Analysis of Polyethylene Surface Sulfonation

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SYNOPSIS

Attachment of —SO_3H groups onto the surface of polymers by treatment with fuming sulfuric acid is a well-known procedure. In the present study we compare the number of —SO_3H groups per unit area measured by a number of methods including weight gain, thickness, FT-IR transmittance spectra, FT-IR surface spectra with ATR method, sodium exchange, and pH measurement of water in contact with the polymer surface. It can be shown that, under the chosen conditions, i.e., room temperature and 32% SO_3 in H_2SO_4, oxidation of PE is the main reaction, while sulfonation accounts for less than 20% of the weight gained during reaction. Differences in the reactivity of high density and low density polyethylenes are dicussed. Deprotonation in water compared with H^+/Na^+ exchange indicates a poor penetration of sodium ions into deeper layers of the polymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The sulfonation of polymers is a common procedure to change the properties of their surfaces from hydrophobic to hydrophillic, which is desirable for many very diversified applications, reaching from electrochemical to medical. Polyethylene, as one of the chemically simplest and ecologically cleanest polymers, has earned special interest. In our studies we aim not only for surface sulfonation but also for penetration of given polymer films in order to form ionic channels for the purpose of solid polymer electrolyte (SEP) production.

Experimental

Polymer films of "high density polyethylene," HDPE, and "low density polyethylene," LDPE, were both treated with fuming sulfuric acid, 'oleum,' containing 32.5% by weight SO_3.

HDPE (Hoechst) was said to contain phosphite, phenol, and stearate as additives and traces of Al, Ti, and Cl as contamination resulting from the po-

lymerization catalyst. HDPE films had a nominal thickness of 20 μm; observed variations were +7, −9 μm. The commercial material was refluxed with chloroform for 24 h and carefully dried prior to sulfonation.

LDPE (Rheinische Kunststoffwerke Worms) contained unspecified "antioxidants" as additives. LDPE films had a nominal thickness of 80 μm; observed variations were +8, −12 μm. The commercial material was refluxed for 24 h with n-hexane, followed by another 24 h refluxing with tetrahydrofuran. Both HDPE and LDPE were submerged into fuming sulfuric acid at room temperature and normal atmospheric pressure. Reaction times ranging from 5 to 80 min were chosen, and the results of the two extreme reaction times will be shown below. After sulfonation we followed the rinsing procedure given by Bergbreiter.[1] Weight control was performed after drying at room temperature under reduced pressure.

Thicknesses were measured using a micrometer screw and were compared with the thickness computed from the fringe pattern of IR transmittance spectra. These computations were performed using a modification of the program RNJ 46 originally published by R. N. Jones[2]

FT-IR spectra were recorded on BRUKER IFS 88 and IFS 66 instruments. A SPECAC Pin 11.000,

Table I   Polymer Film Thickness

Material Sulfonation Time	Thickness, μm Mechanical	Thickness, μm Optical
HDPE 5 min	24	24.8
HDPE 80 min	23	20.76
LDPE 5 min	74	73.31
LDPE 80 min	74	73.2

25 reflections, ATR attachment was used, equipped with a 45 degree KRS-5 crystal.

pH was measured as follows: square pieces of polymer film, 3 by 3 cm, were submerged in 5 mL of distilled water. pH of the water was measured using a commercial microglass electrode before addition of the film and during 2 min after, until a constant value was reached.

RESULTS AND DISCUSSION

The thickness of the polyethylene films was measured before and after sulfonation. The latter estimate was confirmed by evaluation of interference fringe patterns of transmittance IR spectra. Agreement between mechanically and optically determined values is very good. The polymer film thicknesses for a typical set of experiments are collected in Table I. The thickness remained fairly constant through the sulfonation procedure and a net gain of weight was observed, see Table II. This indicates that oxidative cleavage does not lead to a substantial disintegration of the material, though the oleum took on a dark colour during reaction.

For both types of PE the treatment resulted in a gain of weight, as would be expected for the attachment of —SO_3H onto the surface, regardless whether it replaces —H, —CH_3, or —CH_2^-. The net weight gain after 80 min reaction time is 2% of the original

weight for HDPE and 4% for LDPE, despite the higher thickness of the latter, see Table II, column 2.

pH measurements revealed the number of protons released into the aqueous phase in contact with the polymer surface. The number of sulfonic acid groups per square cm was calculated assuming complete dissociation of sulfonic acid and mobility of H_3O^+ in both phases, the polymer and the aqueous phase. Carboxylic acid groups on the polymer would not contribute to the pH change because the pH of the test solution reached values well below 5, except for the HDPE sample after 5 min of sulfonation time. The maximum number of sulfonic acids groups estimated was $\gg 7 \cdot 10^{17}$ particles $\cdot$ cm^{-2}, or roughly 70 particles per every Å^2. A fairly close arrangement of this number of —SO_3^- groups per area would require approximately 1 to 2 μm thickness of the sulfonated layer. These estimates agree closely with the degree of sulfonation reported by Arribas,[3] who used a different sulfonation method. After 80 min reaction time they reached $\gg 9 \cdot 10^{17}$ particles $\cdot$ cm^{-2}, and their estimated penetration depth was 2 μm. Bergbreiter,[1] for comparison, estimated $5.7 \cdot 10^{14}$ particles $\cdot$ cm^{-2}. Considerably higher degrees of sulfonation were, to our knowledge, only reached by Arribas[3] after extended reaction times. Sulfonation corresponded to $\gg 3 \cdot 10^{18}$ particles $\cdot$ cm^{-2} and was, according to electron microscopy, penetrating up to 30 μm into the polymer.

Sodium ion exchange experiments in sodium hydroxide solution were performed to estimate the extent to which carboxylates had been formed on the polymers. Under these alkaline conditions, both —SO_3H and —COOH would form their Na$^+$ salts. Therefore, the difference between the amount of Na$^+$ and H$^+$ exchanged, column 3 in Table II, allows to estimate surface carboxylation. It is, however, very likely that Na$^+$ does not permeate into deeper layers of the polymers. This becomes very obvious if one compares the results of LDPE sulfonation

Table II   Sulfonation and Surface Ion Exchange Reactions

Material Sulfonation Time	Weight Before Sulfonation mg $\cdot$ cm^{-2}	Weight Net Gain mg $\cdot$ cm^{-2}	Weight Na$^+$ Exchange	Surface Reaction Na$^+$ Exchange mol $\cdot$ cm^{-2}	Surface Reaction H$^+$ Exchange mol $\cdot$ cm^{-2}	Surface Modification —SO_3H mg $\cdot$ cm^{-2}	Surface Modification Others mg $\cdot$ cm^{-2}
HDPE 5 min	1.0000	0.0056	0.0611	$2.8 \cdot 10^{-6}$	$2.8 \cdot 10^{-10}$	$2.28 \cdot 10^{-5}$	$5.57 \cdot 10^{-3}$
HDPE 80 min	1.0056	0.0222	0.0055	$2.5 \cdot 10^{-7}$	$4.3 \cdot 10^{-8}$	$3.50 \cdot 10^{-3}$	$1.87 \cdot 10^{-2}$
LDPE 5 min	3.1111	0.0056	0.0222	$1.0 \cdot 10^{-6}$	$7.5 \cdot 10^{-8}$	$6.06 \cdot 10^{-3}$	$-4.60 \cdot 10^{-4}$
LDPE 80 min	2.9278	0.1222	0.0389	$1.8 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$	$9.61 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$

Table III IR Results: Peak Area Relative to $\delta_s CH_2$ of PE at 1370 cm^{-1}

Material Sulfonation Time	ν_s SO$_3^-$ at 1040 cm^{-1} Film Absorbance	ν_s SO$_3^-$ at 1040 cm^{-1} Surface ATR	ν_{as} SO$_3^-$ at 1170 cm^{-1} Film Absorbance	ν_{as} SO$_3^-$ at 1170 cm^{-1} Surface ATR	δ H$_2$O at 1630 cm^{-1} Film Absorbance	δ H$_2$O at 1630 cm^{-1} Surface ATR
HDPE 5 min	0.18	7.83	0.36	9.38	0.13	n.d.
HDPE 80 min	2.22	14.47	3.61	9.66	n.d.	5.18
LDPE 5 min	0.045	5.98	0.045	5.60	0.065	n.d.
LDPE 80 min	2.01	19.15	5.83	26.83	0.86	6.94

n.d. = not detected or not determined.

after 5 and 80 min. Surface sulfonation seems to be nearly complete after 5 min, while during extended reaction times (80 min) sulfonation in the bulk polymer begins. This is especially obvious if the IR spectroscopic observations (Table III) are also taken into account. After 5 min sulfonation there was more than a factor of 100 between surface and bulk, after 80 min there was only a factor of 4 to 9. At the same time the total number of —SO$_3$H groups per square cm increased from $7.5 \cdot 10^{-8}$ to $1.2 \cdot 10^{-6}$ mol. It is easy to calculate from the given difference between refractive indices of KRS5 and PE that the ATR experiment penetrates the top 2 μm of the sample surface. We estimate that after 80 min reaction time the inner 20 μm of HDPE films averaged 2% of the —SO$_3^-$ concentration of the outer 2 μm layers, but for LDPE we estimate that the inner 69 μm average 9% of the —SO$_3^-$ concentration of the outer 2 μm layers, showing that sulfonation reaches the bulk material easier in LDPE than in HDPE. Cleavage becomes a very competitive side reaction for LDPE. During the first 5 min of reaction there is more weight lost by cleavage than weight gained by sulfonation and oxidation; the position in the last column of Table II becomes negative! During extended reaction time there are either no more tertiary carbons left near the surface or they loose reactivity because of the proximity of negatively charged —SO$_3$H groups. Oxidation, then, becomes more important than cleavage.

There are important differences in the molecular structure and, hence, also in solid-state packing between HDPE and LDPE that explain the above findings. HDPE consists, to a high degree, of long hydrocarbon chains that form parallel bundles and give large regions of the solid a crystalline character. Due to the polymerisation conditions, LDPE contains a great number of irregularly branched chains that oppose a systematically ordered arrangement and decrease the crystallinity of the solid. These structural differences give rise to the different sulfonation behavior of HDPE and LDPE. The reaction of H$_2$SO$_4 \cdot$ SO$_3$ with PE is not understood in detail, but the general rules for reactivity of primary, secondary and tertiary carbon atoms of aliphatic hydrocarbons can be applied. Oxidation of —CH$_2$ and —CH$_3$ results in formation of surface functions such as alcohols, ketones, aldehydes, and carboxyles followed by C—C cleavage and CO$_2$ evolution. These reactions are in competition with the insertion of SO$_3$ into primary C—H bonds according to the schematic reaction proposed by Olson and Osterhaas[4]:

$$|\text{---}|\text{-CH}_3 \; \text{---> } (+\text{H}_2\text{SO}_4.\text{SO}_3) \; \text{---> } |\text{---}|\text{-CH}_2\text{-SO}_2\text{OH} .$$
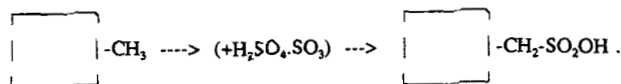
From a critical comparison of all the numbers in Table II, a more detailed explanation of the reaction of oleum with polyethylene can be given. On HDPE, oxidation products account for at least 80 to 90% of the weight gain. This is the lower limit, because the weight loss by cleavage is not known. After 5 min reaction time the observed net weight gain is approximately the same for HDPE an LDPE, but the number of sulfonic acid groups is more than two orders of magnitude higher on LDPE. As outlined above, on LDPE cleavage is very important for short reaction times. Our observations support the following mechanistic arguments: (a) sulfonation takes place preferably at —CH$_3$ end groups. This explains the higher sulfonation numbers of LDPE compared with HDPE, because the former contains a larger amount of branched chains. (b) The most reactive sites are tertiary carbon atoms at chain-branching positions. These are the ones that are first attacked for oxidation followed by cleavage.

Hence, the high Na$^+$ exchange rate on LDPE al-

ready after 5 min sulfonation time, and the 'negative number' for the estimated weight of oxidation products. With HDPE cleavage is not so important. There are only few branched chains. However, when cleavage does occur, a longer part of the chain is lost. This might explain the observed shrinking of HDPE films with prolonged sulfonation time.

Sulfonation experiments with polypropylene[5] confirm the above suggestions. Polypropylene is a model for a regularly branched hydrocarbon polymer with one $-CH_3$ side chain per repetition unit. While all these $-CH_3$ end groups are locations for easy sulfonation, the polymer can also readily been cleaved, because every second C atom on the backbone is a tertiary carbon, apt for cleavage. Reaction with 32.5% oleum for 80 min caused a weight loss of 0.17 mg $\cdot$ cm^{-2} (approx. 10%), while H$^+$ exchange confirmed the presence of $1.7 \cdot 10^{-7}$ mol $\cdot$ cm^{-2} $-SO_3H$ groups.

REFERENCES

1. D. E. Bergbreiter and K. Kabza, *J. Am. Chem. Soc.*, **113**, 1447 (1991).
2. D. G. Cameron, J. P. Hawranek, P. Neelakantan, R. P. Young, and R. N. Jones, Program RNJ46A "determination of optical constants from absorbance measurements on thin liquid films," NRC of Canada, Ottawa Bulletin #16; Modified by J. E. Bertie and C. D. Keefe to run under MS-DOS; Modified by H. H. Eysel in order to interactively remove fringes over a limited range of the spectrum.
3. C. Arribas and D. R. Rueda, *Makromol. Chem.*, **192**, 491 (1991).
4. A. Olsen and A. J. Osteraas, *J. Polym. Sci., Part A-I*, **7**, 1921 (1969).
5. D. Fischer and H. H. Eysel, unpublished.