Radiation-Grafted Polymerization from a Gas Phase to Form Polymeric Layers on Metal Surfaces

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Introduction

Radiation-grafted polymerization from a gas phase (‘gas-phase grafting’) is one of the effective methods for material modification.[1–2] By this method, an initial material (‘substrate’) is irradiated in the atmosphere of non-saturated monomer vapors, so that the energy of radiation is absorbed almost solely by the substrate. This absorbed energy generates active centers of a free-radical nature in the substrate,[2–3] which can initiate a polymerization chain process in a layer of monomer molecules that are absorbed by the surface. As a result of such a polymerization, grafted polymeric structures, chemically connected to the surface of a substrate, are formed. These structures can lead to new functional properties. Such a method of grafted polymerization was performed on a wide range of materials, including monomers of vinyl, vinylidene, acryl, diene, and acetylene types, and substrates of both polymeric and mineral (silicates, alumina, kaolin, oxides, and salts of a number of metals) nature. However, irradiation of pure metals and materials with semi-conductive properties (e.g., silicon and zinc oxide) in the atmosphere of monomer vapors did not result in the initiation of grafted polymerization. This phenomenon might be explained by the dissipation of radiation energy on delocalized charge carriers, which results in the loss of ability to generate the polymerization-initiating centers of a free-radical nature.

At the same time, the formation of chemically connected polymeric structures on metal surfaces and, in particular, on a titanium surface, would allow a number of important problems related to the application of metal products in various areas of modern engineering to be solved. Such problems include: increasing corrosion resistance, changing the adhesive behavior of metal surfaces and, of particular importance, improving the bio-medical characteristics (hemo-biocompatibility, thromboresistance) of titanium products used in surgery (bodies of artificial heart valves, orthopedic products etc.). With this in mind, the work...
presented here addresses the problem of finding opportunities for gas-phase grafting of the surfaces of metal products. While approaching this problem, we relied on the one hand, on the well-known fact that in many cases the surface of a metal is covered by a natural oxide film, the thickness of which can be increased by chemical or electrochemical methods. On the other hand, we relied on the assumption that in such oxide films, the dissipation of radiation energy might be incomplete, allowing for the generation of free-radical centers in these oxide films. The latter assumption is based on the following reasons: during the irradiation of an oxide film, the generation of excited ion-radicals of oxygen is likely, which can migrate on the surface of a metal is covered by a natural oxide film, the superfluous energy (the energy of excitation) dissipates, and the radical essentially perishes, i.e., loses the ability to react and to migrate on the nodes of the oxide crystal lattice. On another (‘free’) border of the oxide, migrating excited ion-radicals can meet the absorbed monomer molecules and initiate the chain process of polymerization, which should result in the formation of macromolecules, which will be chemically connected with the surface of the oxide film. We believe that the effect of grafted polymer formation under irradiation of a aluminium powder in an acrylonitrile atmosphere, mentioned in earlier works, follows such a mechanism.

Our current research concerns the gas-phase grafting on titanium samples. As it is known, the titanium surface is covered by an oxide film. Our choice of titanium is also related to the fact that titanium and its alloys are widely used in the manufacture of different sorts of products for surgical purposes, e.g., cases of artificial valves of heart, stents, fixing details for orthopedic artificial limbs, etc. We expect that the directed modification of titanium products by the formation of polymeric structures that are chemically connected to their surfaces, will allow, in a number of cases, significant improvement of bio-compatibility and thromboresistance of the products that are used in endosurgery.

We have chosen vinylidene chloride, \( \text{CH}_2=\text{CCl}_2 \) (VDC), as a monomer polymerizing compound. The reason for this is that the polymer poly(vinylidene chloride) (PVDC), formed during the polymerization of VDC, can be completely dehydrochlorinated (carbonized). Therefore, the structures of poly(vinylidene chloride) grafted onto the titanium surface should improve the medico-biological characteristics of products after carbonization, because the carbon by itself has high thromboresistance and good hemo-biocompatibility. This effect has already been investigated for the modification of synthetic fibers and textile products for surgical purposes. The study of poly(vinylidene chloride) grafting onto a titanium surface may be a starting point for further research in the field of materials for medical purposes.

**Experimental Part**

Initial titanium samples were made from sheet metal as plates \( 1.2 \times 1 \times 0.05 \text{ cm}^3 \). One surface of each sample was scraped manually by file. Additional oxidation of the samples was carried out by treating with a freshly made boiling mixture of 25% aqueous ammonia, 30% hydrogen peroxide solution, and water in a volumetric ratio of 1:1:5 (SCI solution), for either one or two hours. The gas-phase grafting of vinylidene chloride (VDC) was performed according to the standard technique in a purpose-built glass device consisting of two separately thermostatted communicant vessels. One vessel (reactor) contained the titanium samples. The other vessel (batcher) was filled with a liquid monomer. The batcher temperature determined the monomer vapor pressure in the whole system. Before the experiment, the monomer in the batcher was frozen and the device was evacuated down to approx. \( 10^{-2} \) millimeters of mercury. For complete removal of air dissolved in the liquid monomer, this freeze-evacuation-thaw cycle was repeated three times. Irradiation of the reactor was performed using a panoramic gamma source Co\(^{60}\). In all cases, grafting was performed at \( 30^\circ \text{C} \) and at a VDC vapor pressure of 500 mm of mercury. The dose rate was 0.1 MRad \( \cdot \text{h}^{-1} \), the duration of a reaction was 25 h, total dose was 2.5 MRad. Upon termination of the reaction, the device was pumped out at an increased temperature, over 1 h, in order to remove the non-reacted monomer molecules sorbed on the samples. The samples were then treated with dimethyl sulfoxide at 100 °C for 1 h, in order to remove any residue of non-grafted PVDC. Finally, the samples were washed with water and dried.

X-Ray photoelectron spectroscopy (XPS) was used for surface characterization. XPS spectra were obtained on a MICROLAB MK P X-ray photoelectron spectrometer. The information depth of a method is defined by the photoelectron run, which usually corresponds to approx. 4 nm. Table 1 defines the notation used for each sample.

**Results and Discussion**

Figure 1 depicts the wide range XPS spectra of titanium samples with a natural oxide film (curve 1) and of the samples oxidized by SCI solution (curve 2). Figure 2 shows the fine structure of the Ti 2p peaks for the same samples, after subtracting background noise and renormalization with respect to the maximum. The identification of the main peaks is given in the figures. As can be seen in Figure 1 and 2, all XPS spectra have peaks corresponding to titanium and oxygen atoms. The spectrum of a titanium sample with a natural oxide has peaks corresponding to oxygen-bound

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristic</th>
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<tbody>
<tr>
<td>1</td>
<td>Titanium with a natural oxide film</td>
</tr>
<tr>
<td>2</td>
<td>Titanium oxidized in a solution SCI for 1 h</td>
</tr>
<tr>
<td>3</td>
<td>Titanium oxidized in a solution SCI for 2 h</td>
</tr>
<tr>
<td>2g</td>
<td>Sample 2 after grafting from a gas phase</td>
</tr>
<tr>
<td>3g</td>
<td>Sample 3 after grafting from a gas phase</td>
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titanium atoms (459 eV for Ti 2p3/2 and 465 eV for Ti 2p1/2), and of metal titanium (454 eV for Ti 2p3/2 and 459 eV for Ti 2p1/2). The binding energy values for the titanium oxide Ti 2p3/2 and the titanium metal Ti 2p1/2 peaks coincide. Therefore, the spectrum of a sample with a natural oxide film in Figure 2 consists of three peaks. In the spectrum of samples that were additionally oxidized, the titanium metal peak is absent, and the spectrum consists of only two peaks. This suggests that the artificial oxide TiO2 film completely ‘shields’ the titanium surface and its thickness exceeds the depth of photoelectron output, which is of the order 4 nm.\(^8\) The carbon peak in the spectra shown in Figure 1 is related to the sorption of carboxic compounds from the atmosphere. Apparently, there are other sources of contamination of the sample surface, e.g., by organic compounds, which should be identified and excluded later.

Figure 3 presents the XPS of samples 2 and 3 after their irradiation in an atmosphere of non-saturated VDC vapors (curves 1 and 2 for samples 2g and 3g, respectively). The spectra contain intense Cl 2p, Cl 2s, C 1s, and O 1s peaks. The values of the binding energies and the ratio of intensities of these peaks directly relate to the XPS spectrum of PVDC.\(^8\) This observation allows for an unambiguous conclusion that irradiation of surface-oxidized titanium in VDC vapors results in the formation of a polymeric layer on the sample surface. The very small Ti 2p peak of the titanium oxide layer can be seen in the spectrum of sample 2g. The intensity of this peak is substantially less than the intensity of the carbon and chlorine peaks. The presence of a Ti 2p peak indicates that the thickness of the grafted polymeric layer on this sample is less than 4 nm. This peak is absent in the spectrum of 3g because of the increase of thickness of a polymeric layer with the increase of titanium oxidation. Such a dependence is consistent with the mechanisms (described in the introduction) of formation and migration of the active excited centers that initiate grafted polymerization.

Intense O 1s peaks, which are observed in the spectra of both samples, are apparently related to oxygen atoms that are chemically connected to a polymeric layer. The shape of this peak shows that for sample 2g oxygen is partially related to the TiO2 structure.

**Conclusions**

It has been proven experimentally that irradiation of an oxidized titanium surface in an atmosphere of non-saturated VDC vapors leads to the formation of a grafted polymeric layer on sample surface, and the thickness of the polymeric layer increases with an increase in the oxide film thickness. Such a dependence is consistent with the

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**Figure 1.** Wide range XPS spectra of oxidized titanium samples. 1) Sample 1, and 2) sample 2 and sample 3 (the spectra of these two samples coincide).

**Figure 2.** XPS Ti 2p peaks for oxidized titanium samples. 1) Sample 1, and 2) sample 2 and sample 3 (the spectra of these two samples coincide).

**Figure 3.** Wide range XPS spectra of oxidized titanium samples after PVDC grafting from a gas phase. 1) Sample 2g, and 2) sample 3g.
hypothesis concerning the mechanism of formation and migration of the active excited centers which initiate the grafted polymerization.

In conclusion, our study shows that radiation-grafted polymerization from a gas phase is an effective method for modifying the surface of metal products.

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