

# Study of Sulfonation Mechanism of Low-Density Polyethylene Films with Fuming Sulfuric Acid

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Received 30 December 2002; accepted 14 July 2003

**ABSTRACT:** Sulfonation of low-density polyethylene (LDPE) films with fuming sulfuric acid was studied by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance (ATR) infrared spectroscopy. The ATR spectra showed the formation of C=C double bonds and multiple sulfur atom containing groups for the sulfonation of LDPE films. This led us to propose that the abstraction reaction of hydride ion by sulfur trioxide (SO<sub>3</sub>) in fuming sulfuric acid might account for the formation of the C=C double bonds. It was considered that after the abstraction reaction, these

double bonds react with SO<sub>3</sub>, resulting in the production of alkene sulfonic acids and sultones, along with the formation of sulfate groups as a result of reaction of the double bonds with sulfuric acid. Experimental data by treatment of the sulfonated LDPE films with KOH and thiourea supported the proposed idea, estimating the approximate molar ratio of the products. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2435–2442, 2004

**Key words:** surfaces; modification; polyethylene (PE)

## INTRODUCTION

Surface modification of polymers is of great interest due to the possibilities of their application to functionalization of polymers.<sup>1</sup> Much work with the use of various materials has been done on surface modification of polymers until now. Among polymer materials, in particular, surfaces of polyolefins are nonpolar and very inert, and various surface modification methods have been tried to improve the surface properties.<sup>2,3</sup>

One of them is sulfonation, which has been employed for the improvement of the properties such as adhesion and wettability, changing the hydrophobic surfaces to hydrophilic ones. Sulfonation has several commonly used methods including treatments with gaseous SO<sub>3</sub>,<sup>4,5</sup> hot concentrated sulfuric acid,<sup>6,7</sup> and fuming sulfuric acid.<sup>8,9</sup> With that interest, there have been several attempts to understand the mechanism of the sulfonation of polyolefins. Ihata presented using IR, UV, and Raman spectroscopies that the sulfonation of polyethylene (PE) films with gaseous SO<sub>3</sub> produced sulfonic acids and that with the reaction proceeding the elimination of sulfonic acid groups occurred to form polyene sequences.<sup>4</sup> Idage et al. revealed mainly by use of X-ray photoelectron spectroscopy (XPS) that

the sulfonation of PE films with a gaseous mixture of SO<sub>3</sub> and N<sub>2</sub> showed the formation of sulfonic acids, sulfates, keto, and polyene sequences.<sup>5</sup> Both of them proposed the idea that SO<sub>3</sub> reacted with PE films via radical reactions on the sulfonation. On the other hand, as for the sulfonation of polypropylene, Tada et al. concluded using IR and X-ray photoelectron spectroscopies and molecular orbital calculations that S atoms acting as an electrophilic center reacts with negatively charged C atoms of polypropylene through electrophilic addition of SO<sub>3</sub> in a way similar to aromatic compounds.<sup>7</sup> Although the electrophile varies with the reagent in the reaction system, it is considered that SO<sub>3</sub> is involved in all cases. SO<sub>3</sub> in fuming sulfuric acid is a superacid, which may react with alkanes by hydride abstraction. We applied the idea of reactivity of SO<sub>3</sub> as a superacid to the explanation of sulfonation mechanism of LDPE films with fuming sulfuric acid. In addition, both Ihata and Idage indicated that sulfonation by their experiments involves the formation of C=C double bonds and we confirmed that sulfonation with fuming sulfuric acid in our experiments also gave rise to C=C double bonds. That being the case, reaction of C=C double bonds with SO<sub>3</sub> was carefully examined by reference to reactions of olefins having C=C double bonds with SO<sub>3</sub>, because the reaction is likely similar to the ones of the olefins.

This article presents sulfonation of PE films with fuming sulfuric acid and the mechanisms with due

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consideration of the characteristics of  $\text{SO}_3$  in sulfuric acid.

## EXPERIMENTAL

### Materials and sulfonation procedure

Low-density polyethylene (LDPE) films (30  $\mu\text{m}$  thick, UBE Industries, Ltd., Japan) were used for sulfonation without any pretreatment. The films were soaked in fuming sulfuric acid (10% weight percentage  $\text{SO}_3$ , Wako Pure Chemical Industries, Ltd., Japan) at 60°C for the desired time. The films were quenched in concentrated  $\text{H}_2\text{SO}_4$  (98% weight percentage  $\text{H}_2\text{SO}_4$ , Wako Pure Chemical Industries, Ltd., Japan), rinsed in  $\text{H}_2\text{SO}_4$  aqueous solutions and then distilled water, air-dried at 25°C for 24 h, and stored in the dark in a desiccator.

### X-ray photoelectron spectroscopy

XPS spectra were measured with a JEOL JPS-9010MX photoelectron spectrometer using  $\text{MgK}\alpha$  ( $h\nu = 1253.6$  eV) radiation at 100 W (10 kV, 10 mA). All spectra were collected at an electron take-off angle of 45° with respect to the surface and a pressure of less than  $10^{-7}$  Pa. The spectra peak shift due to the surface charging was corrected by setting the binding energy of C1s to 285.0 eV.

### Fourier transform infrared measurements (FTIR)

Attenuated total reflectance (ATR) infrared spectroscopic experiments were conducted using a Nicolet Magna 560 FTIR spectrometer equipped with a Spectra Teck ARK Model 12 single-beam internal reflection attachment. The reflection element was ZnSe with 45° face angles. The sample compartment was purged with dry air for 5 min before spectra were recorded.

### Contact angle measurements

Contact angles for water drops on treated polymer films were measured by using a Kyowa Kaimenkagaku goniometer Model CA-S Micro II. Sessile drops

TABLE I  
Contact Angles of LDPE Films Sulfonated for  
0 through 80 min

Sample	Contact angle (deg)
0 min	$85 \pm 3$
5 min	$55 \pm 4$
10 min	$48 \pm 4$
20 min	$44 \pm 3$
80 min	$34 \pm 3$

TABLE II  
Elemental Concentrations on Sulfonated LDPE Films

Sample	O/C	S/C	O/S
0 min	0.01	—	—
5 min	0.15	0.046	3.3
10 min	0.18	0.051	3.5
20 min	0.23	0.063	3.6
80 min	0.30	0.081	3.7

of distilled water were placed on the films by a syringe and for each sample the average of five consecutive measurements was noted.

### Treatment with thiourea and KOH

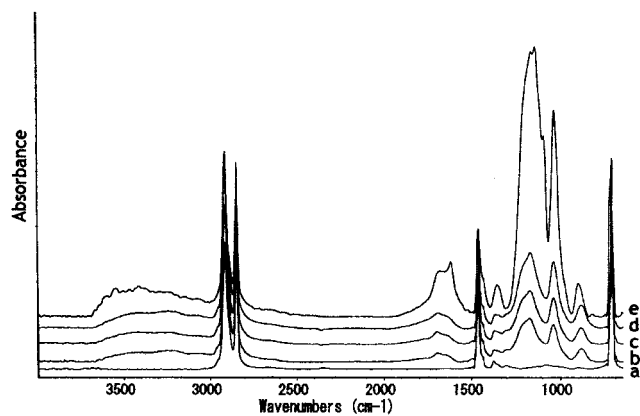
Sulfonated LDPE films were treated with thiourea in ethanol reflux for 2 h. After the reaction, the films were extracted and washed with ethanol and then dried at room temperature. The sulfonated LDPE films were also treated with 0.5N KOH at 40°C for 2 h. After treatment, the films were washed with distilled water and dried at room temperature.

## RESULTS AND DISCUSSION

### Contact angle and X-ray photoelectron spectroscopy results

Contact angle data and elemental concentrations data from XPS measurements for the sulfonated LDPE films are given in Tables I and II, respectively. The contact angles of sulfonated LDPE films significantly decrease after 5 min, and then the decrease rate gradually falls over the period of 80 min. This indicates that sulphonation of the surface of LDPE films has been carried out to some extent during the first 5 min and continues for up to 80 min.

The elemental concentrations were calculated by integrating the area of the atom peaks. It can be seen that because the S/C ratios in the sulfonated LDPE films are still increasing at the 80-min mark, it is clear that the reaction has still continued. Thus, the decrease in contact angles and the incorporation of sulfur atoms demonstrate that the sulfonation has proceeded with the reaction time proceeding over the period to 80 min. The XPS data prove that the S/C ratios in the sulfonated LDPE films during the 5- to 80-min reaction indicates that one repeat unit of 6 to 11 repeat units has a functional group containing a sulfur atom. The O/S ratios in the sulfonated LDPE films are always more than 3 through the sulfonation reaction. It is predicted that this is because not only has the sulfonation reaction proceeded, but the formation of sulfuric ester has occurred, as mentioned later in the mechanism section.



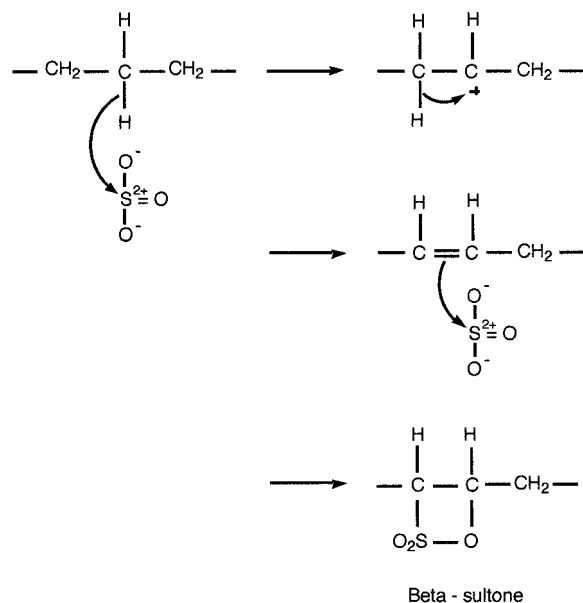
**Figure 1** ATR spectra of (a) LDPE films and LDPE films sulfonated for (b) 5 min, (c) 10 min, (d) 20 min, and (e) 80 min.

### ATR measurements results

Figure 1 shows a series of the ATR spectra of the sulfonated LDPE films before and after treatment with fuming sulfuric acid for 0 through 80 min. They indicate that significant changes in the surface of the sulfonated films took place. The assignments of the new band positions are listed in Table III. There are two absorptions related to O=S=O stretch in the region 1080–1250  $\text{cm}^{-1}$  and at 1040  $\text{cm}^{-1}$ . The intensity of the absorptions in both regions dramatically increases with the reaction time proceeding, compared to the increase rates in XPS, as shown in Table II. The penetration depth for the ATR-IR spectroscopy is a few micrometers for 45° face angles with ZnSe, while the one for XPS is a few nanometers for an electron take-off angle of 45°. From this difference of the penetration depths between them, the increase in the ATR spectra implies that sulfonation has occurred not only in the outermost surface, but in the deeper surface region of the PE films. It can be observed that the absorptions in the region of 1080–1250  $\text{cm}^{-1}$  have at least three peaks in the spectrum of the reaction period of 80 min. The presence of these peaks implies that there is a possibility of the formation of other functional groups having O=S=O stretch except for sulfonic acid groups and the possibility includes the formation of sultones and sulfate groups as discussed later in the mechanism section.

**TABLE III**  
Changes in the ATR Spectra of Sulfonated LDPE Films After Treatment with Fuming Sulfuric Acid

Wavenumber ( $\text{cm}^{-1}$ )	Vibration
900	S—O—C stretch
1040	O=S=O stretch
1080–1250	O=S=O stretch
1600–1700	C=C stretch
1680–1750	C=O stretch

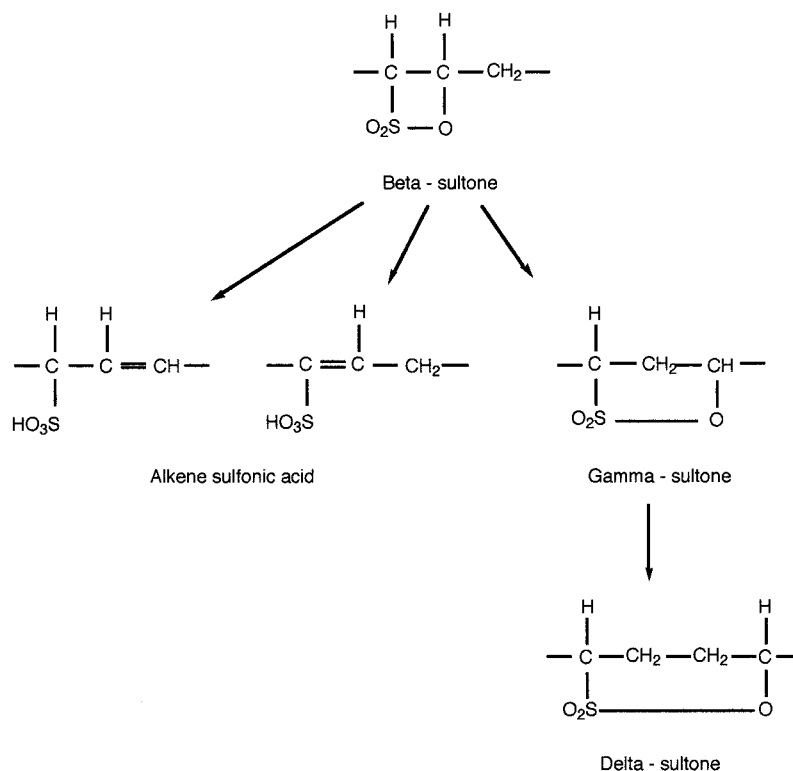


**Scheme 1**

The spectra in Figure 1 illustrate that there are two peaks in the region 1600 to 1750  $\text{cm}^{-1}$ . The higher wavenumber side peak can be assigned to ketones, aldehydes, or carboxylic acids, which probably were produced by the oxidation reaction in the sulfonation process. The lower wavenumber side peak can be attributed to C=C bonds, which were formed through sulfonation of LDPE films. It has been suggested that C=C bonds would be formed by the desulfonation after the formation of sulfonic acid.<sup>4,5</sup> Cameron et al.<sup>6</sup> advanced the sulfonation-desulfonation mechanism, indicating that sulfonic acid groups are thermally unstable in the region of 100°C. Given that the sulfonation reaction temperature of this experiment was 60°C, it is not reasonable to assume that C=C bonds were generated chiefly by desulfonation in the reaction system. In addition to that, considering the results that the intensity in the region 1600–1750  $\text{cm}^{-1}$  and S/C ratios in the XPS data in Table II increased with the reaction time proceeding, there might be a different mechanism on sulfonation of LDPE.

### Mechanism of the sulfonation

Fuming sulfuric acid ( $\text{H}_2\text{SO}_4\text{-SO}_3$ ) is a superacid, which is defined as any acid stronger than 100% sulfuric acid. Superacids are so strong that they can protonate such extremely weak bases as the alkanes.<sup>10,11</sup> In reaction with LDPE films, it can be assumed that sulfur trioxide in fuming sulfuric acid abstracts hydride ion from polyethylene, resulting in the generation of carbocations; the mechanism may be shown in Scheme 1. This mechanism may apply to reaction with polyolefins such as polypropylene in the same man-



Scheme 2

ner. The order of stability is tertiary > secondary > primary among simple alkyl carbocations. According to the stability order, it is considered that in the case of polypropylene, hydride ion is abstracted by  $\text{SO}_3$  most readily from tertiary and least readily from primary positions.

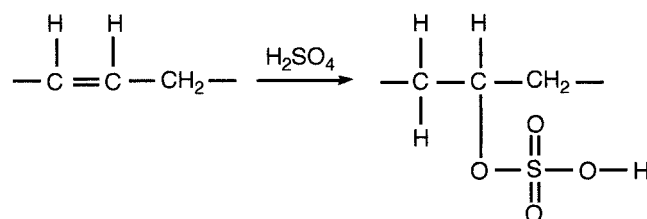
Immediately after the abstraction of hydride ion from polyethylene, it can be assumed that the formation of double bonds occurs on the carbocation site by the loss of a proton from the adjacent methylene carbon. This can account for the generation of  $\text{C}=\text{C}$  bonds of LDPE films in the ATR spectra. Because the  $\pi$  electrons of double bonds are a nucleophilic site that reacts with electrophiles, it is predicted that another  $\text{SO}_3$  attacks these newly formed double bonds and then carbon-sulfur bonds are formed as shown by the reaction sequence in Scheme 1. The electrophilic addition of  $\text{SO}_3$  would proceed through a 2+2 concerted cycloaddition reaction, resulting in the formation of  $\beta$ -sultone. In fact, in the case of low molecular weight compounds such as C14-18  $\alpha$ -olefins, the idea is well-established that  $\text{SO}_3$  reacts with  $\text{C}=\text{C}$  bonds, resulting in the formation of  $\beta$ -sultone.<sup>12,13</sup>  $\beta$ -Sultone is known to be unstable and produce more stable sultones ( $\gamma$ - and  $\delta$ -sultones) and alkene sulfonic acids after rearrangement in the manner shown in Scheme 2.<sup>14,15</sup> However, it should be noted that there is a possibility of the formation of other products which cannot be accounted for by sulfonation products (sulfonic acid

groups, sultones, sulfate groups) in the same way as the case of  $\alpha$ -olefin sulfonation.<sup>14</sup>

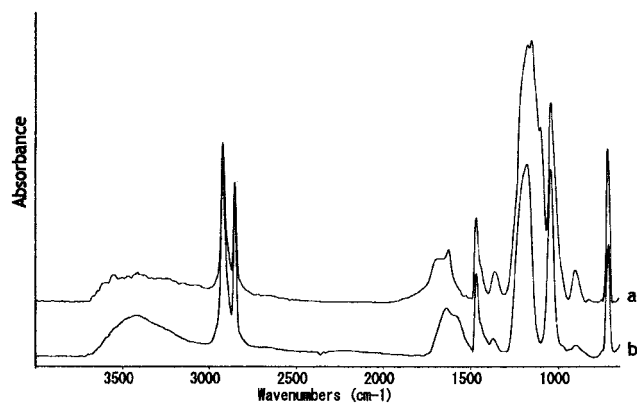
In addition to the electrophilic addition of  $\text{SO}_3$ ,  $\text{C}=\text{C}$  double bonds can react with sulfuric acid as a plausible side reaction in this system where fuming sulfuric acid ( $\text{H}_2\text{SO}_4\text{-SO}_3$ ) is used, to yield alkyl hydrogen sulfate as shown in Scheme 3.<sup>16</sup> The reaction of  $\text{C}=\text{C}$  double bonds with sulfuric acid can be a competing reaction against the one with  $\text{SO}_3$ . However, considering the degree of activities of sulfuric acid and  $\text{SO}_3$  as electrophiles, it is expected that the reaction with  $\text{SO}_3$  would proceed faster than with sulfuric acid.

#### Treatment of sulfonated LDPE films with KOH

To confirm the formation of sultones in sulfonation of LDPE films with fuming sulfuric acid, LDPE films sulfonated for 80 min were treated with 0.5N KOH at



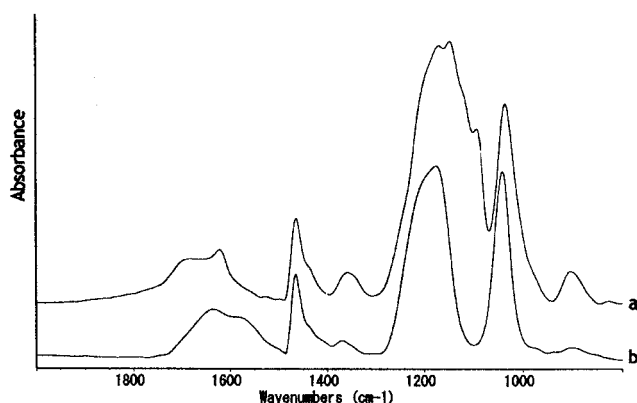
Scheme 3



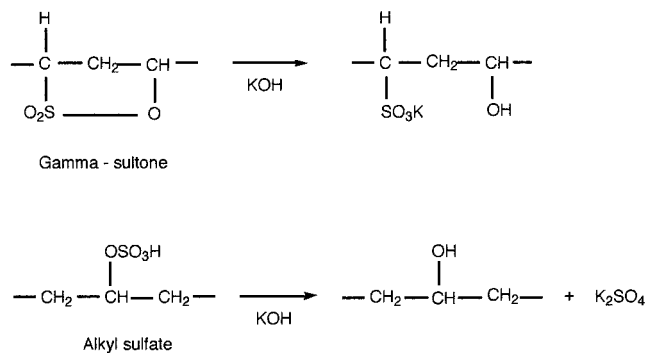
**Figure 2** ATR spectra of (a) sulfonated LDPE films (for 80 min) and (b) sulfonated LDPE films (for 80 min) treated with KOH.

40°C for 2 h. The films were characterized by ATR IR spectroscopy and XPS after the treatment. Figure 2 shows the whole region of the ATR spectra of the sulfonated LDPE films before and after treatment with KOH and Figure 3 shows the narrow region 650–2000  $\text{cm}^{-1}$ . Clearly, there are several remarkable changes between the two spectra. At first, absorptions near 900  $\text{cm}^{-1}$ , which are attributed to S—O—C stretches in sultones, decrease, which raises the possibility of fission of the carbon—oxygen bond in S—O—C bonding by the attack of KOH, as shown in Scheme 4.

Though there seems to be at least three peaks in the range 1080–1250  $\text{cm}^{-1}$  in the spectra which can be attributed to O=S=O stretching, after the KOH treatment, two of the three peaks disappeared and only one broad peak which might be made of multiple peaks at 1180  $\text{cm}^{-1}$  remained. This indicates the possibility of the formation of sulfonic acid groups from sultones and the elimination of sulfate groups as a result of the treatment. Additionally, absorptions near 3400  $\text{cm}^{-1}$  which can be attributed to O—H stretches



**Figure 3** ATR spectra (the narrow range 650–2000  $\text{cm}^{-1}$ ) of (a) sulfonated LDPE films (for 80 min) and (b) sulfonated LDPE films (for 80 min) treated with KOH.



**Scheme 4**

increases, which implies that hydroxyl groups of KOH would bond to C-atoms of S—O—C bonding of sultones and sulfate groups after reaction with KOH. This result supports the expectation of the formation of sulfonic acid groups from sultones and the elimination of sulfate groups in treatment with KOH.

Last, there is a newly formed peak at 1580  $\text{cm}^{-1}$ . This is likely because carboxyl groups which can be prepared through the oxidation in the sulfonation process were converted to the anion forms from the free acid forms with the KOH treatment and due to the resulting form changes the absorptions of the carboxyl groups shifted from 1680–1750  $\text{cm}^{-1}$  to near 1580  $\text{cm}^{-1}$ . Eysel has reported that oxidation occurs in addition to sulfonation in treatment of LDPE films with fuming sulfuric acid, resulting in formation of carboxyl groups, ketones, and aldehydes.<sup>9</sup>

The elemental composition and concentration data obtained from XPS measurements for the sulfonated films before and after treatment with KOH are given in Tables IV and V. The data presented in Table V show that after the KOH treatment, the S/C ratio decreased from 0.081 to 0.066, indicating the elimination of sulfur-containing groups, while the O/C ratio decreased from 0.30 to 0.26, suggesting the elimination of O-atom-containing groups. It is not likely that the elimination of S-atom-containing groups such as sulfonic acid groups or sultones occur easily under the conditions of the 0.5N KOH treatment at 40°C for 2 h. Because it is known that alkyl sulfate can be easily

**TABLE IV**  
Elemental Composition on Sulfonated LDPE Films Before and After Treatment with KOH and Thiourea

Sample	C (%)	O (%)	S (%)	N (%)
A	72.5	21.6	5.9	—
B	74.8	19.4	4.9	0.9
C	69.2	20.4	6.8	3.6

(A) sulfonated LDPE film (for 80 min), (B) sulfonated LDPE film (for 80 min) treated with KOH, (C) sulfonated LDPE film (for 80 min) treated with thiourea.

**TABLE V**  
**Elemental Concentrations on Sulfonated LDPE Films**  
**Before and After Treatment with Thiourea or KOH**

Sample	O/C	S/C	O/S
A	0.30	0.081	3.7
B	0.26	0.066	4.0
C	0.29	0.098	3.0

(A) sulfonated LDPE film (for 80 min), (B) sulfonated LDPE film (for 80 min) treated with KOH, (C) sulfonated LDPE film (for 80 min) treated with thiourea.

Note. The ratios of atoms were calculated based on the values in Table IV.

hydrolyzed in alkali solution, it is likely that the treatment with KOH caused the elimination of sulfate groups produced in the sulfonation. From the amount of S decreased from 5.9 to 4.9% as shown in Table IV, it is assumed that the amount of sulfate groups produced in the sulfonation is about 1% and the ratio of sulfate groups to sulfonic acid groups and sultones would be approximately 1 to 4.9.

#### Treatment of sulfonated LDPE films with thiourea

A further experiment was performed to verify the formation of sultones in the sulfonation by treating the sulfonated LDPE films (80 min) with thiourea in ethanol reflux. After the treatment, the ATR and XPS spectra of the films were measured. Figure 4 shows the ATR spectra of the sulfonated LDPE films before and after treatment with thiourea. They reveal that there are several major changes in the films after treatment. Similar to the case of the KOH treatment, after treatment with thiourea there is a decrease of peak near  $900\text{ cm}^{-1}$  assigned to S—O—C stretches in sultones. This demonstrates that the thiourea treatment caused the cleavage of the carbon—oxygen bond in S—O—C bonding, as shown in Scheme 5. Because the peak near  $900\text{ cm}^{-1}$  has become small but still present, it is likely that the reaction has not been completely finished.

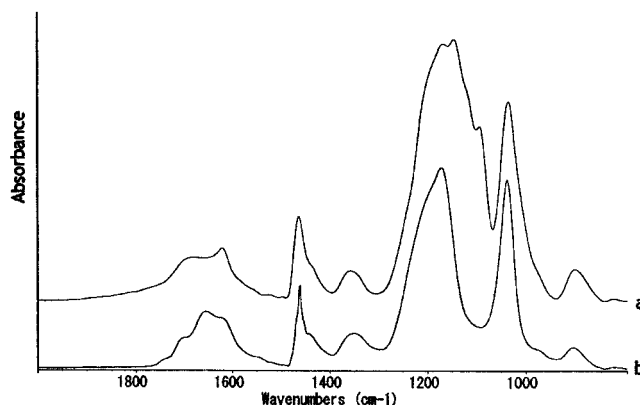
In addition, it can be seen that a new peak is formed at  $1655\text{ cm}^{-1}$ . C=C double bond containing compounds and primary amines are known to show characteristic C=C stretching absorptions and N—H bending absorptions, respectively, in the range  $1600\text{--}1700\text{ cm}^{-1}$ . In the assignment of this new peak, it is not likely that more C=C double bonds were produced in the reaction with thiourea. It seems reasonable to think that thiourea was bonded to the sulfonated LDPE films through the reaction shown in Scheme 5 and the peak at  $1655\text{ cm}^{-1}$  can be attributed to N—H bending absorptions of primary amines in thiourea.

The ATR spectra of the films also show that there are at least three peaks in the range  $1080\text{--}1250\text{ cm}^{-1}$  before treatment. These strong absorptions in this range correspond to O=S=O stretching. As mentioned in the

mechanism section, it can be assumed that sulfonation of LDPE films with fuming sulfuric acid gives rise to sulfonic acid groups, sultones, and sulfate groups as O=S=O-containing products. Accordingly, we assumed that the peaks in the range  $1080\text{--}1250\text{ cm}^{-1}$  can be assigned to one of these groups. As a matter of fact, attempts were made to assign these peaks in the range  $1080\text{--}1250\text{ cm}^{-1}$  by measuring standard materials and by referring to spectra data books.<sup>17,18</sup> Nevertheless, it was too difficult to distinguish the peaks observed in the region, because all those compounds have strong absorptions in this range. The spectra after the thiourea treatment indicate that the number of the peaks decrease in the region  $1080\text{--}1250\text{ cm}^{-1}$  and there seems to be only a broad peak which would comprise more than one peak at  $1180\text{ cm}^{-1}$ . We believe that this is because the reactions of sultones and sulfate groups with thiourea give rise to the formation of sulfonic acid groups and the elimination of sulfate groups, respectively, and for this reason the original peaks of sultones and sulfate groups disappear.

Figure 5 shows the XPS spectra of the films after treatment with thiourea. This region shows chemical shifts of N(1s) and the binding energies range from 399 to 406 eV. It can be seen that there is a newly produced peak near 400 eV where no peaks were present before the treatment. When we take the expected reaction of sulfonated LDPE films with thiourea into account, it seems appropriate to suppose that this peak near 400 eV can be attributed to chemical shift in amine originated from thiourea bonded to sulfonated LDPE films in C—S bonding, as shown in Scheme 5.

Chemical shifts of S(2p) of the sulfonated films before and after treatment with thiourea are given in Figure 6. S(2p) spectrum of (a) sulfonated films displays the presence of one broad peak in the range 167 to 171 eV and its chemical shift can be attributed to S(2p) binding energies for sulfur—oxygen bonds in sulfonic acid groups, sultones, and sulfate groups.



**Figure 4** ATR spectra of (a) sulfonated LDPE films (for 80 min) and (b) sulfonated LDPE films (for 80 min) treated with thiourea.



of a sulfate group, but the molar quantity of N increases at 2 mol. When we take the fact that there is a 1-mol increase of S element in a sultone and no increase of S in a sulfate group by treatment with 1 mol thiourea into consideration, the data in Table 4 that the amount of S increases from 5.9 to 6.8%, at 0.9% after the treatment indicate that the quantity of sultones produced in the sulfonation would be this increment: 0.9%. Because the total percent of sulfonic acid groups and sultones is 4.9% as calculated in the KOH treatment section, the ratio of sultones to sulfonic acid groups would be 0.9 to 4.

Moreover, from the fact that the ratio of the peak at 168.5 eV to the one at 164.5 eV is 5 : 1, the amount of S element of the peak at 164.5 eV is 1.13% by the following calculation:  $6.8\% \times 1/(1 + 5) = 1.13\%$ , where 6.8% is the S amount of sulfonated LDPE films(80 min) treated with thiourea, as shown in Table 4. Because the S amount of thiourea bonding to sultones is 0.9%, the S amount of thiourea bonding to sulfate groups would be 0.23% by subtracting 0.9% from 1.13%. This indicates that as a whole 23% of sulfate groups reacted with thiourea, while 77% of them remained unchanged in the thiourea treatment by the calculation:  $1\% - 0.23\% = 0.77\%$ , because total amount of S of sulfate groups is 1%, as estimated in the KOH treatment section.

In addition to that, considering that the molar quantity of N element increases at 2 mol in both cases of sulfonic acid groups and sulfate groups by the addition of 1 mol thiourea, the increment of N should be double as the amount of S at 164.5eV. Because the amount of S at 164.5 eV is 1.13%, the increment of N is supposed to be around 2.26%. However, as can be seen from Table IV, the actual amount of N is 3.6%, which is about 1.3% higher than the expected value (2.26%). This discrepancy could be due to the finding that N<sub>2</sub> molecules have been attached to the sulfonated LDPE films by adsorption, because there is the possibility that the films were in contact with air for a long period, as described in the report by Tada et al.<sup>7</sup> In fact, XPS spectra in the KOH treatment showed the presence of 0.9% N which was not supposed to be present through the KOH treatment process. We assume that the presence of N after the KOH treatment would be because of the same reason.

In summary, the approximate molar ratios of those S-containing groups produced in the sulfonation reaction may be calculated as follows: sulfonic acid groups : sultones : sulfate groups = 4 : 0.9 : 1. However, it should be noted that the ratios of sultones or sulfate groups to sulfonic acid groups might rise to some extent, owing to the possibilities that the reaction of sultones or sulfate groups with thiourea or KOH have not been finished completely.

## CONCLUSIONS

The characterization of sulfonation of LDPE films with fuming sulfuric acid by XPS and ATR IR spectroscopy

indicated the possibility of the formation of sultones and sulfate groups in addition to sulfonic acid groups. With the results of the ATR and XPS analysis, we demonstrated that sulfonation of LDPE films may be explained by the application of superacid reaction to alkanes with consideration of the characteristics of SO<sub>3</sub> in sulfuric acid as a superacid. In sulfonation of LDPE films with fuming sulfuric acid, it was assumed that SO<sub>3</sub> abstracts hydride ion from polyethylene, forming a C=C double bond. After that, it was predicted that the double bond reacts with sulfur trioxide, resulting in the formation of stable sultones and alkene sulfonic acid after rearrangement and that as a side reaction double bonds might react with sulfuric acid, yielding sulfate groups. To verify the formation of sultones and sulfate groups, treatment of sulfonated LDPE films with KOH and thiourea were performed, respectively. The data analysis of those treatment proved the presence of sultones and sulfate groups as well as sulfonic acid groups and quantified these sulfur-containing groups, providing the approximate molar ratio.

We thank M. Komatsuzaki for helpful discussions with regard to surface analysis of films by using ATR technique.

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