PL-II-3

Novel Plasma Approach for the Synthesis of Highly Fluorinated Thin Surface Layers

[(2)]L. Emilio Cruz-Barba, [(2)]Sorin Manolache, and [(1,2)]Ferencz Denes[*]

[(1)]Biological Systems Engineering Department and
[(2)]Center for Plasma-Aided Manufacturing
University of Wisconsin, Madison, WI 53706

SF_6-RF-plasma environments were employed for the generation of SF_x-oxygen-scavenger species, and used for the synthesis of thin highly-fluorinated paper, polyacrylic acid (PAA), polyethylene (PE), plasma-oxidized polyethylene (OxPE), and polyvinyl alcohol (PVA) surface layers. The concentration of fluorine atoms in the SF_6-plasma was monitored using actinometry. The relative surface atomic concentrations and the surface characteristics of the plasma-modified substrates were evaluated using electron spectroscopy for chemical analysis, contact angle measurements, and atomic force microscopy. It was demonstrated that the plasma-produced SF_x species initiate simultaneous intense surface fluorination, and oxygen extraction mechanisms, and that –C–O, –C=O, and –COOH functionalities are converted into –CF, $–CF_2$, and $–CF_3$ groups respectively. Contact angle (CA) investigations indicate that longer plasma-exposure times result in very high, stable contact angle values. It is suggested that the low stability in time of CA values for the paper samples can be related to the porous nature of the substrates. All plasma treatments generated an increased surface roughness regardless of the nature of the substrates. The results of these investigations open up novel ways for the plasma-enhanced synthesis of thin membrane structures with dissimilar surfaces, which might play a significant role in the area of membrane assisted catalysis (e.g. Nafion-type structures). It is also suggested that pre-oxidized polymer surfaces might lead to more efficient and uniform surface fluorination processes under SF_6-plasma environments in comparison to their non-oxidized counterparts. By selecting plasma-enhanced oxidation reaction mechanisms, which selectively result in the formation of –C=O and –COOH groups, novel routes open up for the synthesis of CF_2 and CF_3-bearing surface layers.

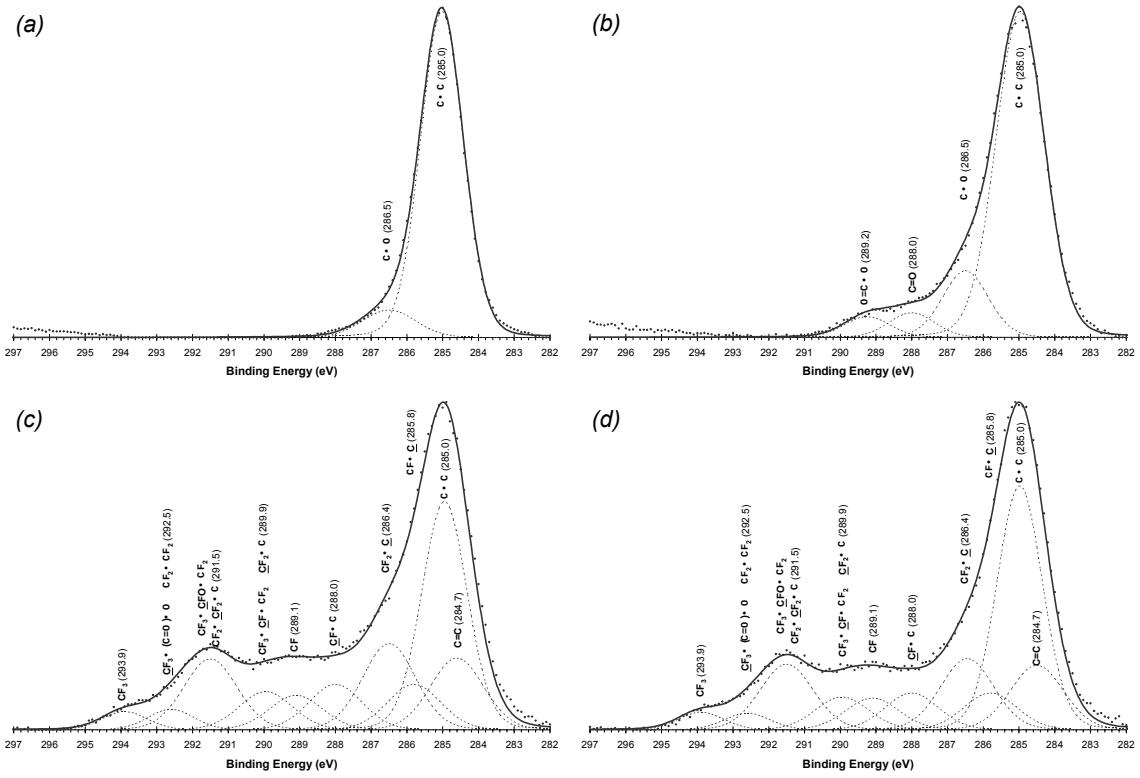

Fig. 1. ESCA C1s spectra of *(a)* virgin PE, *(b)* plasma-oxidized PE, *(c)* SF_6-plasma treated PE, and *(d)* SF_6-plasma treated plasma-oxidized PE.

Table 1. Contact Angle measurements for substrates and SF_6-plasma treated samples.

Sample	***Contact Angle Data (Degrees)***			
Polyethylene (PE)	81.2			
Oxidized PE (OxPE)	68.2			
Polyvinyl-alcohol (PVA)	64.6			
Paper	§			
	1st SF_6-Plasma Treatment Storage Period		***2nd SF_6-Plasma Treatment Storage Period***	
	None	*30 days*	*None*	*30 days*
Plasma Treated PE	143.2	125.8		
Plasma Treated OxPE	143.0	67.4		
Plasma Treated PVA	138.8	64.8		
1 min Plasma Treated Paper	95.4	§	83.0	§
3 min Plasma Treated Paper	99.8	§	93.2	§
5 min Plasma Treated Paper	144.0	§	143.0	§
7 min Plasma Treated Paper	134.4	§	133.0	109.6
10 min Plasma Treated Paper	119.6	103.2	130.8	117.0

§ Indicates that the water droplet was absorbed before a measurement could be made.