

# Controlled Gas-Phase Sulfonation of Low-Density Polyethylene Films

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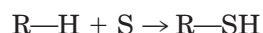
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**ABSTRACT:** In the current research, a highly controllable system operating at low temperatures and for short reaction times is employed for the surface sulfonation of low-density polyethylene. This system provides the advantages of short reaction times and low reaction temperatures, as compared with previous methods of surface sulfonation. Low-density polyethylene films were sulfonated at 40°C for time periods ranging from 5 to 30 min. Subsequently, all films were analyzed by SEM, EDX, horizontal ATR-FTIR, surface roughness, and dynamic contact-angle measurements. Sulfonation was effected at all reaction times. The degree of surface sulfonation increased through 10 min and reached a maximum between 10- and 30-min reaction times with concomitant changes in the physicochemical properties of the material. At 30 min, the film topography changed substantially, indicating that sulfonation was no longer limited to a strictly surface reaction. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1865–1869, 2000

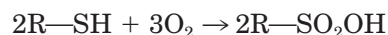
**Key Words:** polyethylene; sulfonation; surface activation

## INTRODUCTION

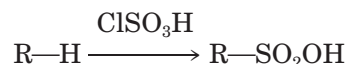
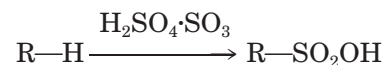
In the early 1960s, Strausz et al. published a series of articles regarding reactions of elemental sulfur with ethylene and propylene to form mercaptans.<sup>1</sup> This reaction proceeds as



Subsequently, they applied this reaction to the insertion of sulfur in the carbon-hydrogen bonds of paraffinic hydrocarbons.<sup>2,3</sup> While this was initially carried out as a bulk-material reaction, Olsen and Osteraas later applied this scheme for the surface sulfonation of polyethylene.<sup>4</sup> Once formed, the surface thiol groups were oxidized to form sulfonic acids:



Next, a scheme was devised to produce surface sulfonic acid groups directly without the need for formation of the intermediate thiol.<sup>5</sup> In this scenario, polyethylene films were immersed in either fuming sulfuric acid or chlorosulfonic acid with the net reactions shown below:



These sulfonic acid surfaces were found suitable for further reaction and functionalization.<sup>4</sup> Surface sulfonation of polyethylene has proven useful

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for the improvement of solvent barrier properties, strengthening of the interfacial bond in ultrahigh strength polyethylene fiber-reinforced composites, production of solid polymer electrolytes, and formation of ion-exchange resins.<sup>5-9</sup>

Limited research has been conducted on polymer surface sulfonation as a gas-phase treatment. In one reaction scheme, polyethylene films were exposed to sulfuric acid fumes in a sealed vessel for up to 20 h at room temperature.<sup>10</sup> In another, a mixture of sulfur trioxide and nitrogen gas was heated to 160°C and then passed over a high-density polyethylene film.<sup>11</sup> While these techniques demonstrated the feasibility of gas-phase surface sulfonation, the required reaction times were lengthy in the first case and production of the gaseous mixture was unwieldy in the second.<sup>10,11</sup> In the current research, a highly controllable system operating at low temperatures and for short reaction times was employed for the surface sulfonation of low-density polyethylene.

## EXPERIMENTAL

Low-density polyethylene (LDPE) (Polymerland, Maumee, OH) was compression-molded into films with an average thickness of  $73 \pm 10 \mu$  using a Carver Model C laboratory press (Fred S. Carver, Inc., Wabash, IN). Prior to molding, the melt characteristics of the polymer were determined using a Perkin-Elmer DSC Model 6 (Perkin-Elmer, Norwalk, CT) to aid in establishing the proper melt cycle. Thin films were obtained by pressing 2.0 g LDPE pellets between 15-cm<sup>2</sup> stainless-steel plates (Fred S. Carver, Inc.) which were covered with aluminum-backed Bytac<sup>®</sup> adhesive (Norton, Akron, OH). The molding assembly was heated in the Carver press to 180°C for 15 min, at which point a load was applied at increments of 1 metric ton per minute to a final load of 11 metric tons. The press platens and molding assembly were then quenched to room temperature with running water.

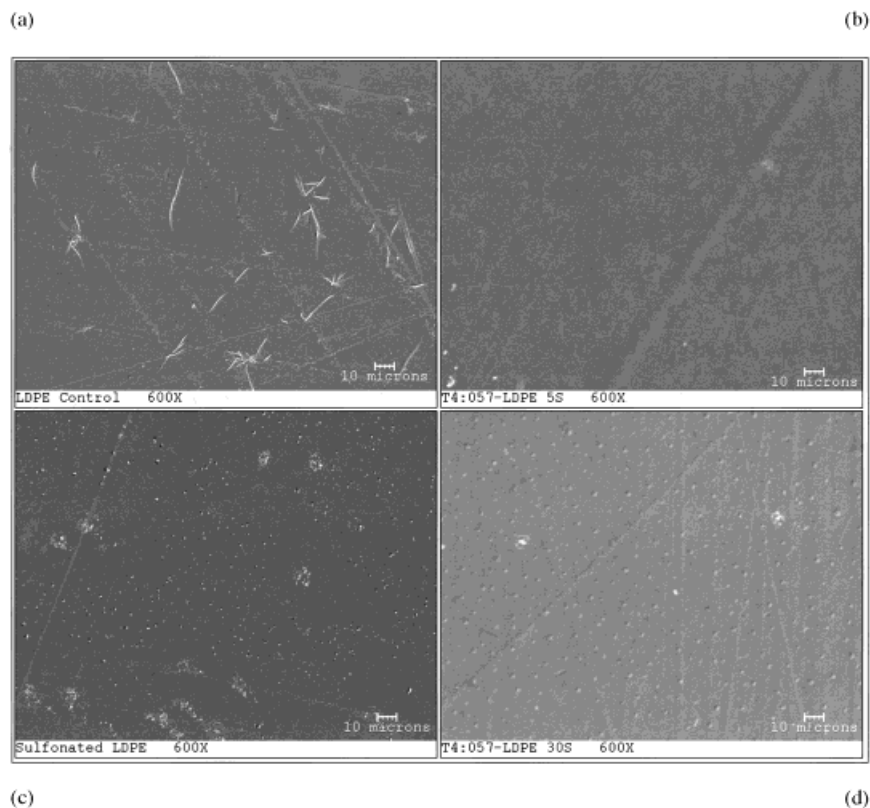
The LDPE thin films were sulfonated in the gas phase using a two-chamber dynamic reactor assembled from standard laboratory glassware: two-neck boiling flask, gas inlet adapter, and adapted pressure filter (Kimble Kontes, Vineland, NJ). The reactor was flame-dried under reduced pressure and purged with argon (HoloX Ltd., Greenville, SC). The lower chamber was immersed in an oil bath which was heated to 40°C using a Digi-Set-Temp (Laboratory Devices, Inc., Hollis-

ton, MA). Five milliliters of fuming sulfuric acid (Aldrich, Milwaukee, WI) was added to the lower chamber, and the argon flow rate was set at 30 mL/min. The reactor was allowed to equilibrate for 15 min; then, the LDPE films were added to the upper chamber. Sulfonations were carried out for 5, 10, and 30 min. After treatment, the films were removed from the reactor, quenched in distilled water, and sonicated in a Branson Model 3210 Ultrasonic Cleaner (Branson Ultrasonics Corp., Danbury, CT) for 30 min. Finally, the films were dried under reduced pressure at 37°C for at least 3 h and stored under argon.

In an effort to fully profile the physicochemical properties of the sulfonated films, several characterization techniques were employed. Initially, the surface was imaged by scanning electron microscopy (SEM) using a JEOL JSM-IC848 electron microscope (JEOL, Peabody, MA). Surface elemental analysis was obtained via electron dispersive X-ray (EDX; JEOL) with a semiquantitative assessment of the amount of sulfur present in each film group. Horizontal attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Perkin-Elmer Paragon 1000 spectrophotometer to confirm the presence or absence of sulfonate groups on the thermoplastic surface.

In an effort to quantify surface variations for different reaction conditions, surface roughness and dynamic contact angles were measured. Surface roughness values were measured using a WYKO NT 2000 Profilometer (Veeco Corp., Tucson, AZ). Roughness measurements were taken in a vertical scanning interferometry mode at a magnification of 25 $\times$ . The root mean square roughness,  $R_q$ , and the average maximum height of the profile,  $R_z$ , were used to compare the roughness of the different film surfaces.<sup>12</sup>

Advancing contact angles were measured using the Wilhelmy plate method in conjunction with the Young equation,  $\theta = \cos^{-1}\{F/(p \gamma_L)\}$ , where  $F$  is the force of the meniscus of the liquid at the film interface;  $p$ , the length of the interface (i.e., perimeter of the sample), and  $\gamma_L$ , the surface tension of the liquid.<sup>13</sup> Small film samples ( $\approx 0.25 \times 0.5 \text{ cm}^2$ ) were immersed in a liquid reservoir at a rate of 3  $\mu$ /min. The force was measured using a Cahn DCA 322 microbalance (Cahn Instruments, Inc., Cerritos, CA) as the liquid in contact with the specimen was increased. Films were tested in both HPLC-grade water and methylene iodide (Aldrich) for comparison of the behavior in polar and nonpolar solvents, respectively.



**Figure 1** SEMs of sulfonated LDPE.

For all tests detailed above, five measurements were taken per group, with the exception of dynamic contact angles for which four measurements were taken. Statistical analysis was accomplished using SAS® System for Windows™ Release 6.12 (SAS Institute, Inc., Cary, NC). Fisher's least significant difference procedure was applied to the data sets to determine statistically significant differences between groups at  $\alpha = 0.05$ .

## RESULTS AND DISCUSSION

The two-chamber dynamic flow reactor proved effective for the surface sulfonation of LDPE. Using this system, surface sulfonation was achieved under relatively mild reaction conditions at short reaction times. The degree of sulfonation was adequately controlled through the film-exposure time in the reactor.

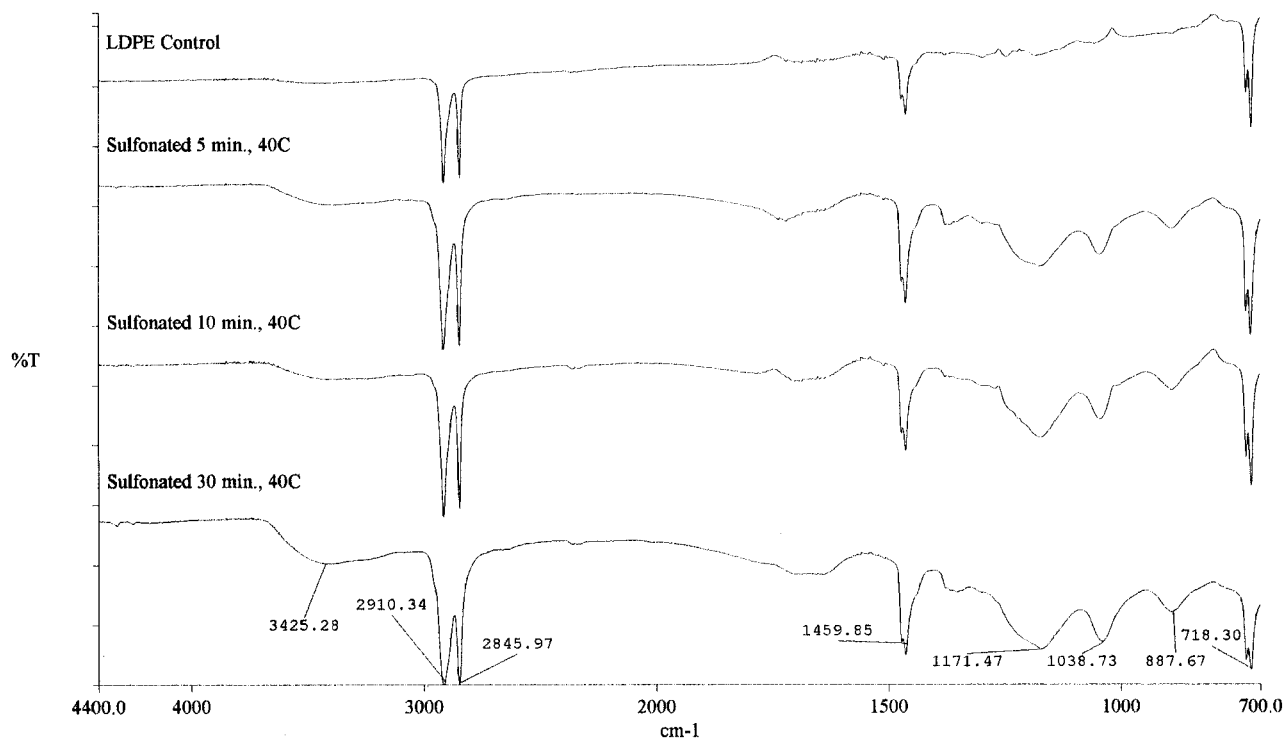
SEMs of the treated films indicate a progressive change in the surface morphology as seen in Figure 1. After 5-min reaction time [Fig. 1(b)], the surface appears somewhat smoother than that of

the control [Fig. 1(a)] due to solubilization of sulfonated ridges which were etched away in hydrolyzation. By 10 min [Fig. 1(c)], submicron-sized blisters appear, and at 30 min [Fig. 1(d)], the defects cover the entire surface and are several microns in diameter.

EDX spectra indicate the presence of sulfur on all treated films and its absence on the control. The results of the semiquantitative analysis computed from five collected spectra are recorded in Table I. The results indicate that the relative concentration of sulfur in these films increases with increasing reaction time with each group being statistically unique ( $p < 0.05$ ). Coupled

**Table I** Elemental Analysis of Sulfonated LDPE

Reaction Time (min)	% P (avg $\pm$ st dev)
0	0.00 $\pm$ 0.00
5	0.16 $\pm$ 0.03
10	0.31 $\pm$ 0.03
30	0.47 $\pm$ 0.03



**Figure 2** Horizontal ATR-FTIR spectra of control and sulfonated LDPE films.

with the SEM images, these initial data suggest that under the given conditions an increasing degree of sulfonation is achieved from 5- to 30-min reaction time.

Horizontal ATR-FTIR spectra of a control and sulfonated films are shown in Figure 2. All sulfonated films indicate characteristic frequencies at 1171 and 1040  $\text{cm}^{-1}$  attributed to the stretching of the S=O bonds of sulfonic groups, in agreement with assignments made earlier.<sup>9,10,14,15</sup> A group frequency at 890  $\text{cm}^{-1}$  closely corresponds to frequencies assigned to sulfur.<sup>14</sup> These bands are not seen in the spectrum of the control film and confirm that the treated film surfaces do, in fact, contain sulfonic acids.

Average surface roughness values are shown in Table II. After 5-min sulfonation time, the overall surface roughness of the LDPE film is less than that of the control ( $p < 0.05$ ). This is due to etching removal of artifactual lines created in compression molding, which results in a smoother surface. The 10- and 30-min time periods show trends toward increasing roughness; however, not all comparisons with the control for these groups result in statistically significant differences. This is due to large standard deviations calculated from measured roughness values which stem

from irregular topographies induced in the sulfonation process. Also, while the root mean square roughness is not statistically different for films sulfonated for 10 and 30 min, the average maximum height of the profile is greater at 30 min ( $p < 0.05$ ). A greater  $R_z$  value than that of the 10-min group is consistent with the larger blister size seen in the SEM images for films sulfonated for 30 min.

Average dynamic contact angle measurements and corresponding standard deviations are shown in Table III. A substantial decrease in the contact angle measured in water is noted for all treated films over the control ( $p < 0.05$ ). The lowered contact angle is expected as sulfonation renders

**Table II** Surface Roughness Measurements of Sulfonated LDPE

Reaction Time (min)	$R_q$ (nm) (Avg $\pm$ St Dev)	$R_z$ ( $\mu\text{m}$ ) (Avg $\pm$ St Dev)
0	75.59 $\pm$ 4.61	1.40 $\pm$ 0.33
5	55.67 $\pm$ 12.81	0.74 $\pm$ 0.05
10	92.54 $\pm$ 12.16	1.59 $\pm$ 0.17
30	86.99 $\pm$ 12.99	2.07 $\pm$ 0.26

**Table III Contact-angle Measurements of Sulfonated LDPE**

Reaction Time (min)	Water (°) (Avg ± St Dev)	Methylene Iodide (°) (Avg ± St Dev)
0	96.81 ± 1.48	69.32 ± 1.39
5	73.71 ± 5.33	67.86 ± 1.66
10	66.11 ± 5.01	63.91 ± 1.53
30	67.47 ± 7.35	63.60 ± 2.63

the LDPE surface hydrophilic. In water, the average contact angle decreases from the 5-min treatment to longer sulfonation times; however, there is no statistically significant difference between any of the treated groups. Compared to those measured in water, only very slight variations are seen for contact angles measured in methylene iodide, an indication that water is a more informative probe liquid. Angles measured in methylene iodide for 10 and 30 min were less than that of the control ( $p < 0.05$ ) while the 5-min treatment time was not statistically different from that of the control.

*In toto*, the data point to an increasing degree of sulfonation from 5- to 30-min treatment time. Horizontal ATR-FTIR together with EDX analysis indicate that sulfonation is effected as a surface treatment and that sulfur concentration increases with reaction time. Changes in surface morphology for longer reaction times are evident in the SEM images. Similarly, the average maximum height of the profile roughness values increase with sulfonation time, while root mean square roughness values initially increase through 10-min sulfonation and then remain constant to 30 min. Dynamic contact angles approximate this trend, decreasing through 10-min treatment time and then remaining constant to 30 min. Given that dynamic contact angles and root mean square roughness measurements do not change substantially from 10- to 30-min treatment, the limit of surface treatment is reached between these reaction times. This claim is further substantiated by increase in the average maximum height of the profile at 30 min, which indicates that sulfonation evokes morphological changes in the film surface at longer reaction times.

## CONCLUSIONS

Surface sulfonation of LDPE was accomplished using a two-chamber, dynamic flow reactor at low temperatures and short reaction times. The degree of surface sulfonation increased through 10 min and reached a maximum between 10- and 30-min reaction time with concomitant changes in the physicochemical properties of the material. At 30 min, the film topography changed substantially, indicating that sulfonation was no longer limited to a strictly surface reaction.

## REFERENCES

1. Strausz, O. P.; Gunning, H. E. *J Am Chem Soc* 1962, 84, 4080.
2. Knight, A. R.; Strausz, O. P.; Gunning, H. E. *J Am Chem Soc* 1963, 85, 1207.
3. Knight, A. R.; Strausz, O. P.; Gunning, H. E. *J Am Chem Soc* 1963, 85, 2349.
4. Olsen, D. A.; Osteraas, A. J. *J Polym Sci Part A-1* 1969, 7, 1913.
5. Olsen, D. A.; Osteraas, A. J. *J Polym Sci Part A-1* 1969, 7, 1921.
6. Shalaby, S. W.; Allan, J. M. U.S. Patent filed 1997.
7. Walles, W. E. U.S. Patent 3 740 258, 1973.
8. Postema, A. R.; Doornkamp, A. T.; Meijer, J. G.; Vlekkert, H. v. d.; Pennings, A. J. *Polym Bull* 1986, 16, 1.
9. Fischer, D.; Eysel, H. H. *J Appl Polym Sci* 1994, 52, 545.
10. Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bello, A. *J Mater Sci* 1985, 20, 3283.
11. Sabne, M. B.; Thombre, S. M.; Patil, A. S.; Patil, S. D.; Idage, S. B.; Vernekar, S. P. *J Appl Polym Sci* 1995, 58, 1275.
12. Schey, J. In *Encyclopedia of Materials Science and Engineering*; Bever, M. B., Ed.; MIT: Cambridge, MA, 1986; p 4806.
13. Lloyd, T. B.; Dwight, D. W. In *Characterization of Polymers*; Tong, H.; Kowalczyk, S. P.; Saraf, R.; Chou, N. J., Eds.; Butterworth-Heinemann: Boston, MA, 1994; pp 156-157.
14. Olsen, D. A.; Osteraas, A. J. *J Polym Sci Part A-1* 1969, 7, 1927.
15. Sowa, M.G.; Fischer, D.; Eysel, H. H.; Mantsch, H. H. *J Mol Struct* 1996, 379, 77.