

Molecular assemblage and characterization of functional polymeric brushes on amorphous metal surfaces

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INTRODUCTION

The tendency of polymeric surfactants to self-organization into ordered and semi-ordered aggregates, hierarchical assemblies, networks, brushes and others nanostructures in liquids and on surfaces provides purposeful construction of functional materials for patterning, self-healing, corrosion inhibition, energy storage, drug carrying. Controlled synthesis of a new generation of surface-active oligomers containing a set of reactive side or/and terminal groups opens perspective ways for molecular assemblage of nanoscale functional brushes including formation of self-ordered sandwich structures on surfaces of various natures: glass, ceramics, metals. In our particular study, two functional oligomers containing side peroxide (which can be used for “grafting from” synthesis), acetate (pyrrolidone) and anchor phosphate or carboxyl groups synthesized in our lab were used as precursors for attachment and formation of the brushes on the sheets of amorphous metal alloys. Oligomer anchor phosphate or carboxyl groups provide grafting to metallic surfaces while free acetate or pyrrolidone fragments interact with the surface and between attached polymer brushes thus showing hydrophilic characteristics as well as self-organization to crystalline structures.

METHODS & MATERIALS

Tethering of functional polymer brushes, synthesized by general approach described in ref. [1, 2], to the amorphous metal alloys [3] were conducted by adsorption from isopropanol solution under different concentration during 20 hours at temperature 15°C. On each step, amorphous metal alloys (Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}) were cleaned in the same solvent without any mechanical influence. Oligomer anchor phosphate or carboxyl groups (fig. 1.) formed coordinated or, possibly, simultaneously salt bonds with metallic surface. After samples modification it were carefully washed in isopropanol and dried under ambient condition. Contact angle analysis and scanning electron microscopy were used to check morphology and stability of the surface films.

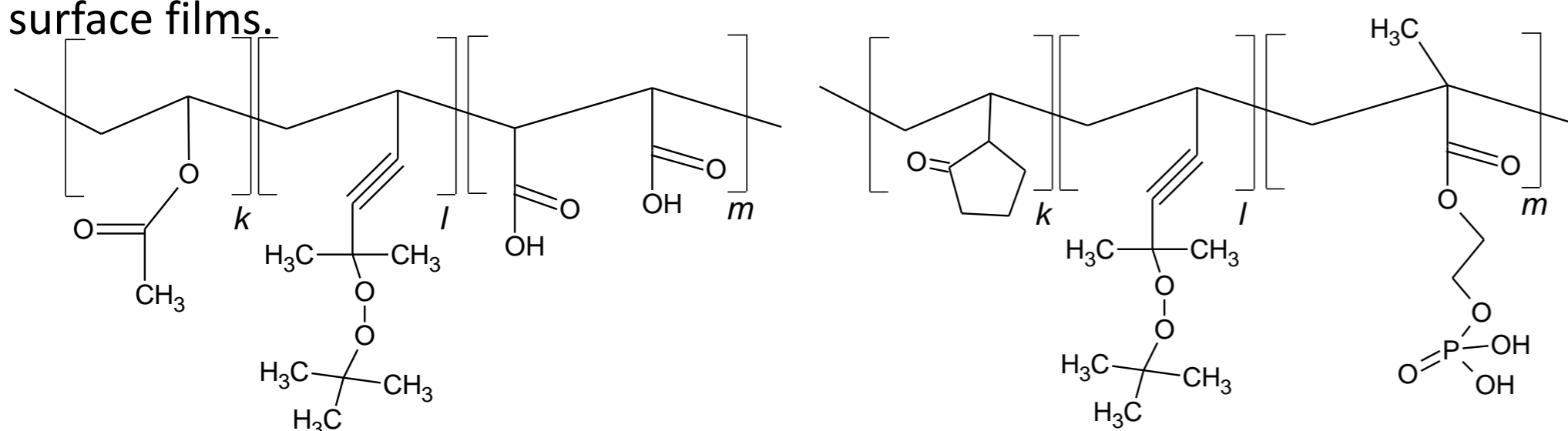
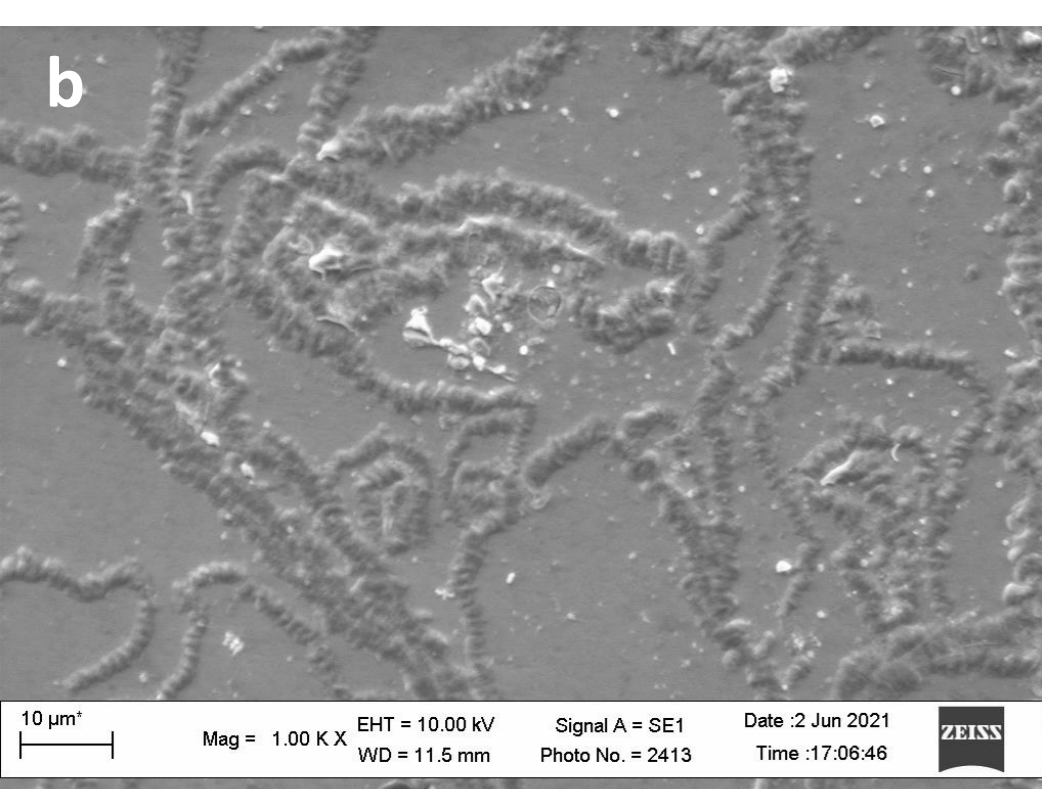
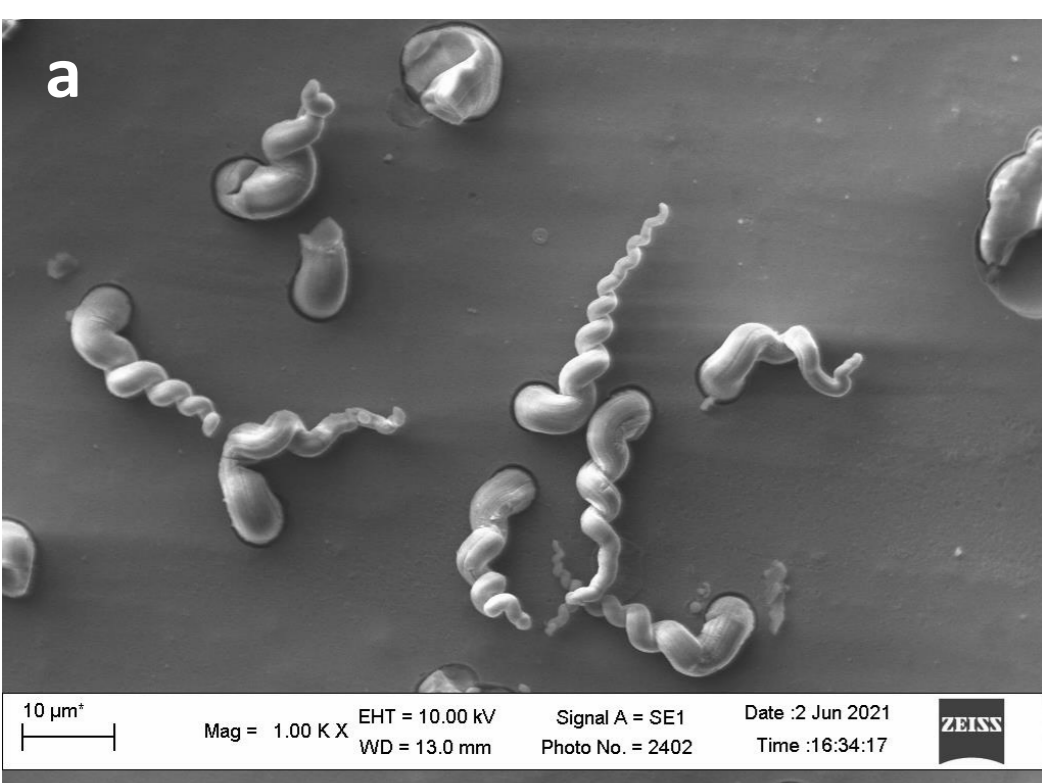


Fig. 1. a) VA-VEP-MA: copolymer of vinyl acetate (VA), peroxide monomer (VEP) and maleic acid (MA) (k=25%, l=45%, m=30%) **b)** NVP-VEP-POEM: copolymer of n-vinyl-pyrrolidone (NVP), peroxide monomer (VEP) and 2-(phosphonoxy) ethyl 2-methylacrylate (POEM) (k=75%, l=10%, m=15%)

RESULTS

Firstly, a quite different picture of surface morphology was noticed for the same sample in relation to its sides. Each individual metal sheet has one con-



tact (back) and one front (shiny) side because of the technology of its obtaining [3]. Surprisingly for us, on the back side of the sheet we revealed large microscopic supramolecular brushes with twisted and strained structure up to 30 μm (fig. 2a). The suggestion that an attraction between neighboring polymer molecules can lead to supramolecular self-organization was proved. Favorable crystallization condition is caused by strong tethering points as well as interaction between polymer brushes and it is the reason of increasing hydrophobicity of the such sample.

Fig. 2. SEM images of VA-VEP-MA grafted sample from 3% concentration solution: a) back side, b) shiny side.

On the other (shiny or front) side of VA-VEP-MA sample, different outgrowths formed due to completely another surface roughness and possibly chemical content distribution on the interface (fig. 2b).

As you can see from the figure 3, the wetting characteristics changed significantly for both sides and the surface become more hydrophilic (from 75–105° down to 40–45°). Availability of the free acetate or pyrrolidone fragments to form easily hydrogen bonds inside the polymer coil and between separated chains provides useful protection from external factors, but in a case when their attraction is much more beneficial than attraction with metal surface the supramolecular self-structuring wins in the molecular forces competition.

In general, the surface tension of NVP-VEP-POEM surface-active oligomer is higher and slowly rises with increasing the concentration of its solution while VA-VEP-MA has a tendency to the surface tension decrease (fig. 4). It corresponds to that VA-VEP-MA samples form crystalline brushes on their surface and do not cover it densely enough like film former NVP-VEP-POEM.

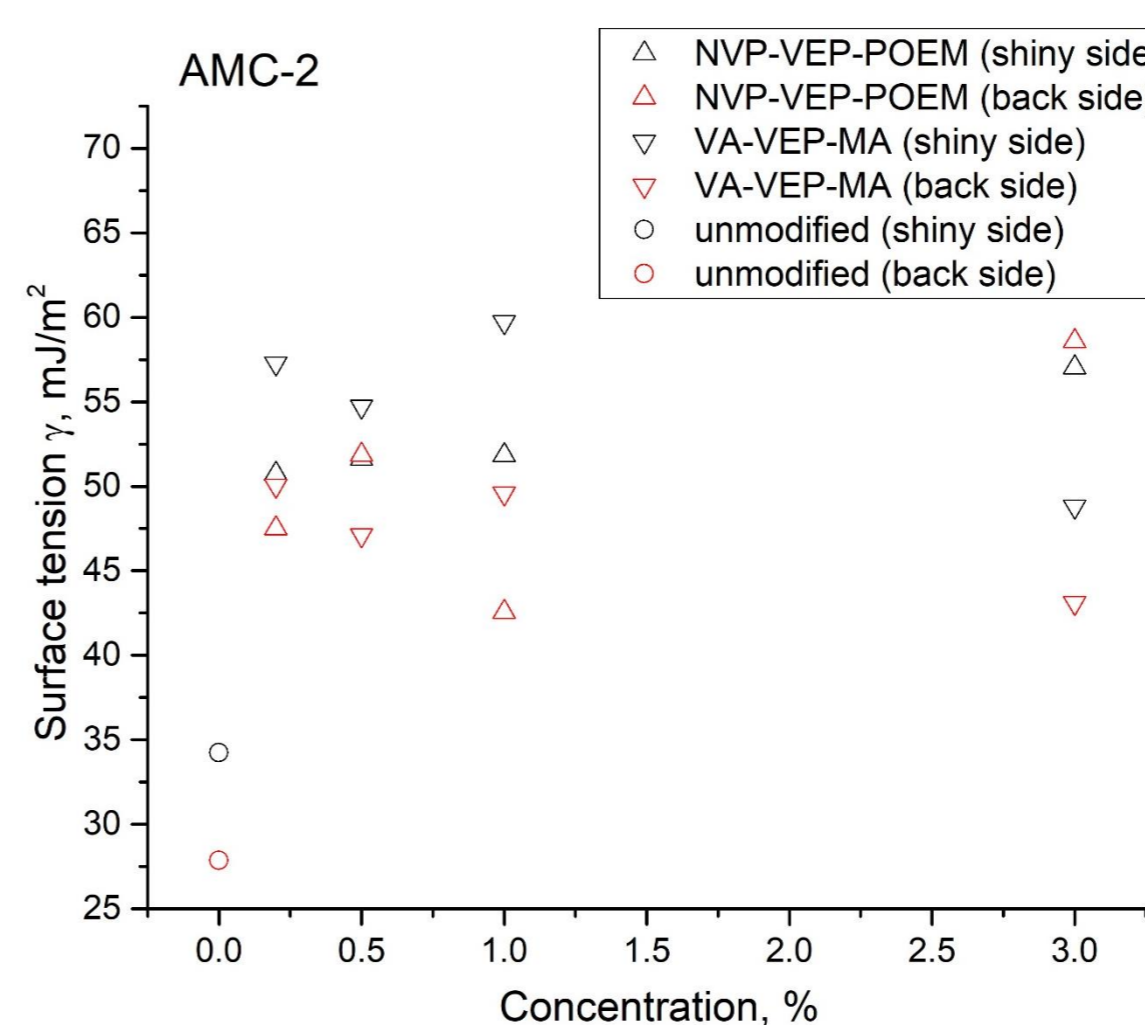


Fig. 4. Surface tension of samples covered by VA-VEP-MA and NVP-VEP-POEM surface-active brushes and its comparison with the unmodified metal surface for shiny and back side.

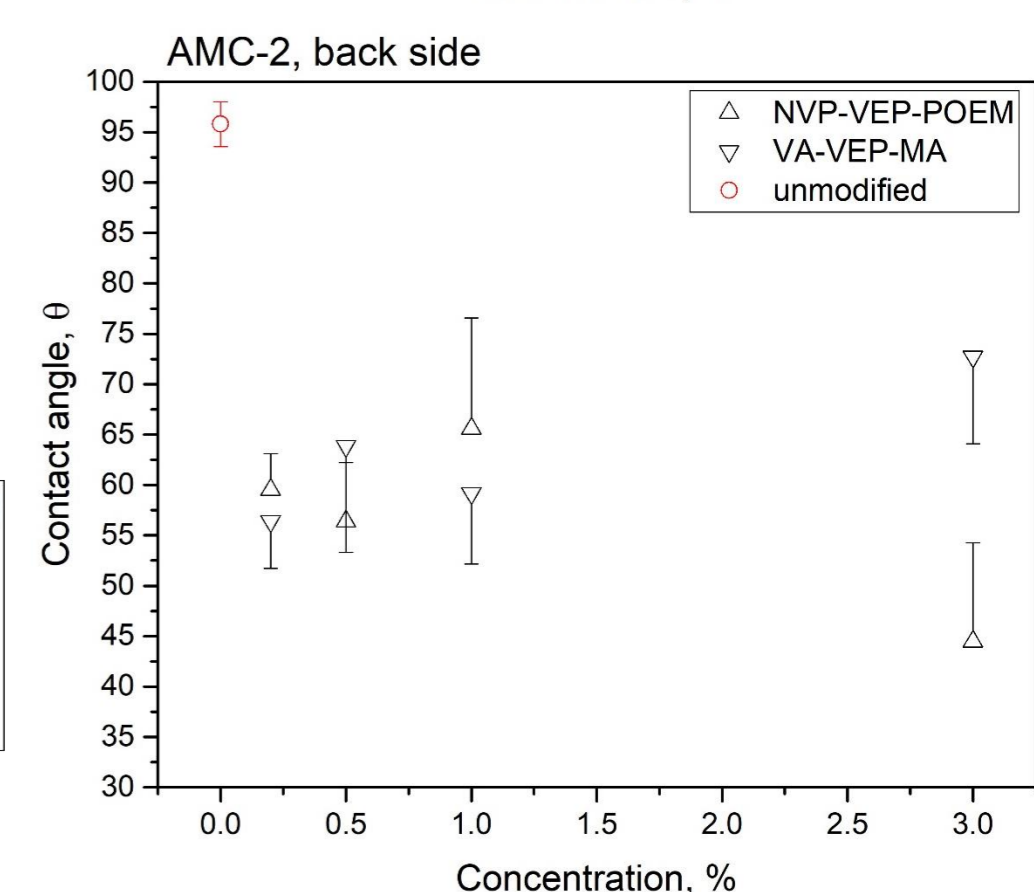
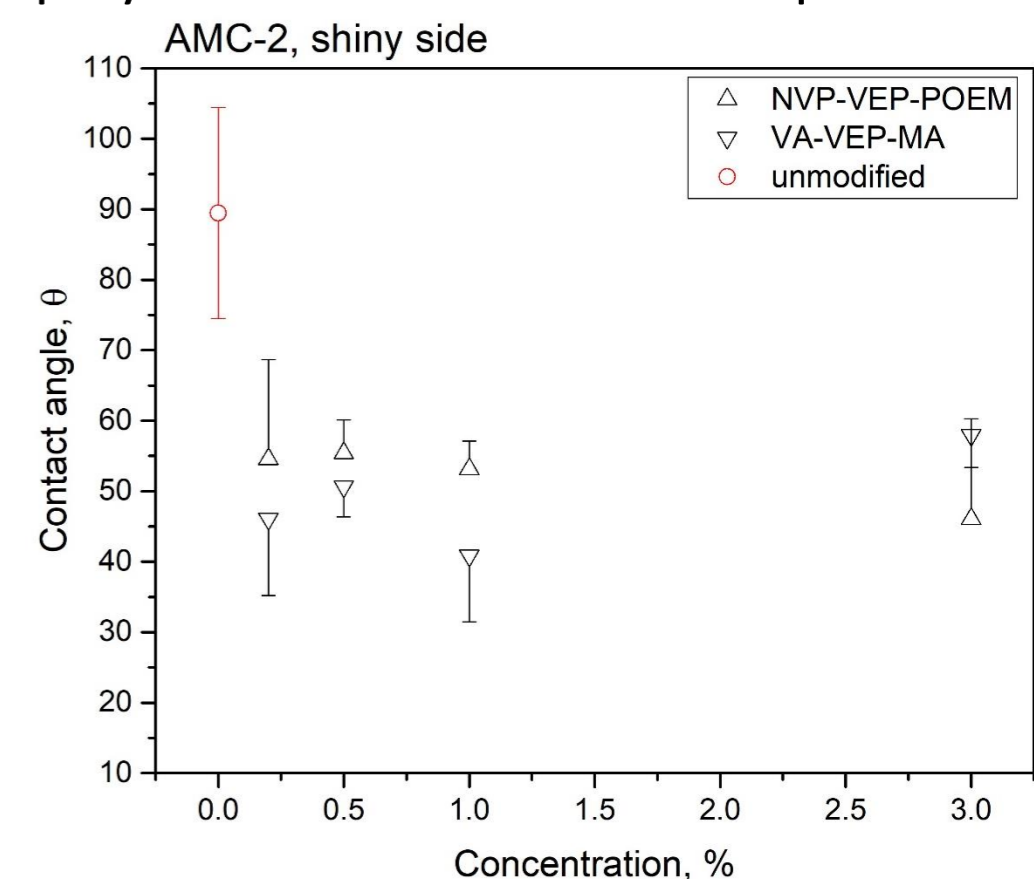


Fig. 3. Contact angle of static drop water measured for the samples prepared from polymer solution of different concentration for VA-VEP-MA and NVP-VEP-POEM and its comparison with the unmodified metal surface: a) shiny side, b) back side.

CONCLUSIONS

In this particular study, we have shown that surface-active functional oligomer are interesting for the surface modification and could form not only dense protective layer on an electrode surface but self-organized nano- and microstructured crystalline objects. It opens a wide range of possible applications in a field of electronics, energy storage, surface protection, biology etc.

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