Sulfur Containing Plasma Treatment for the Introduction of Thiol Groups onto Polyethylene Surfaces

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(Received November 7, 1995)

We propose a novel method of introducing thiol groups onto polymer surfaces of *e.g.* polyethylene by plasma treatment with sulfur-containing organic compounds. X-ray photoelectron spectroscopic analyses of the plasma treated surfaces are presented.

Plasma treatment is an important technique for modifying polymer surfaces while preserving the bulk properties of the polymer. For example, plasma treatment with ammonia,[1] nitrogen[2] or oxygen[3] improves the inert polymer surface's adhesion properties and its wettability. This is because hydrophilic functional groups such as amino, carboxyl, carbonyl, cyano and hydroxyl groups are introduced onto the surface. On the other hand, introduction of thiol (SH) group onto polymer surfaces by plasma treatment is a new type of surface modification. It was reported by Olsen *et al.*[4] that pyrolysis or photolysis of carbon disulfide *etc.* results in polymers comprising thiol groups. In Olsen's report, however, evidence for the existence of thiol groups consisted of IR spectra only and surface analyses were not carried out. Furthermore, very little has been reported regarding the introduction of thiol groups onto polymer surfaces using with plasma treatment. We report here in the introduction of thiol groups onto polymer surfaces by plasma treatment sulfur-containing compounds and the surface analysis of the resulting ones by X-ray photoelectron spectroscopy (XPS).

Experimental: Low-density polyethylene (PE) film was purchased from Scientific Polymer Products Inc. (Mw; 50000, Density; 0.92). All reagents were obtained from Wako or Aldrich. The plasma apparatus used was a reconstructed Ulvac EBH-6 incorporating a Pyrex glass reaction chamber (300 mm long, 80 mmϕ) and an external inductive copper coil (3.5 turns, 50 mm long). A 10 MHz RF generator (Yaesu FT-7676X All Mode Transceiver), coupled to a matching network (Tokyo Hy-Power Antenna Coupler HC-200A) to minimize reflected power, was employed. A PE film (5 X 5 mm) was placed in the center of the reactor, 30 mm under the coil. The reactor was evacuated to a pressure of less than 5 X 10^{-5} Torr. Subsequently, materials for plasma treatment were introduced and plasma glow discharge treatment was carried out (40 W, 35 mTorr, 1 min). Gaseous material (*e.g.* hydrogen sulfide) was supplied from a cylinder at a rate of 15 $\mathrm{cm^3/min}$. Liquid material (*e.g.* ethanedithiol) was supplied from a reservoir at an approximate flow.

The reaction used to tag thiol groups for detection and quantification with XPS is given in Figure 1. The reagent was *p*-chloromercuribenzoic acid (CMB),[5] which is a reagent for the modification of thiol groups. This labeling method was developed by Everhart and Reilley.[6] The treatment is as follows; the sample was placed in a solution containing 0.1 M CMB and 0.2 M NaOH for 7 hours at room temperature. It was then washed with 0.2 M NaOH and immersed in 0.2 M NaOH for 2 hours. The sample was then washed with distilled water and immersed in water for 8 hours. The XPS measurements were performed with a Shimadzu ESCA-750 apparatus using a MgK_α source (8 kV, 30 mA) under high vacuum (< 10^{-7} Torr). The value of 284.6 eV for the carbon (C) 1s of polyethylene was used for calibration.[7] XPS measurements were carried out on two kinds of surfaces. One surface was thiolated (denoted by PE-Pl) and the other was first thiolated and subsequently treated with CMB (denoted by PE-Pl-CMB). The sensitivity factor[8] was C 1s=0.25, O 1s=0.66, S 2p=0.49 and Hg $4f_{7/2}$=3.15.

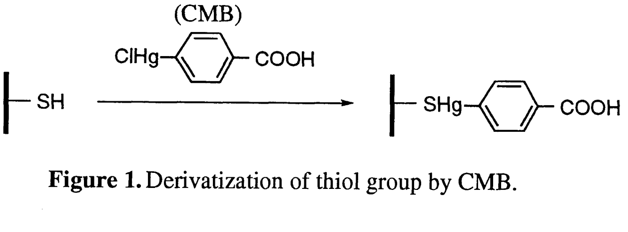

Figure 1. Derivatization of thiol group by CMB.

Table 1. XPS data for the polyethylene surface treated with sulfur containing plasma

plasma gas	PE-Pl-CMB[a] Hg/C	Hg/C[c] (calc)	PE-Pl[b] S/C	O/C	S2p[eV]
Hydrogen sulfide	0.028	0.093	0.27	0.14	163.5
Carbon disulfide	0.037	0.113	0.54	0.26	163.5
Dimethyl sulfide	0.010	0.097	0.30	0.12	163.2
Methyl disulfide	0.017	0.105	0.40	0.13	163.4
Ethanethiol	0.011	0.104	0.38	0.12	163.3
Ethanedithiol	0.047	0.071	0.14	0.20	163.4
Thiophene	0.009	0.090	0.19	0.13	163.3
Control	0.0006				

[a] Plasma treatment and subsequent modification by CMB.
[b] Plasma treatment only.
[c] $\mathrm{Hg/C(calc)} = \dfrac{\mathrm{S/C}}{1 + 7 \times \mathrm{S/C}}$.

Sulfur-containing compounds gas shown in Table 1 were investigated. Among those materials, only thiophene and carbon disulfide were polymerized under the plasma conditions. The properties of plasma polymerized films of thiophene[9] and carbon disulfide[10] have been previously reported. Other reagents were either not polymerized or the rate of polymerization was extremely slow, as shown by IR measurements (data not shown). That methyl mercaptan is difficult to polymerize was reported by Bradley and Hammes.[11] The results of the surface analyses are also shown in Table 1. The XPS spectra of all PE-Pl-CMB showed a mercury (Hg) 4f doublet peak ($4f_{5/2,7/2}$; ΔE=4 eV) around 100 eV while it was not observed in the control. This indicates that plasma treatment containing sulfur atoms can introduce thiol groups onto the polyethylene surface and these thiol groups are selectively modified by CMB.

Although it is possible that residual radicals exist on the surface after plasma treatment, the possibility of the reaction of those radicals and CMB is low because the most active radicals reacted with oxygen in the air after removal of the substrate from the reaction chamber. Note that in all cases an oxygen peak was observed (see PE-Pl in Table 1). If those radical reacted with CMB, there would not be the differences of the Hg/C values between kinds of plasma sources; for example the value Hg/C of ethanedithiol plasma treatment (0.047) is five times larger than that of thiophene plasma treatment (0.009). This is considered that the different amounts of radicals did not sustained but introduced the different amounts of thiol groups; the specific reaction of the thiol groups and CMB occurred.

"Hg/C(calc)" in Table 1 is the value calculated from the S/C ratio of PE-Pl, assuming that all sulfur atoms existed in the form of thiol groups and that they were all modified by CMB (see footnotes in Table 1). However, all Hg/C values were less than those of Hg/C(calc). Apart from incomplete derivatization, one reason is that the sulfur atoms were not always in the form of thiol groups; the chemical shifts of sulfur 2p in Table 1 are near those of the thiol group[7] and C-S-C;[7] it is considered that not only thiol groups but also sulfide "C-S-C" structures exist on the surface; this is reasonable because the plasma process is complicated and includes extremely energetic many kinds of excitations. Another reason is that only thiol groups on the "surface" were modified while those in the "bulk" were not; the surface sensitivity of XPS is *ca.* 10-30 Å.[8] In our study, plasma treatment with ethanedithiol is the best method for the introduction of thiol groups. However, it is difficult to explain the mechanism because the plasma process is complicated; there are many kinds of active species and those contain both homogenous and heterogeneous processes. One hypothetical representation of the introduction of thiol groups is shown in Figure 2. The material *e.g.* ethandithiol is converted to radical species by plasma activation; it is known that the main active species in plasma-polymerization are radicals.[12] The polyethylene surface is activated and the radical species react with the surface (see Figure 2). What radical species are actively produced depends on the reagent. The different amount of thiol groups introduced is related to the amount of the radical species having terminal thiol groups. According to our experiments, there are the most of the excited species having thiol groups in the ethanedithiol plasma.

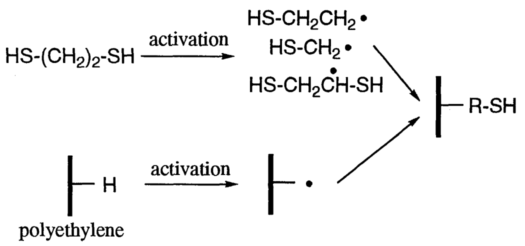

Figure 2. An hypothetical representaion of introduction of thiol groups.

We would like to thank Dr. Tatsuro Hanajiri and Mr. Yoshiya Matsumoto for their helpful discussions and technical assistance. We also thank Mr. Stephen Barker and Dr. Scott McNiven for assistance with the manuscript. This work was supported by Japan Society for the Promotion of Science Research Fellowships for Young Scientists 4184.

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