Surface Free Energy Calculations for the Plasma Modified PMMA Surfaces

Nesrin Hasirci, Canturk Ozcan
Middle East Technical University, Faculty of Arts & Sciences, Department of Chemistry, Ankara 06531, Turkey
nhasirci@metu.edu.tr

Statement of Purpose: Surfaces of materials have great importance in their compatibilities with the environment and in their acceptance by the tissues. In many cases, although the bulk properties are excellent, the surface may need to be modified and engineered in the desired direction. Plasma-glow discharge is one technique used especially for surface modifications and it is possible to alter the wettability and surface free energy as well as the surface chemistry by this method.
In this study, one important biomaterial polymer, PMMA, was prepared in forms of films by solvent casting method and surfaces were modified with application of oxygen plasma. The effects of plasma power on the surface chemistry and surface free energy were examined. Influence of plasma modification on cell attachments was searched.

Methods: Thin films of PMMA were prepared by solvent casting method. Solutions containing 20 percent PMMA in chloroform were casted on microscope glasses, which were dried in an oven around three to five days at room temperature and then vacuumed. ESCA spectra of all samples were obtained by a SPECS SAGE spectrometer. Contact angles of various liquids (water, glycerol, formamide, ethylene glycol, diethylene glycol, tricresyl phosphate) were detected by sessile drop method using a Windows Excel computer program. Surface free energies and its' components were calculated by means of theoretical Fowkes, Berthelot, Geometric Mean and Harmonic Mean approaches.
Cell experiments were carried out by using 3T3 cells and the attached cell numbers were detected by MTS assay.

Results/Discussion: ESCA results demonstrated that oxygen content on the surface of control pristine PMMA sample was 27%. Plasma application caused an increase depending on the applied power. Surface free energy and component values were dependent on the liquids or liquid couples used in calculations. Table 1 gives the dispersive, polar and total SFE values calculated by Geometric Mean Method.
Attached cell numbers increased about 10 times for the samples modified with 100 watt plasma application while a decrease was observed when the power was increased to 300 watts.

Conclusions: Plasma is an effective technique in altering the surface chemistry and surface free energy. The results obtained by Geometric Mean or Harmonic Mean approximations were parallel to each other on surface free energy values. However calculations demonstrated quite deviated results on dispersive and polar components. On the other hand, it can be concluded that, the total SFE and polar component of SFE are effective parameters on the cell attachment and there is a certain critical value for each which gives the maximum adherence of the cells.

Table 1: Dispersive and polar components of pristine and modified PMMA surfaces

Liquid Couple*	Dispersive Component γ^p (mJ/m^2)	Polar Component γ^d (mJ/m^2)	Total SFE (mJ/m^2)
CONTROL PMMA			
W-F	22.51	18.22	40.73
W-G	23.37	17.73	41.10
W-De	19.27	20.25	39.52
G-F	21.63	19.40	41.03
G-De	16.28	25.61	41.89
20 W 15 MINUTE PLASMA			
W-G	12.70	46.64	59.34
W-F	26.32	33.74	60.05
W-Dm	45.75	22.47	68.22
W-De	10.46	49.67	60.13
G-De	8.81	55.76	64.58
100 W 15 MINUTE PLASMA			
W-G	10.89	50.88	61.77
W-Dm	47.07	23.09	70.16
W-De	10.86	50.91	61.77
G-Dm	47.07	11.17	58.24
G-De	10.85	50.98	61.83
Dm-E	47.07	6.05	53.12
Dm-De	47.07	2.26	49.33
300 W 15 MINUTE PLASMA			
W-Dm	49.69	25.43	75.11
W-De	8.62	59.77	68.39
G-Dm	49.69	6.16	55.85
G-De	21.38	25.64	47.02
Dm-De	49.69	1.52	51.21

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