

# A Fluorine Gas Monitoring System for the Direct Oxy-Fluorination of Polyethylene Sheets

Toshi Kasai, Tetsuya Aya, Hidehiko Ohara

Mitsubishi Chemical Corporation, Tsukuba Research Center, Chuou 8-3, Amimachi, Inashiki-gun, Ibaraki 300-0332 Japan

Received 21 September 2000; accepted 14 November 2001

**ABSTRACT:** A new technique is presented to measure the concentration of fluorine in a reaction gas consisting of fluorine, nitrogen, and oxygen in a reaction chamber. The method is described as follows: The gas is directly taken from the chamber using a peristaltic pump and dissolved in a TISAB (total ionic strength adjusted buffer) solution. The concentration of fluorine ion is measured using the selected fluorine ion electrode, the output voltage of which is monitored. The concentration of the fluorine ion and the output voltage follow the Nernst relation so that the measurement of the output voltage of the system enables us to know the concentration of fluorine gas. This technique was applied to

monitor the concentration of fluorine gas in the chamber in which a sheet of polyethylene nonwoven fabric was continuously oxy-fluorinated. The monitored concentration of the fluorine gas as a function of time coincided with the variation of the incorporated fluorine in the sheet measured by X-ray fluorescence (XRF) spectroscopy after the treatment. This technique can be best used for process control of the continuous oxy-fluorination of polymeric materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 684–691, 2002

**Key words:** fluorine gas; oxy-fluorination; polyethylene; TISAB (total ionic strength adjustment buffer); process control

## INTRODUCTION

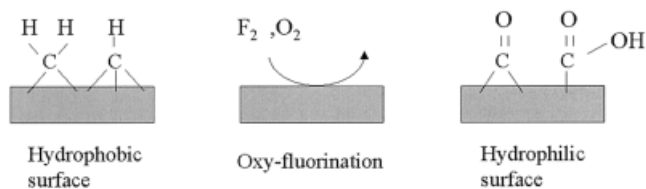
Since fluorine is the element that has the highest electron negativity, it reacts with other materials very easily and rapidly. The gas phase of fluorine is sometimes used to practically alter the surface properties of materials, because it reacts at an ambient temperature and under a normal pressure. The fluorine gas diluted by nitrogen gas is generally employed in order to avoid explosive reactions. This technique is sometimes applied to modify the surface of organic materials,<sup>1</sup> such as polyethylene,<sup>2,3</sup> polyhydrofluoroethylenes,<sup>4</sup> or polystyrene.<sup>5</sup> During the contact between the fluorine gas molecules and the polymers, the fluorine strips the hydrogen bound to the backbones of polymer chains, and then the following reactions can be made: the incorporation of other atoms or molecules and/or polymerization of the base polymers. The species of incorporated atoms or molecules depend on what kinds of gases are included in a reaction gas. When the gas consists of fluorine and nitrogen, fluorine is mainly introduced and F–C bonds are formed on the surface. When the gas contains fluorine, nitrogen, and oxygen, oxygen together with fluorine is likely to be incorporated, and carbonyl or carboxyl groups are created

(Fig. 1), which can be identified by infrared (IR) spectroscopy.<sup>3</sup> The fluorine works as a catalyst to introduce hydrophilic groups on the originally hydrophobic surface. For both cases, unsaturated linkages may contribute to polymerization. As a result, barrier properties, adhesion and printability properties, and friction properties can be improved.<sup>1</sup> When the gas contains fluorine, nitrogen, and oxygen, the reaction is called direct oxy-fluorination. This technique was examined for polyethylene by Toit et al.<sup>3</sup> In this study, authors independently scrutinize the effects of this technique, and find it useful, because the treatment can change the surface property only without affecting the bulk properties of the polymers, e.g., mechanical strength.

Polyethylene has excellent mechanical and chemical properties, but printing and adhesion properties as well as wettability are poor due to its hydrophobic surface. The direct oxy-fluorination alters the surface property to hydrophilic so that those properties can be easily improved.<sup>1</sup> One of the best examples is the surface-modified polyethylene nonwoven fabric, which is used as a separator in nickel metal hydride batteries. The separator needs to be chemically stable in a high alkali solution condition, and have a hydrophilic surface to absorb the alkali solution.<sup>6</sup> The oxy-fluorinated polyethylene nonwoven fabric is considered as one of the materials best suited for this purpose.

The contact between fluorine gas and polymeric materials is usually performed under well-regulated

Correspondence to: T. Kasai, Seagate Technology, NRN 191, 7801 Computer Avenue South, Bloomington, MN 55435, USA (Toshi.Kasai@seagate.com).



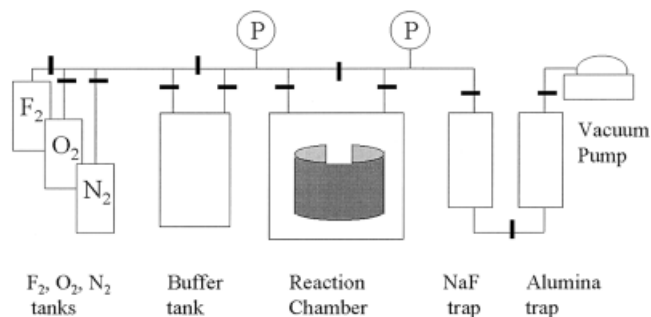
**Figure 1** Schematic pictures of oxy-fluorination. Hydrophobic surface is changed to hydrophilic surface by incorporation of carbonyl and/or carboxyl group.

conditions. A closed reaction chamber is often used to avoid the exposure of fluorine gas to the human body. The experimental evidence shown in an early part of this study suggests that the concentration of fluorine gas is one of the key factors that affect the surface properties. This result is consistent with that in other studies;<sup>3</sup> therefore the monitoring of fluorine gas in the reaction chamber is important. A technique to monitor fluorine gas using ultraviolet ray (UV) has been proposed;<sup>7</sup> however, it might be difficult for continuous use, because the transparent window, which is used to introduce the UV, becomes gradually contaminated by reactant products. That lessens the transparency of the window, and eventually the UV will be blocked. In this article, a new monitoring system for the concentration of fluorine gas is proposed. This technique does not need a window, so the above problem can be avoided. The features of this technique include continuous usability and a reasonable response time. This technique can be used to control the direct oxy-fluorination of polymer materials.<sup>8-10</sup>

**EXPERIMENTAL DETAILS**

**A preliminary study on the direct oxy-fluorination of polyethylene using a batch-type process**

Preliminary tests were performed to examine which experimental conditions most affected the changes of surface and bulk properties of polyethylene. Sheets and nonwoven fabrics made of polyethylene were chosen as test materials because our main interest was to investigate the possibility of the continuous oxy-fluorination of polyethylene nonwoven fabrics used for a nickel metal hydride battery separator. The polyethylene sheets were commercially available, low-density polyethylene, and polyethylene nonwoven



**Figure 2** Schematic diagram of oxy-fluorination used for a fundamental study of the reaction (batch scale).

fabrics that consist of a core-skin structure with a polypropylene core and polyethylene skin (provided by Sanwa Seishi Corp., Japan). The examined factors include the concentration of the fluorine and oxygen gas, the contact time, the reaction temperature, and the moisture contained in the specimens. The factors, analytical methods, and specimens are summarized in Table I. Tensile strength was measured by a standard tester before and after the treatment, and then two values were compared.

A diagram of the batch-type fluorination process is shown in Figure 2. The preliminary tests were conducted using this type. The gas tanks of fluorine, nitrogen, and oxygen were connected to a buffer tank. Air in the buffer tank and in a reaction chamber was first evacuated. The gases were mixed in the buffer tank with a total pressure of 1.5 atm, and then the mixed gas was introduced into the reaction chamber up to 1 atm. The reaction chamber contained the polymeric samples. After the regulated time of reaction, the gas in the chamber was evacuated through a gas trap by a rotary pump. The gas trap system was made of two absorbents: alumina for trapping fluorine gas and sodium fluoride (NaF) for hydrofluoric acid.

The concentration of the introduced fluorine, oxygen, and carbon in the samples was measured by XRF and/or X-ray photoelectron spectroscopy (XPS). Since XRF does not require an ultrahigh vacuum condition, it can be conveniently used compared to XPS. A more surface-sensitive technique, water contact angle (WCA) measurement, could be employed together with XRF, because the detection depth of XRF is deep enough to represent a bulk property in the range used.

**TABLE I**  
**Factors, Specimens, and Analytical Tools Examined in this Study on Oxy-Fluorination**

	Factors	Analytical tools	Specimens
1	Fluorine concentration	Water contact angle XRF	Polyethylene films
2	Oxygen concentration	"	"
3	Reaction time	"	"
4	Atmospheric temperature	XPS	Polyethylene nonwoven fabrics
5	Moisture in samples	"	"

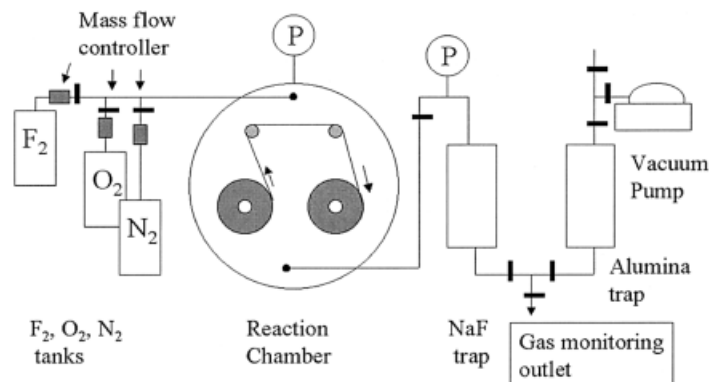


Figure 3 Schematic diagram of oxy-fluorination used for the continuous treatment of nonwoven fabrics.

In the WCA measurement, water (10 mcc) was dropped on the specimens at RT (room temperature) and then, after 5 s, the contact angle was measured using a microscope.

#### The study of a continuous oxy-fluorination process of polyethylene nonwoven fabrics and an *in situ* fluorine gas monitoring system

A diagram of the continuous oxyfluorination process of polyethylene nonwoven fabrics is shown in Figure 3. The polyethylene nonwoven fabrics were 0.45 m in width, 130  $\mu\text{m}$  in thickness and 375 m in length. The fabrics were originally wound upon cores made of polyvinylchloride. Polyethylene terephthalate films, 10 m in length, and 0.45 m in width, were attached at the head and tail parts of the fabrics in order to prevent unnecessary exposure to the fluorine gas when the gas was first introduced to and last evacuated from the reaction chamber.

Two kinds of reaction chamber were employed. Both were made of SUS 304. One had no coatings on the wall (no. 2 reactor), and the other had a tetrafluoroethylene coating (no. 3 reactor) on the wall. The no. 3 reactor was a modified version that prevented fluorine gas from being consumed by reaction with mois-

ture absorbed on the wall. Both reactors had two parallel shafts inside. Fabrics were set at one of the shafts, and wound to the other shaft by a controlled motor to keep a constant speed.

The gas tanks of fluorine, oxygen, and nitrogen were connected to the reaction chamber through mass controllers that introduced a controlled flow of the gases. The pressure inside the chamber was monitored by a pressure gauge. After the treatment, the gas was evacuated by a rotary pump through the gas trap system of two absorbents, NaF and alumina.

The gas monitoring outlet was set between the two absorbent traps to monitor the gas discharged from the reaction chamber (Fig. 3). This setting allowed measuring the fluorine gas in the chamber only by eliminating the effect of hydrofluorine produced from oxy-fluorination of the fabrics. Figure 4 shows a diagram of the fluorine gas monitoring system. TISAB (total ionic strength adjustment buffer) solution was mixed with the sampled gas and then forwarded to the flow cell that measured the generated voltage between the selected fluorine ion electrode and the reference electrode. The output voltage of the flow cell was measured by a voltmeter and monitored by a recorder.

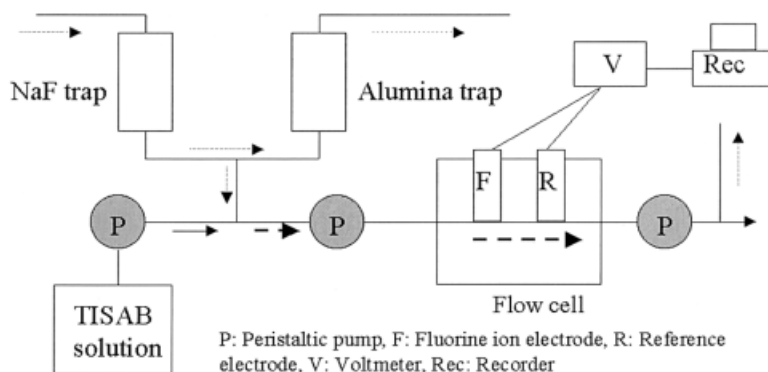
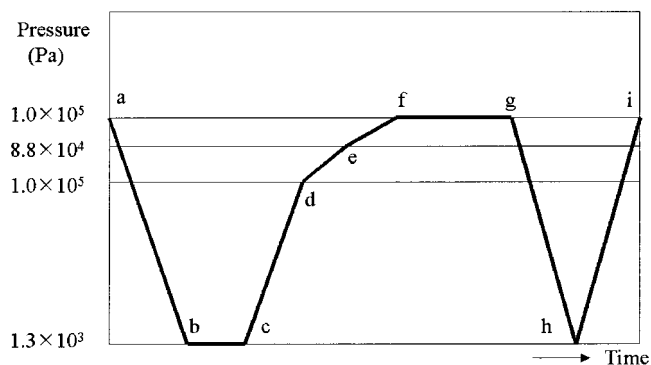


Figure 4 Schematic diagram of fluorine gas monitoring system. The dotted, solid, and bold dotted arrows indicate the flow of gas, TISAB solution, and the mixture of gas and solution, respectively.



**Figure 5** Pressure variation in a reaction chamber during the continuous oxy-fluorination of nonwoven fabrics. Samples are placed in the chamber at (a), and finally removed at (i) after the treatment (see text).

The steps of the continuous treatment are now described with reference to the pressure variation in the reaction chamber (Fig. 5): 1: A fabric was set in the chamber (a). 2: Air in the chamber was evacuated up to  $1.3 \times 10^3$  Pa (b). 3: Oxygen (c–d), nitrogen (d–e), and fluorine gas (e–f) were introduced to 1 atm. 4: The fabric was wound up with a constant speed ( $\sim 16$  m/min), and at the same time, the fluorine gas was fed through the mass flow controller (f–g) and the gas outlet was opened to maintain the internal pressure at 1 atm. 5: After the treatment was finished, the gas was evacuated through the gas trap system (g–h). 6: Nitrogen was introduced into the chamber (h–i) and then the treated fabric was removed.

A general principle of detecting fluorine ion in TISAB is explained as follows: fluorine gas reacts with water, which forms hydrofluoric acid. Hydrofluoric acid is also dissociated in the solution. The reactions are

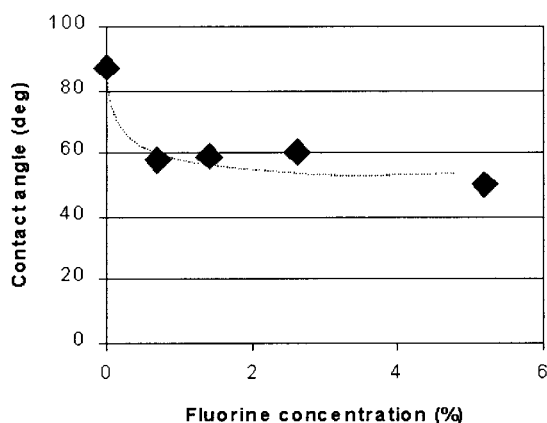


A fluoride ion electrode has a membrane made of a single crystal of  $LaF_3$ , which is emerged in the solution together with a reference electrode. The potential difference ( $E$ ) between the two electrodes is expressed by the following equation:

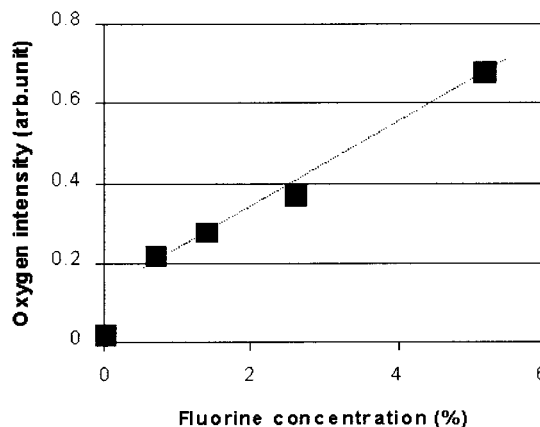
$$E = E_0 + (2.303RT/zF)\log C \quad (3)$$

where  $E_0$  is the constant potential determined by the system,  $R$  is the gas constant,  $T$  is temperature,  $z$  is the magnitude of charge on the species,  $F$  is the Faraday constant, and  $C$  is the activity of fluorine ion in the solution. The fluoride ion electrode shows a linear relationship between  $E$  and  $\log C$  for  $C$  ranging from  $2 \times 10^{-3}$  to  $2 \times 10^5$  mg/L. Activity is nearly equal to the concentration when the value of the activity is small.

The factors that influence the measurement of the concentration of fluorine ion are the temperature, pH, and other ions in the solution. The TISAB solution was used to minimize those factors. It was prepared in advance and kept at room temperature so that the temperature did not affect the measurement. The TISAB contained acetic acid, sodium salts, and distilled water to adjust pH and block the influence from other ions. The pH in the TISAB solution was set to 5.4, because its sensitivity decreased as the pH became higher, and when pH was less than 4, the reaction in (2) progressed backward. Other ions such as aluminium, hydroxide, iron, and calcium can trap fluorine ion. The TISAB was expected to inhibit those unfavorable reactions.

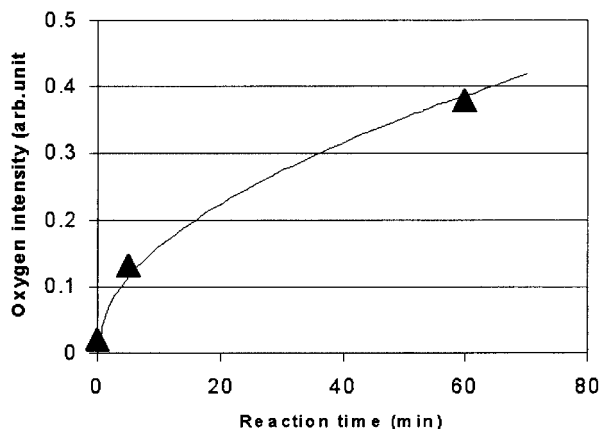


(a)



(b)

**Figure 6** The change of water contact angle: (a) and oxygen intensity incorporated into the sample measured by XRF; (b) as a function of fluorine concentration in the reaction gas. Sample: polyethylene film; oxygen concentration: 73.7%; reaction time: 1 h.



**Figure 7** The relationship between the reaction time and the incorporated oxygen intensity in samples measured by XRF. Sample: polyethylene films; fluorine concentration: 2.6%; oxygen concentration: 73.7%.

## RESULTS AND DISCUSSION

### A preliminary study on the direct oxy-fluorination of polyethylene using a batch-type process

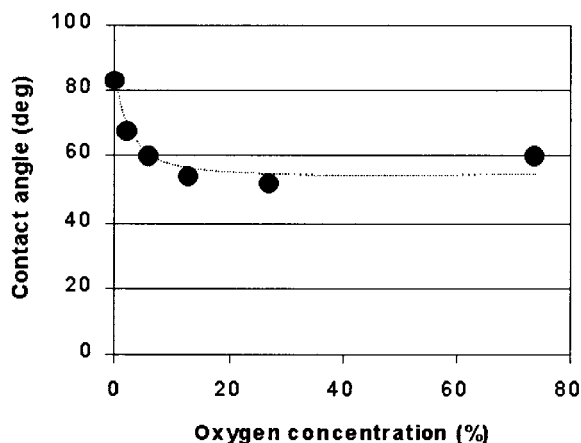
Figure 6(a) shows the relationship between the concentration of fluorine in the chamber and the contact angle of water. The concentration of oxygen was set to 73.7%. The samples were polyethylene films, and the reaction time was set for 1 h. The graph shows that the wettability was greatly improved (i.e., the contact angle of water decreased) when samples were exposed to 0.7% of fluorine and leveled off for further increase of the fluorine content. As shown in Figure 6(b), the incorporated oxygen concentration measured by XRF exhibits a nearly linear slope vs the fluorine concentration. Compared to the contact angle measurement, which is more sensitive to the surface property, XRF can detect oxygen incorporated more deeply, up to around 1  $\mu\text{m}$  from the surface. Therefore, the results

shown in Figure 6(a) and (b) suggest that the number of incorporated hydrophilic groups saturated on the surface when fluorine was more than 0.7% in concentration. Excess exposure to fluorine could lead to the formation of groups inside the materials, which would not affect the hydrophilic property of the surface. This interpretation was supported by the experimental evidence as shown in Figure 7: the relationship between the incorporated oxygen concentration measured by XRF and the reaction time follows a parabolic law, which suggests that the rate determining process of the reaction is diffusion of fluorine. Therefore a one hour exposure of 0.7% fluorine to the samples is enough to obtain a hydrophilic surface of polyethylene in this condition. This critical condition could change depending on the reaction time and the fluorine concentration, so these conditions of the fluorine gas treatment should be carefully controlled to obtain the desired treatment.

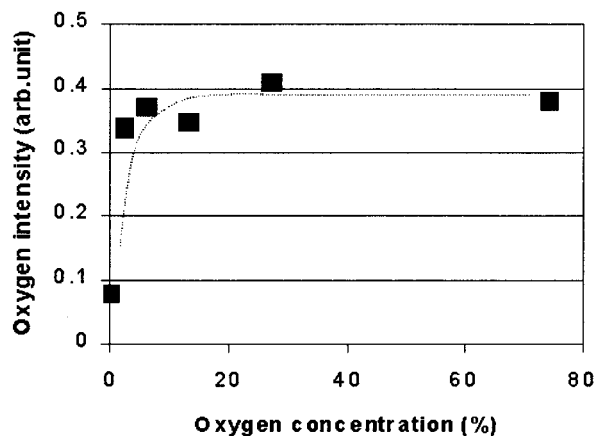
Figure 8 shows the contact angle of water (a) and the concentration of the incorporated oxygen by XRF (b) as a function of the concentration of oxygen in the reaction gas. As long as the concentration of oxygen gas is kept at more than 15%, the value of the contact angle will drop enough to maintain a hydrophilic surface.

The effect of reaction time is shown in Figure 9 and Figure 10 exhibits influence of the moisture contained in the samples. The examined temperature and moisture ranged from 14 to 40°C and from 120 to 400 ppm, respectively. Surface oxygen concentrations in the figures were obtained by XPS. Neither of the effects exhibited a major influence on the incorporation of oxygen for the conditions used in this work.

Surface contaminations such as hydrocarbon could be one of the factors to influence the treatment. Non-woven fabrics dipped in ethanol, washed in 70°C wa-



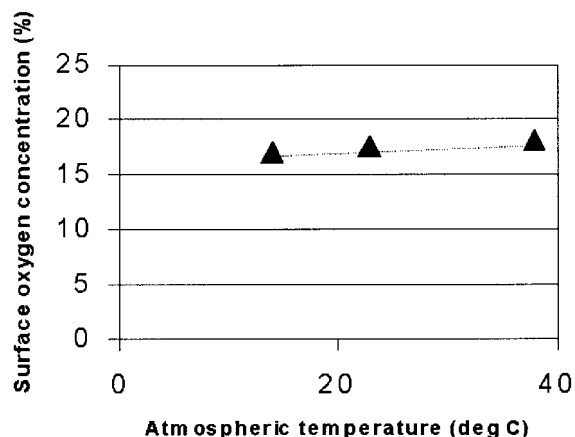
(a)



(b)

**Figure 8** Contact angle of water: (a) and intensity of incorporated oxygen by XRF; (b) as a function of oxygen concentration in the reaction gas. Sample: polyethylene film; fluorine gas concentration: 2.6%; reaction time: 1 h.



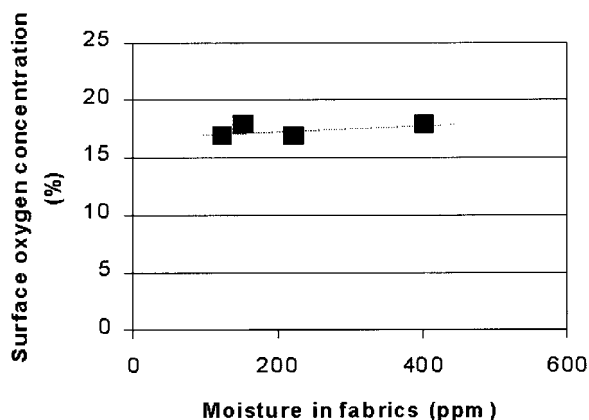


**Figure 9** The relationship between atmospheric temperature and concentration of incorporated oxygen measured by XPS. Sample: polyethylene nonwoven fabrics; fluorine concentration: 1.3%; oxygen concentration: 73.7%; reaction time: 5 min.

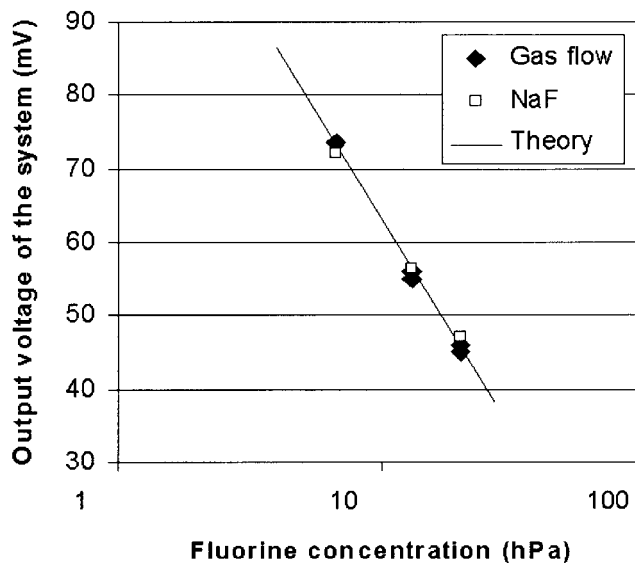
ter, and then dried were oxy-fluorinated to compare with nonwashed fabrics. The concentration of the incorporated oxygen measured by XRF was not significantly different for both samples: therefore, a special pretreatment before the oxy-fluorination was not required.

Mechanical properties were compared before and after the treatment to examine the damage on the treated nonwoven fabrics. No significant differences in tensile strength and elastic modulus were found when fluorine concentration was less than 5.3%.

From the above results, controlling the fluorine concentration and reaction time is crucial for treating polyethylene materials. As long as the oxygen concentration exceeds 15%, critical control of the oxygen concentration is not required.



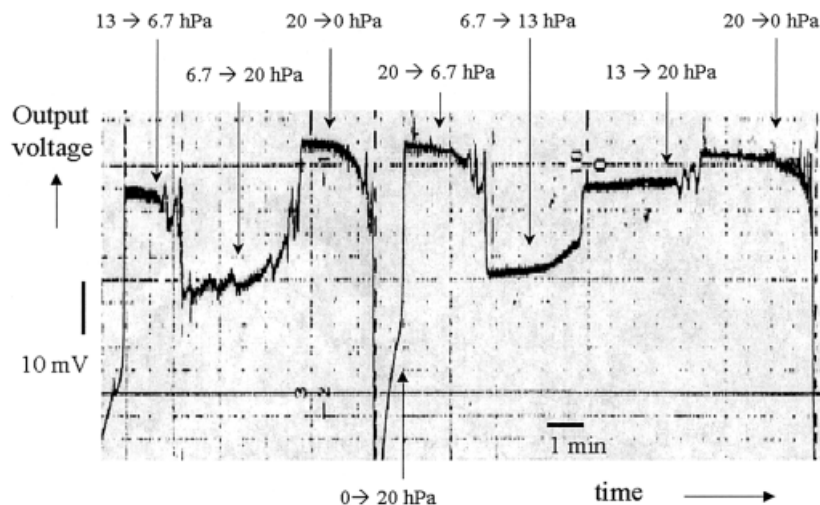
**Figure 10** The relationship between moisture in samples and concentration of incorporated oxygen measured by XPS. Sample: polyethylene nonwoven fabrics; fluorine concentration: 1.3%; oxygen concentration: 73.7%; reaction time: 5 min.



**Figure 11** Calibration line to convert the output voltage of the fluorine gas monitoring system to the concentration of fluorine gas in the reaction gas. Two types of experimentally obtained plots together with theoretical line derived from the Nernst equation are shown (see text).

**The study of an *in situ* fluorine gas monitoring system and the continuous oxy-fluorination process of polyethylene nonwoven fabrics**

In order to confirm that the fluorine gas is dissolved in a TISAB solution, and then dissociated with a conversion rate of 100%, the output voltage of the monitoring system was examined by two methods. The first method was performed in a similar way to sampling the actual reaction gas. The adjusted concentration of fluorine gas, set to  $6.7 \times 10^2$  Pa (0.7%),  $1.3 \times 10^3$  Pa (1.3%), or  $2.0 \times 10^3$  Pa (2.0%), the remainder being nitrogen, was directed to the system using a mass flow controller for the fluorine and nitrogen gases. The outlet of the sampled gas was in between the sodium fluoride and alumina traps (see Fig. 3). The gas was continuously supplied so that the concentration of fluorine gas at the monitoring position was kept constant. The second method was carried out using a solution that had a known concentration of fluorine ion. This solution was prepared by dissolving NaF in a TISAB solution. In this case, the inlet of the gas monitoring system was left unconnected, i.e., air was let in. Figure 11 shows the plots of the output voltage of the fluorine gas monitoring system vs the concentration of fluorine in the gas. The concentration of fluorine ion in the second method was converted to the fluorine gas concentration, assuming the inlet gas contained an equivalent concentration of fluorine. The plots for the two methods are consistent with each other. This suggests that fluorine gas was 100% converted to fluorine ions in the solution. The slope of the indicated line in the figure is  $-59$  mV/div, which was



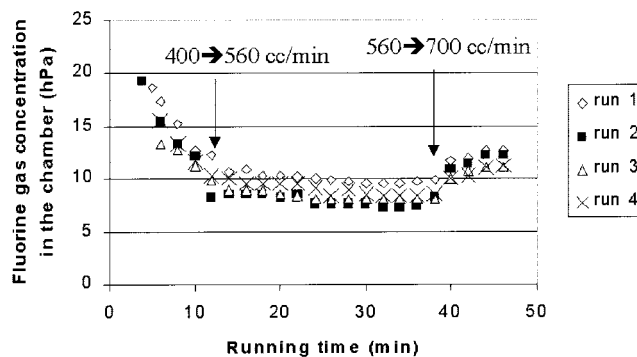
**Figure 12** Variations of the output voltage of the fluorine gas monitoring system when the concentration of fluorine gas was changed stepwise. Each arrow shows a position when the concentration of fluorine gas was changed.

derived from eq. (3). The measured points are on the line, so the Nernst relation was also confirmed. Another experimental result suggested that the tube length between the mixing point of the gas and TISAB and the flow cell should be taken as at least 40 cm or 8 s in time. Otherwise, the conversion of fluorine gas into fluorine ions in TISAB was not well carried out, so the conversion rate dropped.

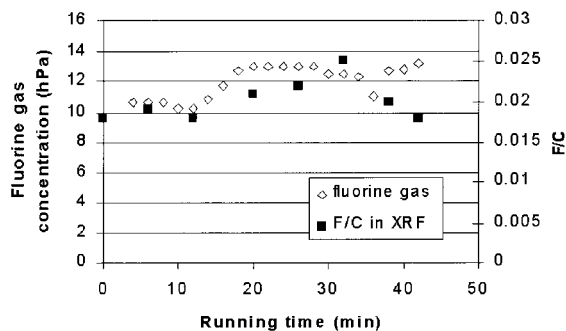
It is also important that the response property of the fluorine gas monitoring system is evaluated, because the concentration of fluorine in a reaction chamber possibly changes during the oxy-fluorination treatment. This was examined as follows: The fluorine gas was fed with different concentrations,  $6.7 \times 10^2$  Pa,  $1.3 \times 10^3$  Pa or  $2.0 \times 10^3$  Pa as described in the previous paragraph. In this test, the concentration of the fluorine gas was changed stepwise, e.g., from  $1.3 \times 10^3$  Pa to  $6.7 \times 10^2$  Pa, and next to  $2.0 \times 10^3$  Pa. The flow rate of the gas was large enough to change the concentration of fluorine gas at the gas monitoring position within 10 s. An example of the response of the output is shown in Figure 12. The figure shows the concentration of fluorine gas vs time with arrows that indicate the time when the gas concentration was changed. The response time for  $\pm 50\%$  change of the fluorine concentration (i.e., from  $1.3 \times 10^3$  Pa to  $6.7 \times 10^2$  Pa, or  $1.3 \times 10^3$  Pa to  $2.0 \times 10^3$  Pa) was 1 min. The output voltage sometimes fluctuated during the transient part of the gas concentration. This presumably resulted from a locally nonuniform fluorine concentration near the inlet of the monitoring system.

The system was applied for the actual treatment of polyethylene nonwoven fabrics. The rolled sample was set in the no. 2 reaction chamber, and originally  $2.0 \times 10^3$  Pa of fluorine gas was introduced. As the winding started, fluorine gas was supplied at the rate of 400 cc/min for the first 12 min, 560 cc/min from 12

to 38 min, and 700 cc/min from 38 to 48 min. This flow rate was empirically determined to obtain a uniform treatment, as indicated in Figure 13. The figure shows the change of the monitored fluorine gas in the reaction chamber. Four independent tests were conducted, and those showed good reproducibility. The initial concentration of the fluorine gas was measured as  $2.0 \times 10^3$  Pa, which was consistent with the initial introduction of fluorine into the chamber. The gas concentration decreased from the beginning, but had a steady value of  $9.4 \times 10^2$  Pa to  $1.1 \times 10^3$  Pa, as the gas flow rate was increased at 12 min. The fluorine gas concentration again increased when the flow rate of fluorine was increased at 38 min. If the fluorine concentration in the chamber were not uniform, the monitored fluorine gas concentration would not be reproduced. Therefore, the result suggests that the concentration of fluorine gas in the chamber was uniform, so the outlet gas that was monitored by the system well represented the concentration of fluorine gas in the chamber.



**Figure 13** Variations of the fluorine concentration in a chamber during the continuous oxy-fluorination of nonwoven polyethylene fabrics. The results of four independent runs are shown.



**Figure 14** Variations of fluorine gas concentration during the continuous oxy-fluorination of polyethylene nonwoven fabrics and F/C (ratio of fluorine to carbon intensity) measured by XRF as a function of running time.

The measured gas concentration in the reaction chamber was compared with the amount of fluorine incorporated into the fabric samples. The concentration of the incorporated fluorine correlated with that of the introduced oxygen, so it can be also used as an indicator of the level of oxy-fluorination. The rolled sample was again placed in the no. 3 reaction chamber (with a tetrafluoroethylene coating) and treated in a similar way. The only difference was an initial fluorine concentration that was set at  $1.3 \times 10^3$  Pa. Figure 14 shows the variation of the F/C ratio from XRF and the monitored concentration of fluorine in the chamber as a function of running time. The F/C ratio from XRF is defined as the ratio of the concentration of fluorine to carbon. The F/C ratio and the fluorine concentration are well correlated. The feed of fluorine gas was again changed from 400 to 560 cc/min at 12 min, so both the F/C ratio and fluorine concentration show increases. At 38 min, the feed was again increased, so the fluorine concentration increased, but the F/C ratio decreased. A similar decrease in the F/C ratio at the front (1 m) was observed, which can be explained as a blocking effect of the polyethyleneterephthalate films wrapped at the head and the tail of the rolls. Since polyethylene nonwoven fabrics have a high air permeability, fluorine gas can easily reach inside the roll by diffusion during the treatment. This effect was confirmed by another experiment. That enables us to set the running speed faster while keeping sufficient reaction time. The head and the tail parts are covered with film; therefore the F/C values decrease toward both ends.

## CONCLUSIONS

1. A basic study was performed to evaluate critical factors that influence the oxyfluorination reaction

of polyethylene. The experimental evidence showed that the concentration of fluorine in the reaction gas and the reaction time should be carefully controlled to obtain the desired level of oxy-fluorination. The reaction was less sensitive to the concentration of oxygen gas as long as it is more than 15%.

2. Polyethylene nonwoven fabrics, 375 m in length, were continuously oxy-fluorinated in specially designed reaction chambers. The incorporated fluorine and oxygen concentration measured by XRF showed the achievement of a constant treatment along the winding direction by continuously supplying of fluorine gas in the chamber.
3. An *in situ* fluorine gas monitoring system was developed to detect the concentration of fluorine in the reaction gas containing fluorine, oxygen, and nitrogen. The output voltage of the system correlated well with the concentration of fluorine gas, and it showed a reasonable response time when the gas concentration was changed.
4. An *in situ* fluorine gas monitoring system was applied to monitor the fluorine gas concentration in the reaction chambers during oxy-fluorination. The monitored fluorine gas concentration reasonably correlated with the variation of fluorine concentration in the sheet measured by a posttest XRF analysis along the winding distance.

We thank Sanwa Seishi Corp., Japan, for the test samples provided. We appreciate the help of Isao Kawakami for his useful suggestions especially on the basic study, and Yuki-chi Kobayashi for his kind support. We also thank Joel Bloch and David. A. Rigney of The Ohio State University for checking our draft.

## References

1. Kharitonov, A. *Fluorine Chem* 2000, 103, 123–127.
2. Schonhorn, H.; Hansen, R. H. *J Appl Polym Sci* 1968, 12, 1231–1237.
3. Toit, F. J.; Sanderson, R. D.; Engelbrecht, W. J.; Wagner, J. B. *J. Fluorine Chem* 1995, 74, 43–48.
4. Shinohara, H.; Iwasaki, M.; Tsujimura, S. *J Polym Sci* 1972, 10, 2129–2137.
5. Kharitonov, A. P.; Moskvina, Y. L. *J Fluorine Chem* 1998, 91, 87–93.
6. Ikeda, H. *Development of a Battery and its Electronics* (in Japanese); Nikkan Kogyo Shinbun, 1996.
7. Toyo Tanso Corp. Personal communication, 1995.
8. Denki Kagaku Corp., TOKO 5101, Technical Report, 1995.
9. Morimoto, S. *Jpn. Patent* S61–23960, 1986.
10. Ogawa, T. *Jpn. Patent* H7–128280, 1995.