

Plasma Surface Modification of Propylene-Based Polymers by Silicon and Tin-Containing Compounds

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SYNOPSIS

Plasma surface modifications of homo-, co-, and terpolymers of propylene films in the presence of selected organosilicon and organotin compounds were investigated. For this, organosilane(stannane) type compounds (such as vinyltriethoxysilane, 3-aminopropyltriethoxysilane, and tetraethylstannane) as well as organosiloxan(stannoxan) type compounds (such as hexamethyldisiloxane and hexabutyldistannoxane) were employed in plasma. Plasma surface modification of polyolefin films with organosilicon plasma has led to increase of the hydrophobicity, while the presence of organotin compounds in 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 organoelement 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(organotinocarboxylate) fragments are formed primarily. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that surface-specific radiofrequency (RF) plasma technique is an important method for the modification of a range of different polymer material surfaces, including polyethylene (PE).¹⁻³ Thin plasma polymer coatings/grfts with given compositions and surface properties can be prepared by plasma polymerization of a range of monomers including silicone⁴⁻⁸ and tin-containing^{9,10} compounds, which are not polymerizable by the usual conventional methods. The effect of several organosilicon and organotin monomers has been studied previously in their plasma polymerizations and plasma surface modification of PE film surfaces.¹¹ By utilizing CO- and CO₂-plasma, it is possible to functionalize PE film surfaces with formation of appropriate functional groups like OH, C=O, and COOH on surface layers.¹² PE surfaces have also been mod-

ified by plasma and by subsequent chemical derivatizations of *N*-vinyl-2-pyrrolidone and allyl alcohol, which provided extra hydroxyl and amine groups.¹³ Plasma surface modification was also used as an effective method, mainly to increase the adhesion of coatings to polypropylene (PP) films.¹⁴ In one study, the surfaces of PP sheet were exposed to a microwave plasma and the ratios of OH, CO, and COOH groups appearing on the surfaces were determined by ESCA. When a modified water-soluble alkyd resin coat was applied on treated PP surfaces and the adhesive strength was determined by cross-cut adhesion test it was found that COOH is the most important in affecting adhesive strength.¹⁵ Degree of wettability of PP films in air after their discharge treatment was found to change considerably¹⁶ by formation of free radicals and hydroxyl groups. Change in the configuration of macromolecules and in the surface roughness, mainly caused by local etching, has been claimed as the main reason for the observed increase in wettability of PP films.¹⁶

Plasma surface modification of PP films with organoelement functional compounds has not been

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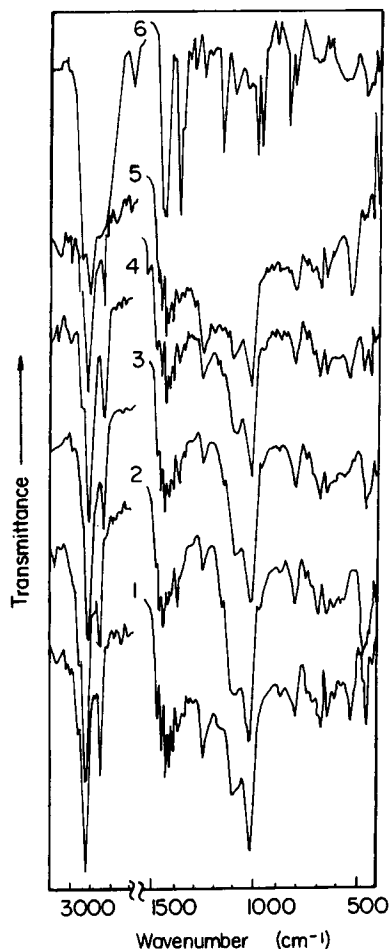


Figure 1 FTIR surface spectra of (1) virgin PP film and plasma surface modified films, (2) poly(VTES)/PP, (3) poly(HMDS)/PP, (4) poly(APTS)/PP, (5) poly(TES)/PP, and (6) poly(HBDS)/PP. Plasma conditions: $FR = 0.15$ g/min, $t = 30$ min, $W = 1200$ J/min, $p = 0.2$ Torr.

studied with enough depth as compared with that of PE. It can be predicted that within polymers of propylene, ethylene-propylene copolymer (EP) and EP-butylene terpolymer (EPB) are probably the most sensitive to plasma action.

The objective of this study is to explore the possibilities for modification of several polyolefin (homo- and copolymers of low α -olefin) surfaces first by plasma polymerization of selected Si- and Sn-containing functional compounds (such as vinyltriethoxysilan (VTES), hexamethyldisiloxane (HMDS), 3-aminopropyltriethoxysilane (APTS), tetraethylstannane (TES), and hexabutyldistannoxane (HBDS), in addition to extended chemical modification of plasma-activated PP film surfaces. For the latter, an oligomer of VTES and maleic anhydride (MA) with chemically active ethoxysilane and anhydride groups was tested.

EXPERIMENTAL

Materials

Chemically pure organosilicon (VTES, HMDS, and APTS) and organotin (TES and HBDS) monomers used were degassed three times by the freeze-thaw method under vacuum before their use in the plasma. The VTES-MA oligomer used was synthesized by radical copolymerization of VTES with MA in bulk, separately, in the presence of benzoyl peroxide at 80°C under nitrogen atmosphere.¹⁷ Low-density PE-, PP-, and EP-copolymer and EPB-terpolymer films ($150 \times 70 \times 0.015$ mm sheets) were used as substrates in plasma, all of which were carefully surface-cleaned in methanol beforehand and were air-dried carefully. Both PP (MH 418, with softening point 150°C) and low-density PE (F-2.12, with softening point 92°C) were products of Petkim (Turkish Petrochem. Ind. Inc.), while EP-copolymer (WF 8166, softening point 126°C) and EPB-terpolymer (WS 709N, softening point 103°C) were products of Simitomo Co. Ltd.

Plasma Modification

For plasma modification, an inductively coupled glow discharge system working at a fixed RF frequency of 13.56 MHz was used. Experimental details of the system and procedure for the plasma modification employed were the same as described previously.^{3,11} Discharge parameters selected and used were as follows: initial pressure in plasma reactor (p) 0.2 Torr, monomer flow rate (FR) 0.15 g/min, power applied (W) 1200 J/min, and discharge duration (t) 30 min.

Plasma modifications on films were applied in either of the following two different modes: (1) plasma was obtained directly in organotin or organosilicon compound selected, which is termed "HMDS plasma . . . etc." and (2) plasma was obtained in vacuum alone without using any monomer, which is termed "plasma in vacuum only." The latter was used for regular surface modifications as well as for surface activation of polymer films, which were retreated by use of VTES-MA oligomer for further modification in some of the experiments.

Measurements

Infrared analysis of virgin and surface-modified polyolefin films were carried out by using a Nicolet-510 FTIR spectrometer equipped with an ATR accessory in the $4000\text{--}400$ cm^{-1} region with a resolution of 2 cm^{-1} .

Table I Surface Energies of Organosilicon and Organotin Plasma-Modified PP and PE Films (Glow Discharge Conditions are as in Fig. 1)

Plasma Polymer Films (Thickness 2.0–2.4 μm) from	Surface Energies (γ_s , Nm^{-1}) as Evaluated from Interactions with Organic Liquids of (at $25 \pm 0.1^\circ\text{C}$)			
	Methylene Iodide		Ethylene Glycol	
	γ_s	$\Delta\gamma_s^a$	γ_s	$\Delta\gamma_s^a$
PP (virgin)	22.24	0.00	0.22	0.00
PP (plasma in vacuum only)	31.79	9.55	0.30	0.08
(VTES) plasma/PP	35.50	13.26	0.13	-0.09
(HMDS) plasma/PP	33.99	11.75	0.46	0.24
(APTS) plasma/PP	34.17	11.93	0.39	0.17
(TES) plasma/PP	28.05	5.81	0.65	0.43
(HBDS) plasma/PP	26.01	3.77	0.50	0.28
PE (virgin)	25.12	0.00	0.79	0.00
PE (plasma in vacuum only)	24.58	-0.54	0.80	0.01
(VTES) plasma/PE	27.45	2.33	0.36	-0.43
(HMDS) plasma/PE	32.98	7.86	0.31	-0.48
(APTS) plasma/PE	30.50	5.38	0.55	-0.24
(TES) plasma/PE	26.96	1.84	0.63	-0.16
(HBDS) plasma/PE	27.17	2.05	1.54	-0.25

* $\delta\gamma_s$ is the difference between surface energy values of plasma-modified and virgin polymer films.

Contact angles were measured by the sessile-drop method using a Rame-Hart goniometer.¹⁸ Solid surface tensions of virgin and films of plasma-modified polyolefin surfaces were obtained from the advancing contact angles of methylene iodide (as non-polar liquid) and ethylene glycol (as polar liquid) in accordance with the known related equations.¹⁹

Swelling tests were done for both virgin PP and for all plasma-modified samples, by use of cyclohexanone at $20 \pm 0.1^\circ\text{C}$. Degree of swelling (Δ) was followed gravimetrically versus time, up to 45 h.

RESULTS AND DISCUSSION

Plasma Surface Modification: Structure–Surface Property Relationships

Figure 1 presents the fragments of ATR-FTIR surface spectra of virgin and plasma-modified PP films. The spectra of surface functionalized PP films prepared by plasma polymerization of organosilicon and organotin compounds differ from virgin PP by the presence of following characteristic bands (cm^{-1}): 955 ($\delta_{\text{Si-O}}$), 460, 750 ($\nu_{\text{Si-C}}$), 1160 ($\nu_{\text{Si-O-C}}$, $\nu_{\text{Si-O-Si}}$) for (VTES) plasma/PP; 450–650, 750 ($\nu_{\text{Si-C}}$), 950 ($\delta_{\text{Si-O}}$), 1150 ($\nu_{\text{Si-O-Si}}$) for (HMDS) plasma/PP; 430, 775 ($\nu_{\text{Si-C}}$), 920 ($\delta_{\text{Si-N}}$), 1145 ($\nu_{\text{Si-O-C}}$), $\nu_{\text{Si-O-Si}}$), 1190 (δ_{NH}), 1545 ($\nu_{\text{Si-N}}$) for (APTS) plasma/PP; 415–570

($\nu_{\text{Sn-C}}$), 660 ($\delta_{\text{Sn-C}}$ rock), 750 ($\nu_{\text{Sn-C}}$), 860 ($\delta_{\text{Sn-O}}$), 945 ($\nu_{\text{Sn-O-C}}$), 1125–1170 ($\nu_{\text{Sn-O}}$), 1205, 1295 ($\delta_{\text{C=O}}$) for (TES) plasma/PP; 430–580 ($\nu_{\text{Sn-C}}$), 635 ($\delta_{\text{Sn-C}}$ rock), 695, 810, 860 ($\delta_{\text{Sn-O}}$), 910, 940, 970 ($\nu_{\text{Sn-O-C}}$), 1210, 1290 ($\delta_{\text{C=O}}$), 1365–1445 (δ_{CH_2} in Bu–Sn) for (HBDS) plasma/PP.

Decrease of the observed intensity for 1255 ($\delta^{\text{S}}\text{CH}_3$) and 2875 cm^{-1} ($\nu^{\text{S}}\text{CH}_3$) bands (Fig. 1) after surface modification indicates that CH_3 groups of PP macromolecules are easily transferred in to the oxidation forms of (OH, CHO, $\text{C}=\text{O}$, and/or COOH) in plasma, which can directly take place during the reaction with Si- and Sn-containing plasma polymers deposition. In fact, the surface structure of organotin-modified PP films contained bands of 1590–1595 and 1205–1295 cm^{-1} corresponding to $\nu_{\text{C=O}}$ and $\delta_{\text{C=O}}$, respectively, in organotin carboxylate, which are absent in the spectra of organosilicon analogues. The details of the possible similar reaction were already described for (organotin) plasma/PE systems in one of our reports.¹¹

Surface properties of plasma-modified polyolefins are expected to depend strongly first on the type of compound used in plasma, i.e., the nature of active element involved in the compound, and on the type of polyolefin films used. Surface energy can be considered as an important criteria to characterize polymer surfaces. In Tables I and II, results of surface energies of virgin and various plasma-treated

Table II Surface Energies (γ_s) Organosilicon-Modified Copolymer (EP) and Terpolymer (EPB) of Propylene (Plasma Condition as in Fig. 1)

Plasma Polymer Films (Thickness 2.0–2.4 μm) from	Surface Energies (γ_s , Nm^{-1}) as Evaluated from Interactions with Organic Liquids of (at $25 \pm 0.1^\circ\text{C}$)			
	Methylene Iodide		Ethylene Glycol	
	γ_s	$\Delta\gamma_s$	γ_s	$\Delta\gamma_s$
EP-copolymer (virgin)	24.07	0.00	0.80	0.00
EP-copolymer ^a	26.26	2.19	0.54	-0.26
(VTES) plasma/EP	29.96	5.89	0.23	-0.57
(HMDS) plasma/EP	30.54	6.47	0.51	-0.29
(APTS) plasma/EP	27.07	3.00	0.76	-0.04
EPB-terpolymer (virgin)	27.28	0.00	0.47	0.00
EPB-terpolymer ^a	29.93	2.65	0.51	0.04
(VTES) plasma/EPB	30.15	2.87	0.27	-0.20
(HMDS) plasma/EPB	31.35	4.07	0.25	-0.22
(APTS) plasma/EPB	34.26	6.98	0.32	-0.15

^a Plasma treatment in vacuum only.

PP substrates are summarized. If methylene iodide component of surface energy (γ_s) is considered as a measure of the degree of hydrophobicity of polymer surfaces, hydrophobicities of homo-, co-, and terpolymers of propylene as well as of PE yielded the following different rows for the virgin and plasma surface treated that PP samples, in general: (for virgin films) EPB > PE > EP > PP and (for films modified by plasma in vacuum only) PP > EPB > EP > PE.

As evidenced from these data the hydrophobicity of PP surface after plasma treatment in vacuum in-

creases considerably, while corresponding values for PE and copolymers of propylene tested change slightly. These results for a series of plasma surface-modified films (Table I) show that the highest degree of hydrophobicity is achieved in the case of use of organosilicon plasma. However, PP, EP, and EPB films modified by organotin plasma gained much smaller degrees in hydrophobicities (Table II). The highest hydrophobicities obtained for PP surfaces were with VTES, APTS, and HMDS plasma; for EP and EPB copolymers HMDS and APTS plasma have yielded similar results. As a result, silicon-rich surfaces produced are found to be more hydrophobic than those for polyolefin surfaces treated with organotin plasma at similar conditions. This fact can best be explained by the possible expected differences in the structure of deposited thin plasma polymer coatings or grafts produced. In addition, if the predominating polar nature of organotin carboxylate fragments in comparison with the organosiloxane fragments is considered at the surfaces modified, lower γ_s values for the treated polyolefin film surfaces for the latter can be ensured.

Surface Modification of Plasma-Activated Polyolefins by VTES-MA Oligomer

The results obtained for the dependency of surface energies for PP and PE films on the condition of modification are summarized in Table III. Thin coatings with characteristic thicknesses of 10–15 μm on plasma-activated surfaces of PP (or PE) films are formed easily from a 5% solution of VTES-MA oligomer in methyl ethyl ketone by centrifugation, which was then dried in vacuum until constant weight. From Table III it is seen that for these samples, there is a monotonic increase of surface ener-

Table III Surface Energies (γ_s) of Polyolefin Films Treated with VTES-MA Oligomer after Surface Activation in Vacuum

Polyolefin Films Treated with VTES-MA Oligomer Right after Their Plasma Surface Activation in Vacuum	Condition of Modification with Oligomer		(γ_s) Evaluated from Interaction with Methylene Iodide ($25 \pm 0.1^\circ\text{C}$)	
	t (min)	T ($^\circ\text{C}$)	γ_s	$\Delta\gamma_s$
	Oligo(VTES-MA)/PE	15	60	25.96
30		60	26.54	1.42
60		60	27.38	2.26
60		90	29.11	4.42
Oligo(VTES-MA)/PP	15	60	23.65	1.41
	30	60	25.22	2.98
	60	60	26.96	4.72
	60	90	30.06	7.82

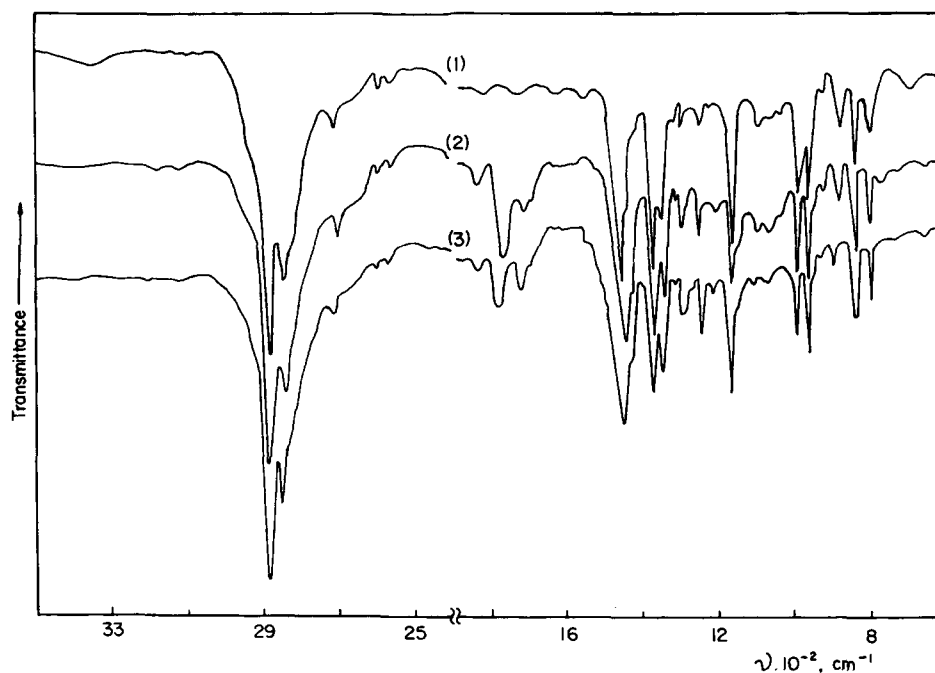
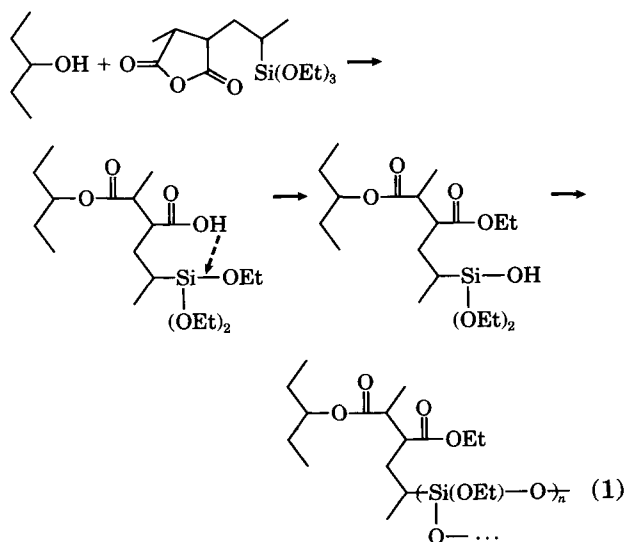


Figure 2 FTIR spectra of (1) plasma surface-treated PP film and PP film surface modified with VTES-MA oligomer at (2) 60°C during 30 min and (3) 90°C during 60 min.

gies with increase of modification times and temperatures. The observed systematic increase of surface energies both by increase of modification times and temperature allows one to suggest that the chemical modification expected is accomplished. Increases of time and temperature are expected to increase the probability of formation of hydrophobic organosiloxane fragments of a crosslinked character. The coat and/or grafts obtained on PP and PE films were found to be durable. A similar, thin and yet durable coating was found to be impossible to obtain on virgin PE and PP films without use of plasma, even if the same procedure is applied afterwards.

Data from FTIR spectroscopic studies can be used to speculate on the proceeding of the chemical reaction between plasma-activated polyolefin surfaces and VTES-MA oligomer (Fig. 2). As seen from these data, new bands at 1720, 1770, and 1835 cm^{-1} consisting of $\nu_{\text{C}=\text{O}}$ (ester) and $\nu_{\text{C}=\text{O}}$ (anhydride), respectively, appear in the spectra of surface-modified PP films. Moreover, it is observed that increases of both modification temperature and of duration of surface treatment increased the intensity of the ester band and decreased that of the hydroxyl band (3360 cm^{-1}), which allows one to demonstrate the probable reaction steps for the plasma-treated PP with VTES-MA, as follows: (1) intermolecular esterification, (2) intramolecular reaction between carboxyl and ethoxysilyl groups, and (3) polycondensation of

ethoxysilyl fragments, as initiated by the free carboxyl group, by formation of crosslinked poly-(organosiloxane) structure. These can be presented schematically as follows:



Swelling

Swelling test results are presented in Figure 3. From the dependency of degree of swelling on time, it is observed that for virgin and for the plasma- (in vac-

uum only) treated PP films there are standard types of diffusion curves obtained, showing a rapid diffusion first followed by a slowed-down plateau region.

When diffusion curves of (organosilicon) plasma-modified PP systems are considered, curves with similar characteristics with very low diffusion levels are obtained. The levels of diffusion in the (organosilicon) plasma/PP systems were much lower than the reference curve, pointing out the existence of effective crosslinks introduced.

The characteristic diffusion curves for (organotin) plasma/PP systems had some basic differences from that of PP and (organosilicon) plasma/PP systems. Swelling of (organotin) plasma/PP takes an intermediate position between virgin and (organosilicon) plasma/PP systems. For the difference observed between Sn- and Si-containing compounds used, one can consider first the existence of organotin carboxylate groups in the former with high polarities.

On the other hand, low levels of swelling observed for (HBDS) plasma/PP film in comparison with (TES) plasma/PP can be explained if different activities of plasma-sensitive $\text{CH}_2\text{-Sn}$ group of HBDS: ($\text{CH}_2\text{-Sn-O}$) and TES: ($\text{CH}_2\text{-Sn-CH}_2$) in the formation of thin plasma polymer coatings/grfts with different crosslink densities, are considered.

The results obtained parallel the data of structure-surface energy relationships considered in the previous part of this work.

CONCLUSIONS

The following concluding remarks can be summarized in relation to the glow discharge polymerization of selected organosilicon and organotin compounds on the surfaces of homo-, co-, and terpolymers of propylene, as well as for the reaction of plasma-activated polyolefin films with VTES-MA oligomer:

1. Hydrophobicities of homo-, co-, and terpolymers of propylene surfaces after plasma treatment with silicon- and tin-containing monomers increased, the change being highest for the organosilicon case for polypropylene substrate; for the organotin case as well as for other substrates the changes were much smaller.
2. Further modification of plasma-activated polyolefin surfaces by use of VTES-MA was shown to proceed mainly via esterification and polycondensation reactions, as traced by

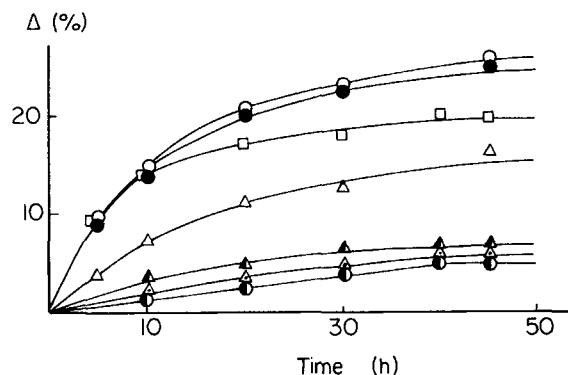


Figure 3 Plots of degree of swelling (Δ) vs time for (○) virgin PP film, (●) plasma-treated (in vacuum only) PP film, and the following organosilicon(tin) plasma surface modified films: (△) poly(VTES)/PP, (●) poly(HMDS)/PP, (▲) poly(APTS)/PP, (□) poly(TES)/PP, and (△) poly(HBDS)/PP; all in cyclohexanone at $20 \pm 0.1^\circ\text{C}$. Plasma conditions as in Figure 1.

the carboxyl and ethoxysilyl fragments, leading to crosslinked poly(organosiloxane) structures.

3. Swelling and FTIR experiments have shown that coats with highly polar organotin carboxylate groups were produced with much lower degrees of crosslinking, in the case of modification with organotin plasma.

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