Colloid Polym Sci (2009) 287:541–548
DOI 10.1007/s00396-009-2000-9

ORIGINAL CONTRIBUTION

# Surface treatment of LLDPE and LDPE blends by nitric acid, sulfuric acid, and chromic acid etching

**Hao Wang · ShuangJun Chen · Jun Zhang**

Received: 17 July 2008 / Revised: 21 December 2008 / Accepted: 8 January 2009 / Published online: 27 January 2009

**Abstract** Surface treatment of linear low density polyethylene and low density polyethylene blends is investigated herein using nitric acid, sulfuric acid, and chromic acid. These chemical treatments not only make the surface rough but also introduce polar groups. A new method, "sulfonic groups index" (SI) is employed to quantify the newly generated polar groups in the wavenumber of 1,250–840 $\text{cm}^{-1}$ in the Fourier transform infrared spectra. The SI values effectively indicate that the most polar groups are incorporated into the chromic acid-etched samples among the three inorganic acids, which is also confirmed by scanning electron microscopy and roughness tests. Besides, annealing treatment can enhance the crystallinity $X_c$ of all etched samples which plays a predominant role in the increase of roughness within 2 h. As etching time increases, chain scission and destruction of amorphous parts happen and roughness increases a lot for chromic acid-treated samples, but for sulfuric acid- and nitric acid-treated samples, the destruction of amorphous parts may not happen so that the roughness has not many changes.

**Keywords** Surface treatment · Linear low density polyethylene · Low density polyethylene · Sulfonic groups index · Blend · Inorganic acids · Roughness

H. Wang · S. Chen · J. Zhang (✉)
College of Materials Science and Engineering,
Nanjing University of Technology,
Nanjing 210009, People's Republic of China
e-mail: zhangjun@njut.edu.cn

## Introduction

Surface treatment of polyolefin has been widely studied because many properties of polyolefin such as adhesion, wettability, printability, transparency, lubricity, and biocompatibility can be improved by introducing polar groups or making rough surface [1, 2]. Several techniques of surface modification have been applied to polyolefin, for example, chemical [3–7] or physical etching [8, 9], flame [10, 11], corona discharge [12, 13], plasma treatment [14–17], and photografting [18]. Among these techniques, chemical etching of polyolefin by nitric acid, sulfuric acid, and chromic acid in different treating conditions has been well investigated and these treatments not only make the surface rough but also introduce the polar groups [19–21]. Researchers mainly concern about the mechanical properties and surface element constitutes of the etched polyolefins. However, there is little work to quantify the introduction of multiple polar groups.

Low density polyethylene (LDPE) is generally applied in packing films due to its good processability and mechanical properties [22]. LDPE is produced by high-pressure polymerization through free radical reaction. It contains alkyl branches and long chain branches. These alkyl substituents cannot be accommodated in the crystalline lattice, which results in the lower crystallinity [23]. Linear low density polyethylene (LLDPE), produced by copolymerization of ethylene and α-olefin, contains short chain branches. The crystallinity of LLDPE is higher than LDPE. LLDPE has been widely used as plastic films and in injection molding due to its excellent mechanical properties such as tear and impact strength as well as high tensile strength [22, 24]. By blending LDPE with LLDPE, the good processability, excellent mechanical properties, and high crystallinity can be obtained. The films of the blends will be produced without the need for extruder modifications [25–27].

In this paper, LLDPE and LDPE blends, which have been blown into smooth films, are chosen as typical complexes because of their comprehensive applications in industry. A new method, “sulfonic groups index”, is employed to quantify the newly generated polar groups in the wavenumber of 1,250–840 cm$^{-1}$ in the FTIR measurements. The molecular structures and morphology of LLDPE/LDPE films etched by nitric acid, sulfuric acid, and chromic acid have also been discussed.

## Experimental

### Materials

The blends of LLDPE/LDPE (1:1, mass ratio) were blown into smooth films (with a thickness about 0.13 mm) by the extrusion film blowing technique [28–30]. The LLDPE was purchased by Sinopec Yangzi Petrochemical Company Ltd. (China) and the LDPE was purchased by BASF-YPC Company Ltd. (China). Nitric acid (65%, AR) was supplied by Shanghai Chemical Reagent Co. Ltd. (China). Sulfuric acid (98%, AR) was obtained from Nanjing Chemical Reagent Co. Ltd. (China). Potassium dichromate (GR) came from Sinopharm Chemical Reagent Co. Ltd. (China). The chromic acid with different concentrations [$K_2Cr_2O_7$/$H_2O$/$H_2SO_4$ (1:2:18, 1:5:184 and 4:5:184, mass ratio)] was freshly prepared by mixing potassium dichromate, hot distilled water, and sulfuric acid prior to use.

### Preparation of samples

The LLDPE/LDPE films were soaked into distilled water, nitric acid, sulfuric acid, and chromic acid at 75 °C for different times (1, 2, 4, and 8 h), respectively. After etching by three acids, the films were immediately washed with running distilled water and ethanol. Then the films were dried in a vacuum oven at room temperature for 24 h.

### Fourier transform infrared (FTIR) measurements

FTIR spectra were obtained by attenuated total reflectance technique. The scanning range of the spectrometer (IFS 66/S, Bruker, Germany) was 4,000–580 cm$^{-1}$ with a nominal resolution of 4 cm$^{-1}$ at 32 scans.

### Differential scanning calorimetry (DSC)

The crystallization behaviors of LLDPE/LDPE films before and after treatment were studied using differential scanning calorimetry (DSC-7C, Perkin-Elmer, USA) with appropriate samples sealed in aluminum pans. The heating rate was 10 °C·min$^{-1}$ with the temperature ranging from 50 to 150 °C under a dry argon blanket. The relative crystallinity ($X_c$) of the samples was calculated as follows:

$$X_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\%$$

Where $\Delta H_f^*$ is the enthalpy of fusion of the perfect polyethylene (PE) crystal and $\Delta H_f$ is the enthalpy of fusion of the samples. The value of $\Delta H_f^*$ for PE is 277.1 J g$^{-1}$ [31].

### Scanning electron microscopy (SEM) observation

The surface morphology of LLDPE/LDPE films before and after etching were taken by a SEM (JSM-5900, Japan Electron Optics Laboratory, Japan) with the pretreatment of Au deposition. The accelerating voltage of the SEM was 15 kV.

### Surface roughness measurements

The surface roughness of the treated films was determined using a portable roughometer (TR200, TIME, China). The roughness was measured according to ISO 4287-1997.

## Results and discussion

### FTIR measurements

FTIR spectra are used to identify the functional groups and quantify chemical changes on the surface after acid treatment. Figure 1 indicates the differences of the etched films in different conditions.

There are little changes of nitric acid-etched sample before and after etching (Fig. 1a), which means that the films are essentially resistant to nitric acid. After etching by chromic acid, there is a broad band near 3,035 cm$^{-1}$, which is referred to as hydroxyl groups. The new absorption bands between 1,250 and 840 cm$^{-1}$ of the samples etched by sulfuric acid and chromic acid (Fig. 1b and c, respectively) can be attributed to multiple sulfonic groups ($O{=}S{=}O$, $S{=}O$, $S({=}O)_2OH$, $-SO_3H$, $S-O-C$, etc.) [32–34]. Other new main absorption bands of the sample etched in chromic acid (Fig. 1c) are in 1,800–1,500 cm$^{-1}$. The new bands are mainly assigned to groups containing carbonyl such as ketones, aldehydes, carboxylic acids, and even some $C{=}C$ bonds [2, 6, 32–34]. The intensity of these new absorption bands increases when the etching time is increased. The appearance of the oxidized substances on the surface of the etched samples is an indication of oxidative reactions, which provides supporting evidence of chemical composition changes of the

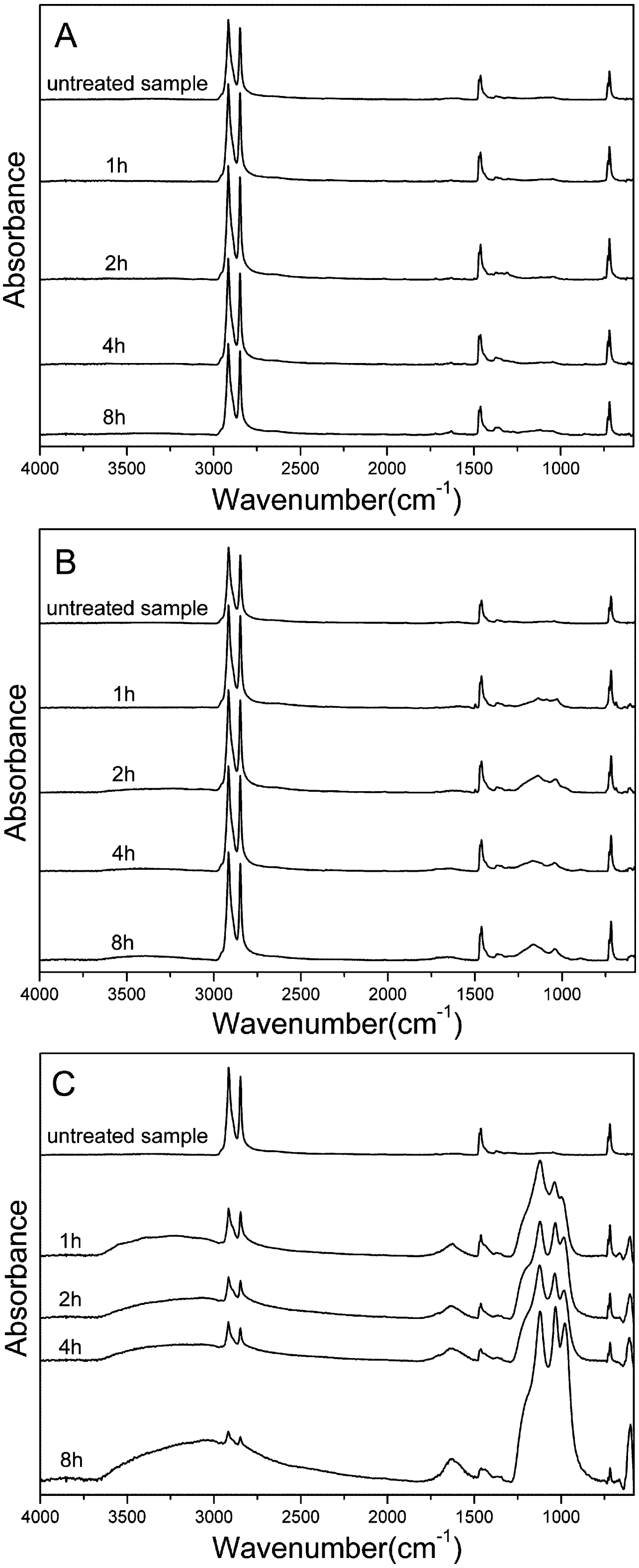


**Fig. 1** FTIR spectra of **a** nitric acid-etched LLDPE/LDPE films, **b** sulfuric acid-etched LLDPE/LDPE films, and **c** chromic acid-etched LLDPE/LDPE films

surface. The schematic mechanism of the oxidative reactions by chromic acid is depicted as Figure 2.

The attack to the molecular chains by hexavalent chromium in acid medium proceeds through the formation of the tetravalent chromium ester intermediate, which hydrolyzes to an alcohol. The alcohol then undergoes oxidation to form chain scission products, such as an olefin, an aldehyde, and a ketone, which may be further oxidized to carboxylic acid [7, 35, 36].

Other investigators have also proved that the sulfonation procedure of polyolefins by fuming sulfuric acid or hot concentrated sulfuric acid is accompanied by oxidation of polymers [32, 34, 37, 38]. However, these two absorption bands between 1,250–840 and 1,800–1,500 cm$^{-1}$ are complex because there are a lot of new polar groups generated during oxidative reactions. In order to quantify the effect of acid etching time on oxidation of the films, the carbonyl index [39, 40] (CI) is introduced at first.

The CI is calculated using the following equation:

$$CI = \frac{A_{(1800-1500)}}{A_{(760-660)}},$$

where $A_{(1800-1500)}$ are the integrated areas of the absorption bands of carbonyl groups from 1,800 to 1,500 cm$^{-1}$ of each etched sample and $A_{(760-660)}$ are the integrated areas of the absorption bands of methylene from 760 to 660 cm$^{-1}$ of each etched sample. The reason for division by integrated methylene peak areas is to eliminate the effect of film thickness.

Table 1 shows the CI changes of LLDPE/LDPE films etched in three acids for different times. From Table 1, it can be seen that CI values of all untreated samples are not equal to zero. It is assumed that there may exist very few C=C bonds due to the synthesis procedures of LLDPE and LDPE. When the treating time is not much, the C=C bonds may react and be diminished, resulting in the little decrease of CI values of nitric acid-treated samples. As the treating

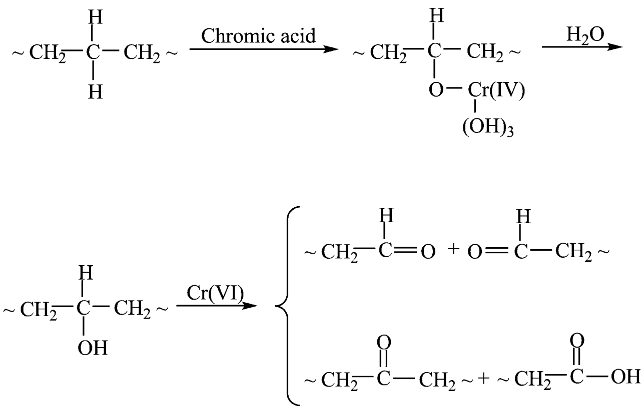


**Fig. 2** The schematic mechanism of polyethylene oxidized by chromic acid [2]

time increases long enough, some new groups like carbonyl, C=C bonds, and ether may form by oxidation. The oxidation may enhance the CI values little for nitric acid-treated sample. However, the CI values of nitric acid-etched sample have no considerable changes which are due essentially to the ethylene copolymers' resistance to nitric acid.

The CI values of sulfuric acid-etched sample have a minor change from 0.38 (untreated sample) to 0.79 (8 h), while the CI values of chromic acid-etched sample grow from 0.38 (untreated sample) to 2.64 (1 h), 4.09 (2 h), 7.98 (4 h), and 16.81 (8 h). The changes of CI values suggest the newly generated carbonyl groups [39]. It can be observed that the sample etched in chromic acid has the largest CI values among the three acids. This can be ascribed to the strong oxidation of chromic acid. However, CI is not enough to illustrate the introduction of functional groups, especially the sulfonic groups. A new method, sulfonic groups index (SI), is employed to semi-quantitatively measure the sulfonation by acids. The SI is similar to CI, and it is calculated using the following equation:

$$SI = \frac{A_{(1250-840)}}{A_{(760-660)}},$$

where $A_{(1250–840)}$ are the integrated areas of the absorption bands of sulfonic groups from 1,250 to 840 cm$^{-1}$ of each etched sample.

Table 2 shows the SI changes of LLDPE/LDPE films etched in three acids for different times. As mentioned, the untreated samples may have very few C=C bonds, which also results in the SI values of the untreated samples not equal to zero. The little decrease and then little increase of SI values also exist which is covered by the increase of sulfonic groups. For the SI values, the original groups and other newly formed groups have to be considered. So the original SI values should be revised by subtracting the control data of nitric acid-treated samples.

The SI values of the chromic acid-etched sample have increased drastically from 0 to 32.49, 54.76, 83.67, and 215.33, when etching time changes from 0 (untreated sample) to 1, 2, 4, and 8 h, respectively. The SI values of sulfuric acid-etched sample have increased from 0 (untreated sample) to 2.55 (8 h). The SI values of nitric acid-etched sample are similar to its CI values, which have no considerable changes. The increase of SI values of the etched samples suggests that there are sulfonic groups generated during the treating procedure. It indicates that the chromic acid-etched sample has much more sulfonic groups than that of the sulfuric acid-etched sample, which may also result from the strong sulfonation and oxidation of chromic acid. This possibly points out that chromic acid is a stronger oxidizing etchant than sulfuric acid and nitric acid for polyethylene [2].

**Table 1** CI changes of LLDPE/LDPE films etched in three acids for different times

| Etching time (h) | Carbonyl index | | |
|---|---|---|---|
| | Nitric acid | Sulfuric acid | Chromic acid |
| 0 (untreated sample) | 0.38 | 0.38 | 0.38 |
| 1 | 0.21 | 0.35 | 2.64 |
| 2 | 0.20 | 0.45 | 4.09 |
| 4 | 0.26 | 0.70 | 7.98 |
| 8 | 0.50 | 0.79 | 16.81 |

**Table 2** SI changes of LLDPE/LDPE films etched in three acids for different times

| Etching time (h) | Sulfonic group index | | | | |
|---|---|---|---|---|---|
| | Nitric acid | Sulfuric acid | | Chromic acid | |
| 0 (untreated sample) | 0.77 | 0.77 | 0[a] | 0.77 | 0[a] |
| 1 | 0.66 | 2.40 | 1.74 | 33.15 | 32.49 |
| 2 | 0.64 | 4.44 | 3.80 | 55.40 | 54.76 |
| 4 | 0.67 | 3.17 | 2.50 | 84.34 | 83.67 |
| 8 | 1.55 | 4.10 | 2.55 | 216.88 | 215.33 |

[a] The SI values are obtained by subtracting the control data of corresponding nitric acid-treated samples

Compared to CI, SI is more appropriate to quantify the concentrations of sulfonic groups introduced by strong oxidative acids. In addition, SI can be a complementary measurement to quantify the sulfonation and oxidation degrees resulting from other strong oxidative substances.

## DSC analysis

Figure 3 and Table 3 compare the DSC melting curves of untreated, distilled water-treated, and acid-etched LLDPE/LDPE films. All curves show two distinct melting characteristics including a premelting plateau and a main melting peak. The onset melting temperature $T_m^{on}$ and the premelting plateau temperature $T_m^{P_1}$ of the untreated sample increase after treating either in distilled water or in all three acids for 1 h. After treating for 8 h, the $T_m^{on}$ and $T_m^{P_1}$ of all samples have another minor increase, which probably results from the continual growth of smaller crystals during the treating procedure at 75 °C. The treatment here is mainly an annealing procedure [41]. The main melting peak temperature $T_m^{P_2}$ and the final melting temperature $T_m^f$ of the sample treated in distilled water for 8 h (111.9 and 117.2 °C, respectively) are approximate to the untreated sample (112.5 and 117.9 °C, respectively). The $T_m^{P_2}$ and $T_m^f$ of three acid-etched samples for 8 h are lower than the samples etched for 1 h and the untreated sample. The lower $T_m^{P_2}$ and $T_m^f$ of the acid-etched samples suggest the etching of the

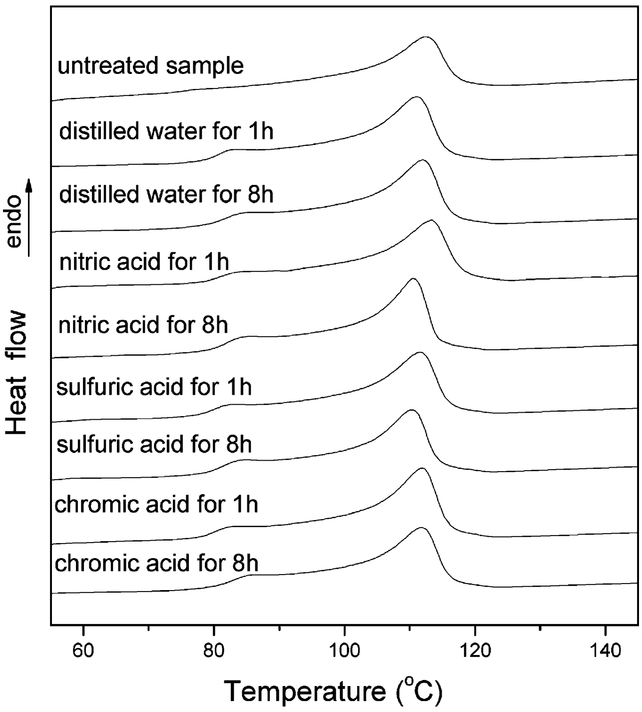


**Fig. 3** DSC melting curves of untreated LLDPE/LDPE films, distilled water-treated LLDPE/LDPE films for 1 and 8 h, and LLDPE/LDPE films etched by three acids for 1 and 8 h

amorphous regions and the crystal structures [42, 43]. The $\Delta T_{\mathrm{m}}\left(\Delta T_{\mathrm{m}}=T_{\mathrm{m}}^{\mathrm{f}}-T_{\mathrm{m}}^{\mathrm{on}}\right)$ appears to be similarly affected, which reduces from 44.2 °C (for the untreated sample) to around 36 °C (for the samples etched by acids for 8 h). It indicates that the spherulite size distribution in the blends becomes narrow, which results from the etching of the bigger spherulites.

The crystallinity $X_{\mathrm{c}}$ of all other samples has increased after acid etching for 1 and 8 h, except the sample etched in chromic acid for 8 h (35.56%), which has a minor decrease compared to the same sample for 1 h (36.04%). After etching for the same time, 8 h, the $X_{\mathrm{c}}$ values of the chromic acid- and sulfuric acid-etched samples (35.56% and 36.57%, respectively) are less than that in distilled water (37.06%). This demonstrates that the acids may etch not only the amorphous regions but also some crystal structures. However, after etching for 8 h, the $X_{\mathrm{c}}$ values of all etched samples are much larger than the untreated sample (32.98%). Therefore, it suggests that the annealing procedure plays a predominant role during this acid treating procedure.

## Surface morphology

The surface morphologies of the LLDPE/LDPE films before and after acid etching are presented in Figure 4. The surface of untreated film is essentially smooth and neat on the submicron scale. After a short acid etching time by nitric acid and sulfuric acid for 1 h (Fig. 3b and d, respectively), there appear some protuberance on the surface. After a longer etching time for 8 h (Fig. 3c and e, respectively), the surface becomes rougher. In contrast, the samples etched in chromic acid for 8 h (Fig. 3g) have a severe surface situation that the trenches and hills cover the entire surface. This is attributed to the stronger oxidation of chromic acid than that of nitric acid and sulfuric acid. The amorphous regions of LLDPE/LDPE films which have a looser chain packing structure may easily be etched by the oxidative acids, especially chromic acid [42].

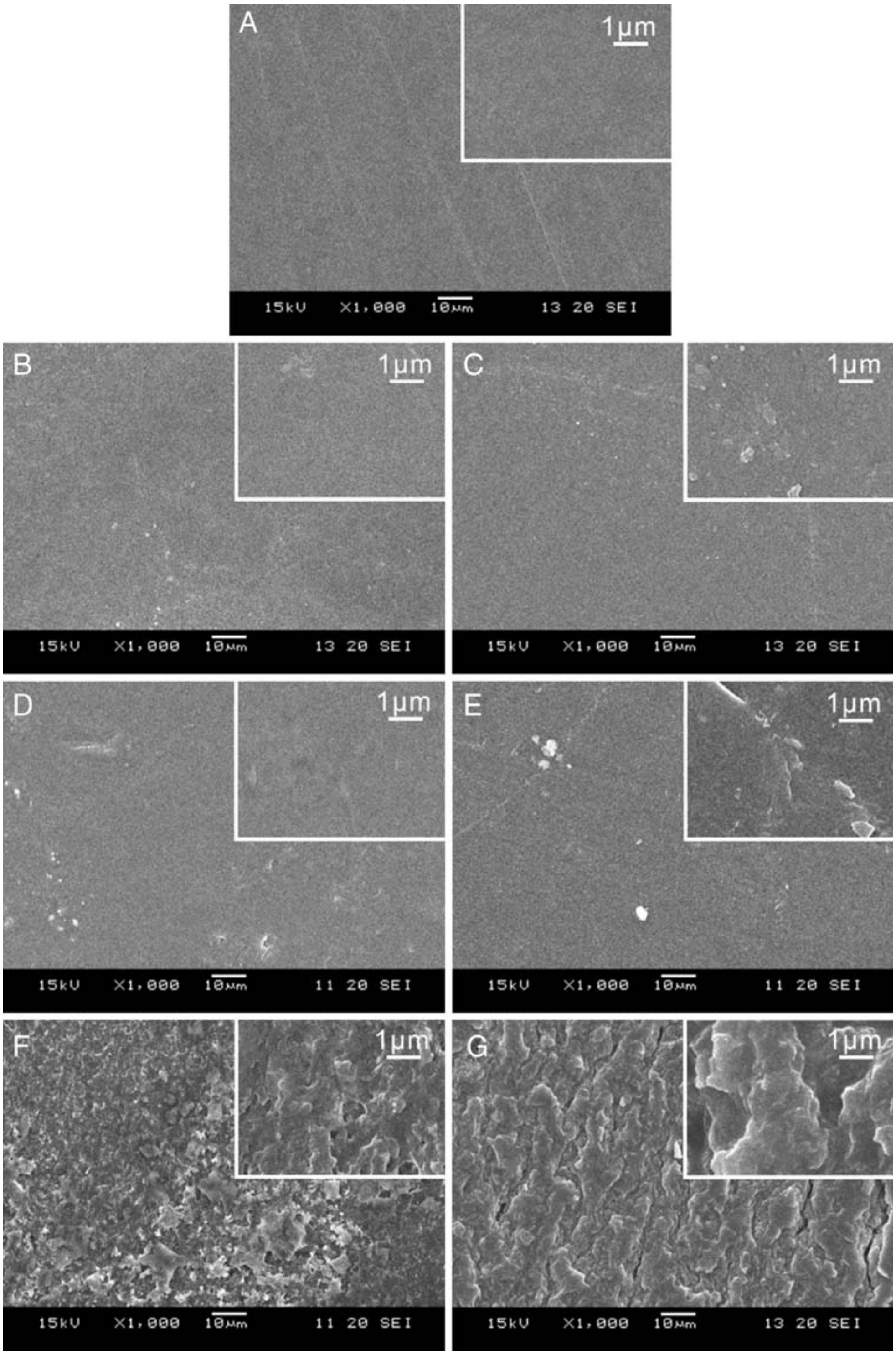
Figure 5 shows the morphology of etched LLDPE/LDPE films in different chromic acid concentrations for 1 h at 75 °C. It can be seen that the holes and trenches on the surface increase when the concentrations of chromic acid become higher. This is consistent with the previous FTIR spectra analysis that the samples etched in chromic acid for 8 h have the largest carbonyl index and sulfonic group index.

**Table 3** DSC data derived from melting curves of untreated, distilled water-treated, and acid-etched LLDPE/LDPE films

| | Etching time (h) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | | | | 8 | | | |
| | Untreated sample | Distilled water | Nitric acid | Sulfuric acid | Chromic acid | Distilled water | Nitric acid | Sulfuric acid | Chromic acid |
| $T_{\mathrm{m}}^{\mathrm{on}}$ (°C) | 73.7 | 77.8 | 78.1 | 77.2 | 77.9 | 78.4 | 78.7 | 78.5 | 79.5 |
| $T_{\mathrm{m}}^{\mathrm{P}_1}$ (°C) | 76.7 | 83.7 | 84.0 | 82.4 | 83.0 | 86.2 | 85.2 | 84.4 | 85.9 |
| $T_{\mathrm{m}}^{\mathrm{P}_2}$ (°C) | 112.5 | 111.2 | 113.3 | 111.6 | 112.0 | 111.9 | 110.6 | 110.3 | 111.8 |
| $T_{\mathrm{m}}^{\mathrm{f}}$ (°C) | 117.9 | 116.6 | 119.5 | 117.2 | 116.9 | 117.2 | 114.9 | 115.1 | 116.9 |
| $\Delta T_{\mathrm{m}}$ (°C) | 44.2 | 38.8 | 41.4 | 40.0 | 39.0 | 38.8 | 36.2 | 36.6 | 37.4 |
| $\Delta H_{\mathrm{f}}$ (J g$^{-1}$) | 91.38 | 97.79 | 97.85 | 100.86 | 99.86 | 102.68 | 104.07 | 101.34 | 98.53 |
| $X_{\mathrm{c}}$ (%) | 32.98 | 35.29 | 35.31 | 36.40 | 36.04 | 37.06 | 37.56 | 36.57 | 35.56 |

$T_{\mathrm{m}}^{\mathrm{on}}$ Onset melting temperature of LLDPE/LDPE films, $T_{\mathrm{m}}^{\mathrm{P}_1}$ the premelting plateau temperature of LLDPE/LDPE films, $T_{\mathrm{m}}^{\mathrm{P}_2}$ the main melting peak temperature of LLDPE/LDPE films, $T_{\mathrm{m}}^{\mathrm{f}}$ the final melting temperature of LLDPE/LDPE films, $\Delta T_{\mathrm{m}}=T_{\mathrm{m}}^{\mathrm{f}}-T_{\mathrm{m}}^{\mathrm{on}}$, $\Delta H_{\mathrm{f}}$ enthalpy of fusion, $X_{\mathrm{c}}$ crystallinity of LLDPE/LDPE films

**Fig. 4** SEM images of **a** untreated LLDPE/LDPE films, nitric acid-etched LLDPE/LDPE films for **b** 1 h and **c** 8 h, sulfuric acid-etched LLDPE/LDPE films for **d** 1 h and **e** 8 h, and chromic acid-etched LLDPE/LDPE films for **f** 1 h and **g** 8 h



## Surface roughness measurement

Roughness is characterized by means of *Ra*, expressing the arithmetical mean deviation of the profile within the sampling length [44, 45]. The roughness of the film etched in three acids for different times is presented in Figure 6. The initial roughness of the untreated film is 0.126 μm. After etching by sulfuric acid for 8 h, the roughness of the sample has increased to 0.258 μm. The nitric acid-treated sample has a similar change, but the roughness 0.240 μm is lower than that of the sulfuric acid-treated sample. The chromic acid-etched sample has the maximum of 0.545 μm when treating for 4 h. However, at the end of the treating procedure of 8 h, the roughness drops to 0.340 μm.

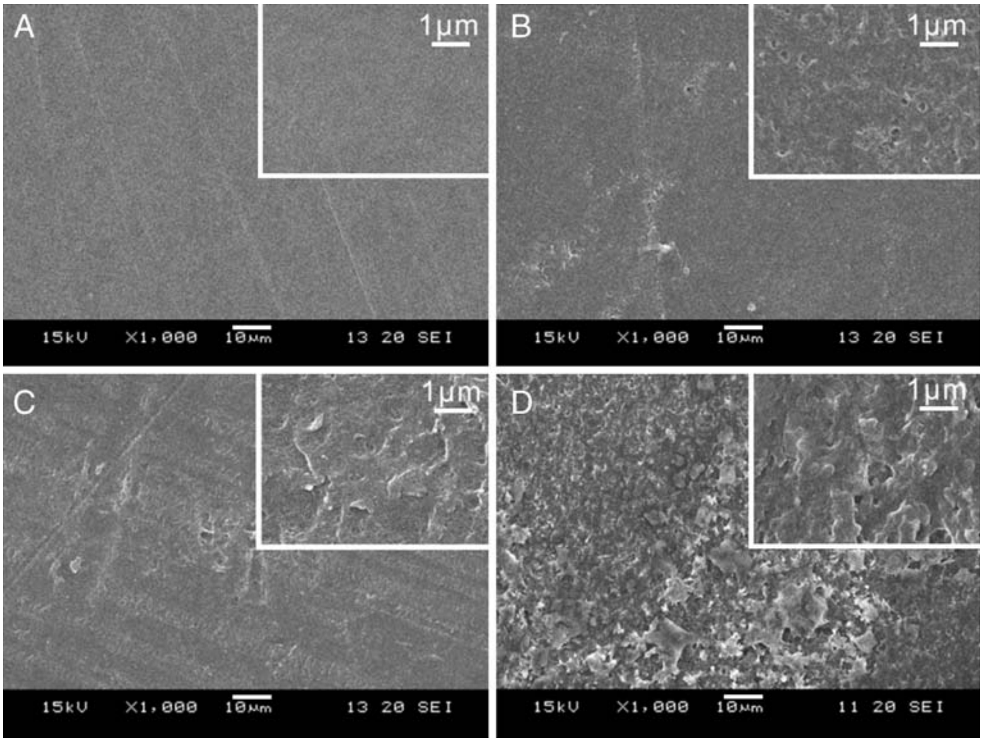


**Fig. 5** SEM images of **a** untreated LLDPE/LDPE films and etched LLDPE/LDPE films in different chromic acid concentrations for 1 h at 75 °C: **b** $K_2Cr_2O_7/H_2O/H_2SO_4$ (1:5:184, mass ratio); **c** $K_2Cr_2O_7/H_2O/H_2SO_4$ (4:5:184, mass ratio); **d** $K_2Cr_2O_7/H_2O/H_2SO_4$ (10:20:180, mass ratio)

When etching time is within 2 h, the increase of roughness may be attributed to the annealing of the samples, so the roughness of the three samples changes almost to the same extent. As etching time increases, for sulfuric acid- and nitric acid-treated samples, the destruction of amorphous parts may not happen, so the roughness has not many changes. However, for chromic acid-treated sample, as etching time increases from 2 to 4 h, chain scission and destruction of amorphous parts happen and roughness increases a lot. As etching time continues, chain scission and destruction of crystalline parts happen. This is like smoothing so that the roughness decreases. So the etching process may include three stages: the first is oxidation and groups introduction of amorphous parts of semi-crystalline polymer or blends; the second is chain scission and destruction of amorphous parts; the third is chain scission and destruction of crystalline parts.

## Conclusions

The new FTIR absorption bands between 1,250 and 840 $cm^{-1}$ of the chromic acid- and sulfuric acid-etched samples can be attributed to the multiple sulfonic groups such as O=S=O, S=O, $S(=O)_2OH$, $-SO_3H$, S−O−C, etc. A new method, “sulfonic groups index” (SI), is employed to quantify the newly generated polar groups in the wavenumber of 1,250–840 $cm^{-1}$ in the FTIR spectra. The SI values effectively indicate that the most polar groups are incorporated into the chromic acid-etched samples among the three inorganic acids, which is also confirmed by SEM and roughness tests. Besides, annealing treatment can enhance the crystallinity $X_c$ of all etched samples which plays a predominant role in the increase of roughness within 2 h. As etching time increases, chain scission and destruction of amorphous parts happen and roughness increases a lot for chromic acid-treated samples, but for sulfuric acid- and nitric acid-treated samples, the destruction of amorphous parts may not happen so that the roughness has not many changes.

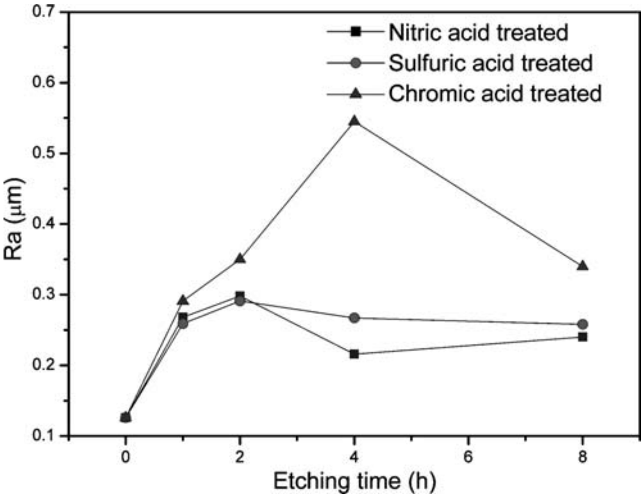


**Fig. 6** The roughness changes of LLDPE/LDPE films etched in three acids for different times

## Reference

1. Vasconcellos AS, Oliveira JAP, Neto RB (1997) Eur Polym J 33:1731
2. Blais P, Carlsson DJ, Csullog GW, Wiles DM (1973) J Colloid Interface Sci 47:636
3. Silverstein MS, Breuer O (1993) Polymer 34:3421
4. Silverstein MS, Dodiuk OBH (1994) J Appl Polym Sci 52:1785
5. Bag DS, Kumar VP, Maiti S (1999) J Appl Polym Sci 71:1041
6. Bag DS, Ghosh SN, Maiti S (1998) Eur Polym J 34:855
7. Holloway F, Cohen M, Westheimer FH (1951) J Am Chem Soc 73:65
8. Reding FP, Walter ER (1959) J Polym Sci 38:141
9. Mackie JS, Rudin A (1961) J Polym Sci 49:407
10. Sheng E, Sutherland I, Brewis DM, Heath RJ (1994) Appl Surf Sci 78:249
11. Song J, Gunst U, Arlinghaus HF, Vancso GJ (2007) Appl Surf Sci 253:9489
12. Overney RM, Lüthi R, Haefke H, Frommer J, Meyer E, Güntherodta HJ, Hild S, Fuhrmann J (1993) Appl Surf Sci 64:197
13. Zhu LP, Zhu BK, Xu L, Feng YX, Liu F, Xu YY (2007) Appl Surf Sci 253:6052
14. Guruvenket S, Rao GM, Komath M, Raichur AM (2004) Appl Surf Sci 236:278
15. Wei QF, Gao WD, Hou DY, Wang XQ (2005) Appl Surf Sci 245:16
16. Yu HY, Hu MX, Xu ZK, Wang JL, Wang SY (2005) Sep Purif Technol 45:8
17. Yu HY, Xie YJ, Hu MX, Wang JL, Wang SY, Xu ZK (2005) J Membr Sci 254:219
18. Rånby B (1999) Int J Adhes Adhes 19:337
19. Idage SB, Badrinarayanan S, Vernekar SP, Sivaram S (1996) Langmuir 12:1018
20. Cheikh RB, Askeland PA, Schalek RL, Drzal LT (2002) J Adhes Sci Technol 16:1651
21. Bentjen SB, Nelson DA, Tarasevich BJ, Rieke PC (1992) J Appl Polym Sci 44:965
22. Kontou E, Niaounakis M (2006) Polymer 47:1267
23. Basfar AA, Idriss KM (2006) Polym Degrad Stab 91:437
24. Lacoste J, Carlsson DJ (1992) J Appl Polym Sci 30:493
25. Zhao BY, Yi XW, Li RY, Zhu PF, Hu KA (2003) J Appl Polym Sci 88:12
26. Cordonnier M (1987) Plastics Rubber Process Appl 8:23
27. AbdelBary EM, Ismail MN, Yehia AA, AbdelHakim AA (1998) Polym Degrad Stabil 62:111
28. Harper C (2000) Modern plastics handbook. Technology Seminars, Lutherville
29. Fan D (2004) Polym Eng Sci 44:1811
30. Francesco P, Graziana C, Paolo M (2005) Macromol Mater Eng 290:105
31. Brandrup J, Immergut EH, Grulke EA (eds) (1999) Polymer handbook. Wiley Interscience, New York
32. Tada H, Ito S (1997) Langmuir 13:3982
33. Kaneko M, Kumagai S, Nakamura T, Sato H (2004) J Appl Polym Sci 91:2435
34. Kaneko M, Sato H (2005) Macromol Chem Phys 206:456
35. Wiberg KB, Eisenthal R (1964) Tetrahedron 20:1151
36. Sager WF (1956) J Am Chem Soc 78:4970
37. Cameron GG, Main BR (1985) Polym Degrad Stab 11:9
38. Fischer D, Eysel HH (1994) J Appl Polym Sci 52:545
39. Kim M (2003) Polym Carbohydr 54:173
40. Albertsson AC, Andersson SO, Karlsson S (1987) Polym Degrad Stab 18:73
41. Wang LY, Fang PF, Ye CH, Feng JW (2006) J Polym Sci B 44:2864
42. Hsieh YL, Barrall G, Xu SQ (1992) Polymer 33:536
43. Ueharaa H, Nakaea M, Kanamotoa T, Ohtsub O, Sanoc A, Matsuurac K (1998) Polymer 39:6127
44. Toshio O, Satoshi O (1999) J Appl Polym Sci 71:243
45. Yoshiki H, Yayoi S, Ikuo U (1999) J Biomed Mater Res 48:301