

PLASMA COPOLYMERIZATION – A RECOMMENDED WAY FOR FORMATION OF DEFINED FUNCTIONALIZED SURFACES

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INTRODUCTION: The chemical fixation of biological molecules onto functionalized surfaces demands an arbitrary adjustable number of monotype functional groups on the surface to avoid undesirable interactions by redundant functionalities. Common surface treatments as silanization, plasma treatment or plasma polymer deposition of OH, NH₂ or COOH groups-bearing monomers give rise to random functionalized surfaces, which are not perfectly adapted to large molecules. Usual plasma polymer layers, prepared by continuous wave RF plasmas, are often chemically irregular in their structures and chemical compositions. To minimize irregularities low wattages and the pulsed plasma technique was applied to avoid a high degree of fragmentation¹. Using the pulsed plasma technique we investigated the plasma-initiated chemical copolymerization of allyl alcohol (Aal) with “neutral” molecules (“chain extenders”) as butadiene (BD), ethylene (E), acetylene (AC) and styrene (St). The copolymer layers were characterized by XPS, FTIR and contact angle measurements.

METHODS: The copolymerization experiments were performed in a stainless steel reactor (Ilmvac, Ilmenau, Germany) using a RF plasma of 100W/300 W and a duty cycle $t_{on}/(t_{on}+t_{off}) = 0.1$. The X-ray photoelectron spectra (C1s, O1s, F1s) before and after derivatization were recorded with a Sage 150 spectrometer (Specs, Berlin, Germany) using a non-monochromatic Mg K_α radiation for excitation. The energy analyzer was operated at 20 eV pass energy. The analysis area was about 35 mm², the pressure in the analysis chamber was hold at $<5 \cdot 10^{-8}$ mbar. Core-level signals were obtained in the constant analyzer energy (CAE) mode at 90° take-off angle. The X-Ray source was run at a power of 225 W (12,5 kV and 18mA). The contact angles were measured using the Sessile Drop Method with the Contact Angle Measuring System G2 (Krüss, Hamburg, Germany) and interpreted following Owens et al.². The FTIR-spectra were recorded using the Nexus Spectrometer (Nicolet, USA).

RESULTS: In Figures 1-4 the chemical composition of TFAA-derivatized layers of copolymers Aal/BD and the surface energy of the copolymers are shown. Dependent on the applied power different regions of plasma deposition of copolymer or homopolymers were found. Applying 100 W Aal and BD copolymerize, if the concentration of Aal exceeds 30 mole% in the precursor. At lower concentrations of Aal exclusively BD was deposited. The deposition at 300 W restricts the copolymerization region. (cf. Fig. 3). When E

instead of BD was used, the copolymerization takes place if the precursor contains 1-30 mole% Aal (100 W). A further increase of the Aal percentage gives rise for deposition of pure Aal layers. The copolymerization regions of Aal with BD, E, AC and St are compared.

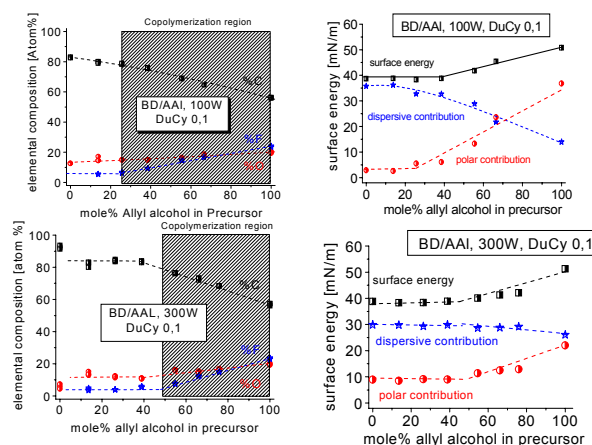


Fig. 1-4: Chemical composition of Aal/BD copolymers (derivatized with TFAA) and surface energy of the (original) copolymers for different Aal concentrations in the precursor.

DISCUSSION & CONCLUSIONS: The copolymerization of Aal with ‘neutral’ monomers like BD, E, AC or St in pulsed plasmas shows an interesting way to produce defined functionalized surfaces such as equipped with hydroxy groups. Depending on the reactivity of the applied comonomers the copolymer formation occurs only in a distinct range of comonomer composition in the precursor. The width of the copolymerization region is mainly influenced by the plasma power.

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