

Talk prepared for the AATN XXXI th Annual Meeting, B.Aires (Nov. 2004)

**REVIEW OF SOME RESEARCH WORK ON
SURFACE MODIFICATION & POLYMERIZATIONS
BY NON-EQUILIBRIUM PLASMA
IN TURKEY**

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1. INTRODUCTION

Plasma state, known also as the fourth state of matter, refers to an *electrically neutral mixture of positive ions and electrons*. Considering the gas (T_g) and electron temperatures, (T_e); there can be either:

- (1) *equilibrium plasma* ($T_e \sim T_g$); (hot plasmas in arcs, corona discharges and in plasma jets, with high temperatures of $>5 \times 10^3$ K), or
- (2) *non-equilibrium plasma* ($T_e \gg T_g$); (cold plasma/glow discharge).

Within these, the latter “*non equilibrium plasma*” is of main interest for studies with polymers and they will be presented here also, where pressures are low [typically $0.1 P \cdot 10^3$ Pa], (T_e/T_g) ratio is in the range of (10-100), average electron energies and electron densities are (10 eV) and (10^9 - 10^{12} cm⁻³), respectively

The absence of thermal equilibrium makes it possible to work at near ambient gas temperatures [the temperature of heavy particles (ions, molecules, molecular fragments) remain near ambient (300 K, or 0.025 eV)] with sufficiently energetic electrons [the value of T_e is high, typically above 10^4 K (~1 eV)], which makes non-equilibrium plasma well suited to work with thermally sensitive materials.

“Among the most important parameters which characterize such discharges are,

- (a) the charged particle density, n (electrons or positive ions), and
- (b) the electron temperature, T_e (or mean kinetic energy,)”.

In the plasma state, hot electrons, which acquire their kinetic energy directly from the applied EM field, collide with gas molecules and thereby transfer energy through ionization, bond breakage (molecular fragmentation), and other forms of excitation. Excited molecular and atomic species in the plasma, in turn, can emit photons over a very broad portion of the electromagnetic spectrum, ranging from X-rays to the infrared (IR). Photons in the vacuum ultraviolet (VUV) or ultraviolet (UV) range, which have energies comparable to or exceeding those of covalent bonds (a few eV, typically), can also initiate photochemical reactions in polymers, readily.

There are two major current trends worldwide in the plasma research:

(a) **Surface Modification Studies**

Surface modifications can be applied to a range of *different substrates of different nature* (from inorganic to organic); *with different physical shapes* (from powder, fiber and scrap forms to film structures).

As a result of proper surface modifications in cold plasma, surface properties are shown either to be modified or changed completely on wish within the very thin immediate surface layers, without altering bulk properties of the substrate at all.

Surface modifications by plasma are mainly done to change surface energies and surface chemistry of the substrate, to improve properties like adhesion, absorbancy, wetting, biocompatibility..; as well as flame resistance and thermal stabilities.

As regards the interaction of plasma with a polymer surface, following four major effects may be distinguished: (1). surface cleaning, that is, removal of contamination from the surface;

(2.) ablation,-or etching-, of surfaces; (3). cross-linking (or branching) of macromolecules in the uppermost surface layer; and (4). modification of surface-chemical structure. Modified and activated surfaces can also react further with the atmospheric oxygen and water vapor upon re-exposure of the polymer to air.

(b) **Plasma State and Plasma Polymerisation Studies**

In plasma polymerization and copolymerisations , a number of conventional (unsaturated) and unconventional (i.e., saturated) monomers can be used, in the gas-liquid (or even in solid) phases. However plasma polymerization studies are mostly concentrated for the gas phase reactions (plasma state polymerizations), whereas for the liquid or solid states, plasma- initiated polymerizations are also possible.

Plasma systems for industrial processing of polymers is made possible with both (rf) and (mw) plasma systems [1], *mostly for the treatment of flexible substrates* (e.g. films, fabrics, etc.), and *large objects such as moulded automotive parts*, i.e., (PP) or (PP/EPDM) bumpers, *as well as for many small parts and particulates*, mostly basing on oxidizing plasmas.

Both “surface modification” and “plasma polymerization” effects, can coexist; and depending on the processing parameters employed, one or the other effect can be made to dominate.

2 NON EQUILIBRIUM PLASMA STUDIES IN TURKEY

Non equilibrium plasma studies in Turkey can also be considered on two different lines: (surface modification studies) and (plasma polymerization studies).

(i) ***Plasma modification studies***

In this group of studies, there are studies with *fiber/fabrics, biomaterials-food oriented ones*, and *others*.

studies with modification of fibers/fabrics

In this group, there are surface modification studies of various fibers (Carbon, [1a,b,c,d], PAN [2]), and fabrics (PET [3a,b], (PET)/cotton [4], (PET) , (PA) [5] and cotton [6]).

In Carbon fiber (CF) studies, fibers are treated by Ar, as carrier gas, and air, as a reactive component; in addition to a number of different monomers as gases in plasma (allylcyanoide, xylene/Ar, xylene/air, xylene/air/Ar, toluene/air/argon, dioxane... at 5 min. treatment time and at three different (rf) powers of 50, 100 and 200 W). (SEM) micrographs of carbon fiber surfaces showed that the surface striations and surface roughnesses are improved after any of these treatments. *A qualitative agreement between the increase in the strength of fibers with increase in surface energies was established*, [1a,b,d].

Fibers were subjected to single filament tests, and epoxy-CFR composites (60% fiber, unidirectional) prepared to ILSS and flexural strength tests through three point bending measurements. *It is concluded that plasma treatment at selected conditions led to significant improvement of ILSS and flexural strengths in composites*, [1c,d].

Studies with PAN fiber, [2] were done mainly to check the possibility of altering flammability characteristics by proper grafting of flame retardant groups to the surface layers by plasma, without affecting the bulk properties of the fiber. For this, Ar gas, HMDS, ethyldichlorophosphate and tris(butoxyethyl) monomers are tested separately in plasma, and *appreciable decreases in the burning rates and increase in oxygen index (OI) values of PAN fibers are obtained*, only with some negative effects in the case of Ar use, which is believed mainly due to the crosslinking.

Studies with fabrics are done either to decrease the flammability[3a], or to increase hydrophilicities (thereby imparting soil resistances, and improving dyeabilities), [3b]; and for these studies, firstly *PET fabric* is used. For flammability studies, plasma is either applied in air, or the plasma in the presence of different monomers like HMDS, 1.1.2.Trichloroethane, Trichloroethylene, Tetrachloroethylene, PCl_3 and Allylamine are used *which yielded decrease in burning rates at different levels*. During hydrophilicity studies, fabrics are either directly treated in acrylic acid plasma (I), or they are first treated in Ar plasma and then immersed in an aqueous acrylic acid bath(II). The plasma conditions (exposure time and discharge power) are changed in (I), while the acrylic acid content and the incubation time are changed in (II). *It is found that, the wettability, and therefore the dyeability and soil repellency are significantly improved by both of these methods. The method (II) resulted in better dyeability and soil repellency in contrast to lower surface wettabilities*.

(PET)/(Cotton) & (PET) and Polyamide (PA) fabrics are also treated in low-temperature plasmas to increase hydrophilicities,[4,5].

For the first[4], Acrylic Acid and water plasma is used with two alternative procedures: either (a) plasma conditions (exposure time & discharge power) are varied, or (b) Acrylic Acid content and incubation times are changed. It is observed that *glow-discharge treatment significantly improves the wettability of the fabrics, and higher hydrophilic surfaces are created, hence, the dyeability of the fabrics are improved*. No significant colour change of fabrics, neither with repeated washing cycles nor with long period of storage, is observed.

For(PET) and (PA) fabrics[5], five different modifications are tried separately: treatments are done either (i) in acrylic acid, (ii) in water, (iii) in air, (iv) in O_2 and (v) in Ar plasma; with the changes in exposure times and discharge power to control the extent of plasma surface modification. More hydrophilic surfaces were created by all of the methods used. *Wettability, soil resistance and dyeability of (especially PET) fabrics are significantly improved*.

Cotton fabrics are treated [6] in two different plasma procedures: (a) In the first, fabrics are directly treated in Amine plasmas (Ethylenediamine or Triethylenetetramine). (b) In the second, they were first treated in Ar plasma, followed by their immersion into an aqueous Amine bath. Treated fabrics were then dyed with a reactive dye (Remazol Black B) and the colour yields and fastness properties of the resulting fabrics are measured. *The K/S values obtained were significantly improved when compared to the untreated fabric.*

Biomaterials-food oriented plasma surface modification studies

In this group of studies, there are “oxygen/air plasma surface modification” of various films, and “studies for enzyme immobilization” and “studies to increase blood-protein interaction on PU films”.

In the first group, (i) a biological polyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate), [7], (ii) a PU membrane[8], and (iii) a denture Acrylic resin base material[9], are used.

*In (i) the effect of plasma power (10 W or 100 W, 15 min) on the surface hydrophilicity and on the attachment of Vero cells are studied. Water contact angles of the modified surfaces (67-46) decreased with the increase of applied plasma power. Virgin PU (42-45 cells/cm² attached) showed an increase in the number of attached cells first (60-70 cells/cm² at 10W) which is then decreased (27-40 cells/cm² at 100 W), as the applied power increased ;which showed that *optimum levels of cell attachment to PU can be achieved by plasma successfully*[7].*

In (ii), the effect of oxygen (rf)-plasma treatment on surface and bulk properties of a biological polyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate), is studied by (XPS) and (SEM). The plasma-treated films became more hydrophilic due to increases in the oxygen-containing functional groups on the surface of the polymer; and a direct relation is observed for O/C ratio versus the total power (duration x power) [8].

*While in (iii), denture Acrylic resin base materials are surface modified in air to improve wettabilities, [9]. (FTIR), (XPS), and contact-angle measurements revealed an increase in the O/C atomic ratio, due to the formation of-COH groups on surfaces during plasma treatment. The O/C ratio decreased upon heating the samples at 100 C in vacuum for 1-2 mins and exposing to liquid CH₂Cl₂ for an another 1-2 min. Exposure to distilled water for prolonged periods causes a slight decrease during the initial 1-20 days but levels off to a constant value up to a period of 60 days. Contact angles of treated samples are always lower than untreated. *Plasma treatment seems to offer a durable increase in the wettability for these materials left in air or in distilled water.**

In enzyme immobilization studies, (PC) membranes plasma treated with dimethylamine, n-pentylamine or n-heptylamine are prepared. Amino group concentrations produced on (PC) membranes are then assayed by binding radiolabelled [1-C-14]acetic anhydride to the membrane, followed by scintillation counting. For differently treated membranes, different degrees of radiolabelled (I-125) glucose oxidase or rennet binding are observed and which is directly related to the surface amino-group concentrations for the appropriate membrane[10a,b].

In a food-oriented study, (CA) membranes are plasma treated for its use as a glucose electrode in the food industry,[11]. Development of a single-layer glucose enzyme electrode with extended linearity to be used to determine glucose contents. The single surface of (CA) membranes are modified with amylamine. Plasma-treated surface of membranes are activated with glutaraldehyde, then glucose oxidase (GOD) immobilised onto this site. *The linearity and response time of these electrodes are investigated at pH 4 and 6, and these membranes treated with amylamine: at 5 W/20 min showed the best result (with linearity acid response time as 320 mM glucose and 500 s, respectively at pH 4).*

Other plasma surface modification studies

In several compatibility studies [12-16], various selected surfaces are attempted to be modified by plasma in order to enhance the adhesion between different components, hence to improve interface & interphases.

In the case of plasma surface modification studies in connection with polymer blends and composites, there are followings:

(a) (LDPE,powdered) & (PVC) [12a], as well as (LDPE) & (PVC powder) blends [12b], where CCl₄ and vinyl chloride (VCM) plasma are applied for the first and acetylene plasma for the second. Mechanical properties showed appreciable increases in all, for(VC) plasma treatment case being the highest; and these increases in mechanical properties had a very nice parallel trend with the increase in surface energies, indicating increases in the work of adhesion as a result of the plasma surface modifications.

(b) blends prepared from (PET,powdered).& (PVC powder) [13a,b], where plasma in a series of chlorine-containing monomers [like CCl₄, VCM, 1.1.2.2.tetrachloroethane (TCE), 1.1.dichloroethylene (DCE)] at two different plasma operational conditions, are applied. From the intrinsic viscosities of blends in the phenol/tetrachloroethane-mixed solvent system, degree of compatibility of blends are characterized by the use of the Krigbaum-Wall.parameter (Δb), which showed improvements after treatment. A series of mechanical, thermal and surface energy analysis done yielded similar improvements in connection to plasma treatments.

(c) surface-modified recycled rubber & Epoxy systems [14a,b], where car tire regrinds (355-500 μ m in sizes, used as the toughening phase) are surface modified by oxygen plasma, showed improvements in fracture toughness values of the blend; although some decreases in tensile properties are also introduced to these systems by modification. Fractographic surfaces by SEM indicated that increase in fracture toughnesses are due to improved interfaces leading to crack deflections and secondary rubber toughening observed are shear deformation and some debonding initiated at the interfaces.

and in other plasma surface modification studies, where an inorganic component in the polymer matrix is involved, there are following ones:

(d) some performance characteristics of plasma surface modified carbon black in the (SBR) matrix [15]. which is aimed to check the limits of applicability of plasma surface modification of (CB) for its use in the tire manufacturing industry. For this,

styrene or butadiene cold plasmas are utilized for (CB) surfaces. Tensile strengths and percent elongations of vulcanizates are found to respond differently if modified fillers are used as compared with those prepared by the unmodified fillers. Glass transition temperatures of vulcanizates are found to correlate well with the results of mechanical properties. Findings are also supported by the SEM pictures.
and

(e) *studies with surface-modified (powder CaCO_3) & (PP)*, [16], where surface modifications are done by acetylene plasma at two different plasma conditions. Mechanical and thermal properties of the composites prepared were evaluated and the effects of surface modification on the extent of adhesion of filler to the matrix, as well as on polymer phase, are investigated with the help of (SEM). Some of the samples prepared are found to yield at higher strains and they are mechanically superior as compared to those prepared with unmodified filler.

In addition to the following studies:

(f) *Plasma surface modification of PE with organosilicon and organotin monomers*, [17], where plasmochemical modification of a (PE) film surface by several selected silicon and tin containing monomers [such as vinyltriethoxysilane (VTES), hexamethyldisiloxane (HMDS), 3-aminopropyltriethoxysilane (APTS), tetraethylstannane (TES) and hexabutylstannoxane (HBDS)], are all examined. The structure and properties of plasma polymers obtained and plasma modified PE film surfaces were studied by FTIR, photoacoustic FTIR spectroscopies and by using surface energy and swelling measurements. It is shown that the structure of plasma polymers formed either on the inorganic non-active (KBr and glass) or on the organic active (PE films) surfaces do not differ much from each other. Organosilicon plasma polymers, are mainly with polysiloxane type fragments; while organotin analogs are primarily carboxylate fragments. The plasma of organosilicon and organotin compounds were used to modify PE film surfaces to produce thin, hydrophobic, biologically active and inactive surfaces. The results of surface energy studies as followed by the interaction with methylene iodide (non-polar) and ethylene glycol (polar components), and degree of swelling studies for both unmodified as well as plasma modified PE films, in xylene showed a decrease in the latter, and an increase of hydrophobic components as expected.

(g) *Plasma Surface Modification of PP-Based Polymers By Silicon And Tin-Containing Compounds*, [18a,b]; where homo-, co-, and terpolymers of several PP films are treated in a series of selected organosilicon [i.e., organosilan (stannan)e type compounds (such as vinyltriethoxysilane, 3-aminopropyltriethoxysilane, and tetraethylstannane)] and organotin [i.e., organosiloxan(stannoxan)e type compounds (such as hexamethyldisiloxane and hexabutylstannoxane)] plasma.

Plasma surface modification of (PP) films with organosilicon plasma led to increase of hydrophobicities, while organotin plasma produced less hydrophobic surfaces. Reaction of plasma-activated polyolefin films further with vinyltriethoxysilane-maleic anhydride oligomer also led to an increase in the hydrophobicity of polypropylene surfaces. It is observed that the degrees of swelling of (virgin, plasma-treated, and plasma-modified) polypropylene films in cyclohexanone strongly depend on the nature of the organo-element compounds used, organosilicon plasma causing lower degrees of swelling. The changes of surface properties observed are explained by

different surface structures produced in plasma: in the case of organosilicon compounds, it is believed that poly(organosiloxane) and for organotin compounds poly(organotin carboxylate) fragments are primarily formed.

(ii) Plasma (initiated and state) Polymerization studies

(a) *Plasma initiated polymerization and copolymerization of Styrene and MMA* [19-21a,b,c]. In these studies, plasma initiated polymerization is applied to two model compounds, styrene and methylmethacrylate, in a series of experiments, both in gas and in liquid states; and mass spectrometric study is used extensively in gas phase analysis, where the kinetics and nature of plasma chemical reactions of monomers alone as well as their mixtures are studied.

In case of Styrene alone in gas plasma, the most significant reaction observed was the *plasma state polymerization* with some decomposition and formation of a small amount of C_2H_4 , whereas MMA under the same conditions, decomposed mainly to CO, CO_2 and C_2H_4 .

From plasma-initiated studies in the case of MMA in liquid state, done with high resolution NMR; it is found that there is a free radical mechanism involved [20], and that they are not as monodisperse,[22] as predicted before.

Gas phase plasma plasma reactions of their mixtures indicated a catalytic effect of Styrene on the polymerization of MMA, with the inhibiting effect of MMA observed on polymerization of Styrene. There are appreciable decomposition of both monomers observed,[21a,b,c].

For the plasma initiated copolymerization reactions in liquid, tubes with break seals in the middle having two different compartments are used. For samples without and with break seals-the latter is broken right after discharge-a random copolymer rich product; while for the others with break seals broken after certain times, a block copolymer is obtained, as traced out by NMR and IR studies[19].

(b) *Plasma-initiated polymerizations* of Acrylamide(AA) in solid-state and in solution are also examined [23], and the effects of plasma operational parameters, amount of water, post polymerization period and temperature are verified; products are characterized by IR, X ray diffraction and viscosity studies.

(c) *In other plasma state polymerization (PSP) studies*, there are (PSPs) of ethane[24] and some simple saturated hydrocarbons[25], of (HMDS)[26a,b,c], of benzene & cyclohexane, [27], and a series of selected organic compounds [28].

Plasma state polymers of ethane, when coated on (NaCl) optical components are found to provide effective protective coats for their use in CO_2 laser windows with negligible absorbances at and around $10.6 \mu m$ and high scratch resistances,[24].

The kinetics of polymer deposition of several selected saturated hydrocarbons, such as methane, ethane, propane and n-butane are found to give powdery (highly crosslinked) as well as transparent film products, depending on the plasma operational parameters employed, as characterized by "characteristic maps" of corresponding systems. The rates of polymer depositions are found to depend strongly on pressure, flow rate of monomer and (rf) power applied, and an empirical equation is proposed relating these parameters to the deposition rates of these monomers[25].

(PSP) of (HMDS) is rather extensively studied in these works. Characteristic map of (HMDS) contained only film product. Formulation of operational parameters

affecting the polymerization of this monomer is made by use of rotatable central composite (RCC) statistical design[26a,b,c].

Selected organic compounds -alone or mixed with different inert gases (Xylene/air, Xylene/Ar., Xylene/air/Ar., toluene/air/Ar, dioxane and allyl cyanide)- are subjected to (PSP), and their plasma characteristics as well as products are examined[28].

In one diagnostic study[29], Acrylonitrile and (HMDS) are selected and used as two model compounds to clarify the effects of electrode type (inner Cu, Zn, Ni and Al as well as outer), reactor configuration and substrate temperature on (PSP). It is found that electrode type or reactor geometry does not effect deposition rates for these two monomers, whereas an inverse relationship is found between the substrate temperature and deposition rates.

(d) Plasma initiated polymerization (PIP) of allyl alcohol and 1-propanol are studied, where the effect of composite parameters [the ratio of plasma power (P)-to-monomer flow rate (ϕ), (P/ ϕ)] on deposition rates are examined. (XPS) is used for analysis of products. Surfaces of the films produced demonstrated the importance of double bond in monomers for good C-O group retention, and that the double bond is involved in the deposition mechanism,[30].

(e) a nucleic acid sensor is prepared by plasma polymerization by treating the piezoelectric quartz crystal surfaces with ethylene diamine (EDA) plasma (about 43 Angstrom) [31] to follow hybridizations with this piezoelectric crystal microbalance system (QCM). Created amino groups on crystal surface are then converted to aldehydes by reacting with glutaraldehyde (GA) to reach to the optimum (GA) concentration of about 270 ng/cm². A (GA) concentration of 2.5% and an incubation time of 2 h were selected as optimal values at this step, corresponding to (GA) surface concentrations of about 270 ng/cm². A double strand Oligonucleotide, having one extra base on 5-end of one of the complementary strands, are immobilized through the amino groups onto (GA)-modified crystals.. The (QCM) sensor carrying the covalently bound strand is used in hybridization experiments, which showed that equilibrium is achieved in about 5 min, and the frequency shift measured is related to the concentration of the target strand to be measured within the medium.

(f) an amperometric alcohol single-layer electrode is prepared by (EDA) plasma polymerization,[32], which incorporated amino groups on tract-etched polycarbonate membranes, and it's performance is tested on commercial alcoholic beverages. Sensitivity, linearity and response time are 5.6 nA/mM, 2 mM and 50 s, respectively.

(g) (PSP) and (PIP) studies related to activated charcoal [34-36] are done to explore their applications in hemoperfusion.

Activated charcoal has been used in medicine as an oral antidote in cases of acute poisoning, as well as the removal of toxins and metabolites from the blood, known as "charcoal hemoperfusion".

Charcoal granules can be microencapsulated by a bio-compatible plasma polymer without any significant loss of the adsorptive capacity of the substrate [hence, (i) avoiding the release of carbon fines (resulting emboli formation) and damage to cells due to warpage in the case of their use if not coated; or (ii) avoiding decrease in the adsorptive capacity through pore blockage and avoiding introduction of certain toxic impurities into blood, both in the case of coating from solution].

HMDS plasma is used to produce plasma-state, (PSP) [by direct application of monomer and plasma at the same time] as well as plasma-initiated polymers (PIP) [either (a) by applying discharge to charcoal in the absence of monomer which is let to enter the system after discharge is off, or, (b) after PSP monomer flow is maintained after the plasma is off] as very thin-biocompatible coats on charcoal. ESCA and IR (from depositions on NaCl crystals) characterization studies of (PSP) and (PIP) polymers showed similar results, with monomer structure kept more intact in the latter. From the adsorption capacity tests, where creatinine and vitamin B12 are used; there is no alteration in the adsorptive capacities exhibited for treated samples. Whereas from hemoperfusion tests, where fresh sheep blood with oxalate anticoagulant are used and both hemolytical activity and cell counts are applied; no appreciable hemolysis is traced.

It is concluded that plasma polymer produced is an effective enough bio-compatible coat, saving the platelets, erythrocytes and leucocytes during hemoperfusion while adsorbing the toxins.

(h) There are also several collaboration (international) projects to note as regards to (PSP) studies, such as, “preparation of high performance enzyme electrodes by plasma polymerisation technique”,[37a]; “preparation of mass sensitive immunosensors and single layer multienzyme electrodes by plasma polymerisation technique”,[37b]; “infection free biomaterials and high performance biosensors by plasma polymerisation technique”,[37c];

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