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Natural weathering of rape straw flour (RSF)/HDPE and nano-SiO_2/RSF/HDPE composites

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Abstract

The use of wood polymer composites (WPCs) in industries has been growing, and this is fueled in part by the use of WPCs in the construction industry. Rape straw flour (RSF)/high-density polyethylene (HDPE) composites as WPCs can also be applied in the construction industry. As a result, the durability of RSF/HDPE composites after natural exposure becomes a concern. Fourier transform infrared (FTIR) spectroscopy is used to monitor the development of degradation products, such as carbonyl groups and vinyl groups, and to determine changes in HDPE crystallinity. Differential scanning calorimetry (DSC) is also used to analyze changes in HDPE crystallinity. The results indicate that the carbonyl index was roughly lower for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites, and the concentration of vinyl groups was generally much larger for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites. At the same time, carbonyl index and vinyl index decrease with an increasing depth of composites, particularly decreasing strongly from 100 to 200 μm. The crystallinity of the samples increase because of natural aging, and the values of crystallinity derived by DSC are smaller than those derived by FTIR.

Keywords: Rape straw flour; High-density polyethylene; Weathering; FTIR; DSC

1. Introduction

High-density polyethylene (HDPE) is currently the most widely used commercial polymer due to its superior mechanical and physical properties. However, its toughness, weather resistance, processability, and environmental stress cracking resistance are not good enough, which have thus limited its application in many high-technology fields. One measure to improve its properties is to reinforce it with some fillers to form a composite (Gungor, 2006; Liu, Kwok, Li, & Choy, 2002; Zhang, Fang, Zhang, Wang, & Wang, 2003).

Wood fiber plastic composites (WPCs) have gained significant popularity in the last decade. However, there have been few recent investigations on rape straw flour/high-density polyethylene composites as WPCs. When rape straw flour is added to plastics, it increases stiffness which is an advantage in certain areas of use. There are also economical and environmental reasons for replacing part of the plastic with rape straw flour.

Some residential construction applications of WPCs, such as in windows, sidings, and roof tiles, are quickly entering the market or are currently being developed. Particularly, the use of WPCs in the construction industry has resulted in concern about the weathering of these products when exposed to outdoor environments. Of particular concern is the weathering of WPCs after ultraviolet (UV) exposure. In light of this, scientists have begun to investigate the UV weathering of WPCs (Matuana & Kamdem, 2002; Matuana, Kamdem, & Zhang, 2001; Stark & Matuana, 2003).

The photodegradation of polyolefins is mainly caused by the introduction of chromophores such as hydroperoxide groups, carbonyl groups, and double bonds during polymer manufacture. The degradation reactions proceed from carbonyl group precursors according to Norrish type

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I and II reactions (Jabarin & Lofgren, 1994; Wypych, 1995).

Fourier transform infrared (FTIR) spectroscopy has been recently used to study the changes in surface chemistry of polyethylene after weathering. FTIR spectroscopy has been used to monitor carbonyl group formation (Jabarin & Lofgren, 1994; Tidjani, 2000), vinyl group formation (Jabarin & Lofgren, 1994; Tidjani, 2000), and changes in crystallinity (Kaci, Sadoun, & Cimmino, 2001) of weathered polyethylene.

We used FTIR spectroscopy to monitor the changes in chromophores of RSF/HDPE and nano-SiO_2/RSF/HDPE composites after accelerated weathering, and used FTIR spectroscopy to monitor changes in crystallinity. We also monitored changes in crystallinity using DSC.

2. Experimental method

2.1. Materials

Rape straw flour (RSF) with a size of 74 μm was provided by the National Engineering Research Center of Rapeseed, China. It was first dried in 105 °C for 24 h. HDPE (5000s) is a product of Daqing Petrochemical Co. with a melt index of 0.7 g/10 min and was used without any treatment. The silica nanoparticles used were obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area, particle size, and silanol group content were 640 m^2/g, 10 nm, and 48%, respectively. They were dried in vacuum at 105 °C for 48 h before use.

2.2. Preparation of the RSF/HDPE composites and nano-SiO_2/RSF/HDPE composites

The HDPE and rape straw flour were mixed in a roller at 145–150 °C for 15–20 min. The resulting sheet was compression molded at 170 °C into a 0.5-mm thick sheet under a pressure of 9 MPa for 15 min and then was kept at room temperature. Then the nano-SiO_2/RSF/HDPE composites were also prepared under the same conditions. The ratio of the HDPE/rape straw flour (RSF) particle was 100/100 according to weight. Meanwhile, the ratio of the HDPE/RSF particle/nano-SiO_2 was 100/100/2 according to weight.

2.3. Natural (outdoor) weathering

The specimens (4 × 4 cm) exposed to sunshine were cut from the laminates. The boards were then placed on the rooftop facing southward at a 30° angle with the roof or plane of the earth. The exposed samples were periodically taken out for analysis after 15, 30, 45, 60, 75, and 120 days, respectively.

2.4. Analysis by fourier transform infrared spectroscopy

The FTIR instrument used was a Nicolet 470. The method used to prepare the samples involved consolidating the composites ground in a KBr matrix. The ratio used was 10 mg of the sample in 250 mg of KBr. Some reports recommended a low ratio, however no absorbance values close to one for the most intense band of the spectrum were achieved on using ratios 3/300 and 6/600. So the ratio of 10/250 was chosen and good absorbance values can be derived. The solid blend was submitted to 10-ton compression samples. Then scans were run at a resolution of 4 cm^{-1}. Each sample recorded consisted of 32 scans recorded in absorbance units from 4000 to 400 cm^{-1}.

2.5. DSC analysis

Analyses of the samples were carried out on a Nexus DSC 204F1 in nitrogen atmosphere. The temperature and melting enthalpy were calibrated with standard indium at each cooling rate in the measurement. The samples of 5–10 mg were encapsulated into aluminum pans and were heated first up to 170 °C rapidly from 50 °C, and this temperature was maintained for 5 min in order to eliminate the thermal history of the samples. Then the samples were cooled down to 50 °C at the cooling rate of 10 °C /min.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy analysis of the samples at various exposure times

Fourier transform infrared (FTIR) spectroscopy was used to monitor the development of degradation products, such as carbonyl groups and vinyl groups, and to determine the changes in HDPE crystallinity of both the RSF/HDPE composite and nano-SiO_2/RSF/HDPE composite samples. The FTIR curves at different exposure times are shown in Figs. 1 and 2. Table 1 shows the wave numbers

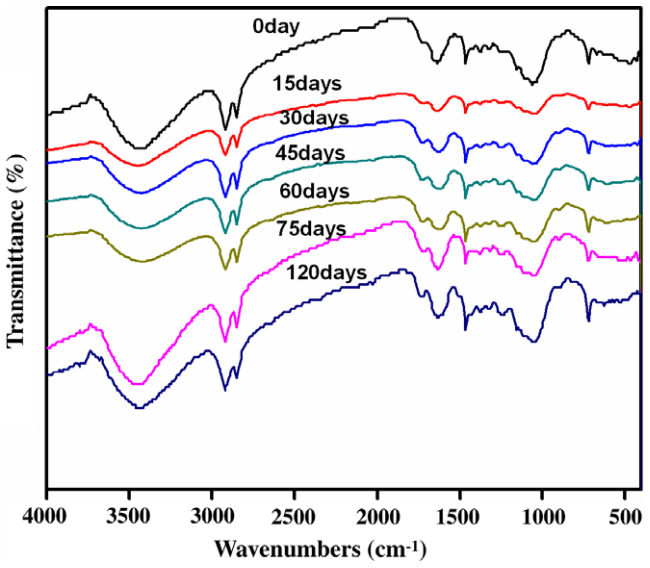

Fig. 1. FTIR spectra of RSF/HDPE composites at various exposure time.

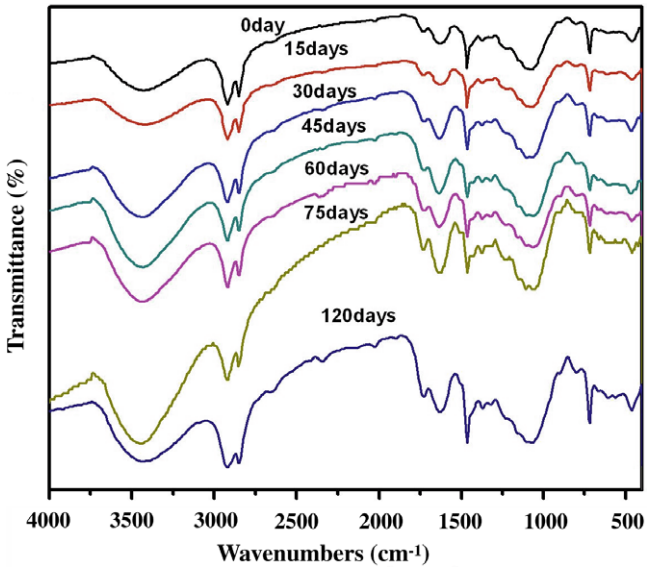

Fig. 2. FTIR spectra of nano-SiO_2/RSF/HDPE composites at various exposure time.

Table 1
Wavenumbers of peaks used for FTIR analysis and corresponding functional groups and vibrational types (Pagès, Carrasco, Saurina, & Colom, 1996; Tidjani, 2000)

Wavenumber (cm^{-1})	Functional group	Vibrational type
2920	$-CH_2-$	C–H stretching
1723	R(C=O)OH	C=O stretching
1474	$-CH_2-$	C–H bending, crystalline
1464	$-CH_2-$	C–H bending, amorphous
899	$RCH=CH_2$	C–CH_2 out of plane bending
729	$-CH_2-$	C–H rocking, crystalline
717	$-CH_2-$	C–H rocking, amorphous

of the peaks monitored with their corresponding functional groups and vibrational types.

3.1.1. Carbonyl group formation

Carbonyl index was calculated using the following equation:

$$\text{carbonyl index} = \frac{I_{1723}}{I_{2920}} \times 100 \quad (1)$$

where I is a peak intensity of the FTIR spectra. The peak intensities were normalized using the peak at 2920 cm^{-1}, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was chosen as a reference peak because it changed the least during aging. The increase in carbonyl group concentration (calculated from Eq. (1)) over exposure time is plotted in Fig. 3. The carbonyl index was roughly lower for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites. As the exposure time increased, the carbonyl index increased for the RSF/HDPE composites and nano-SiO_2/RSF/HDPE composites. The increase in carbonyl group formation for polyethylene after weathering is known to be proportional to the number of chain scissions that occur in the polyethylene (Wypych, 1995). The results indicate that chain scission may have occurred upon exposure and that the number of chain scissions increased with the increase in exposure time (Fig. 3).

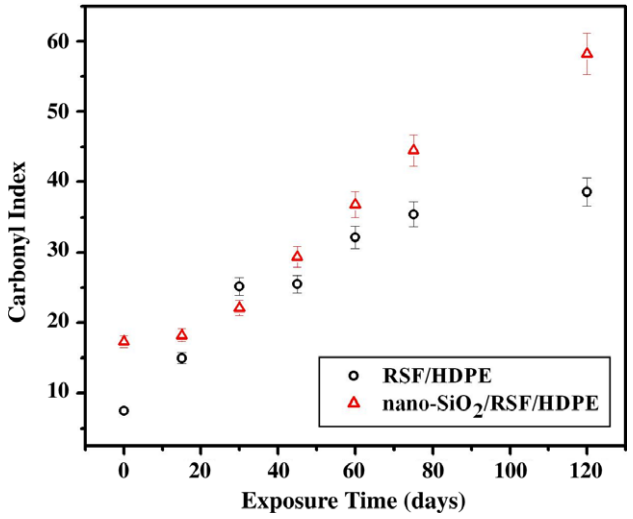

Fig. 3. Carbonyl group formation as a function of exposure time for RSF/HDPE and nano-SiO_2/RSF/HDPE composites.

3.1.2. Vinyl group formation

Vinyl index was also calculated based on the following equation:

$$\text{vinyl index} = \frac{I_{899}}{I_{2920}} \times 100 \quad (2)$$

where I represents a peak intensity of the FTIR spectra. Vinyl group formation is an indication of polymer chain scission (Jabarin & Lofgren, 1994) of HDPE, which can be a result of carbonyl degradation via Norrish II. Fig. 4 shows the increase in vinyl group concentration based on the peak at 899 cm^{-1}. The concentration of vinyl groups was generally much larger for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites. There was no significant vinyl group formation during the exposure of the RSF/HDPE and nano-SiO_2/RSF/HDPE composites through the initial 15 days (Fig. 4). After 15 days, vinyl group formation significantly increased with UV exposure time, leveling after 75 days. Other investigators have also found an initial delay in vinyl group formation in the early stages of naturally weathered HDPE (Jabarin & Lofgren, 1994), followed by a steep increase as weathering progressed. Vinyl groups at longer exposure times are thought to be caused by degradation via the Norrish type II mechanism, which causes vinyl groups to be the major products in the first stage, followed by a slower conversion to carbonyl groups (Jabarin & Lofgren, 1994). Similarly, for RSF/HDPE composites and nano-SiO_2/RSF/HDPE composites, the vinyl group concentration was not significantly larger than that of the unexposed sample through 15 days

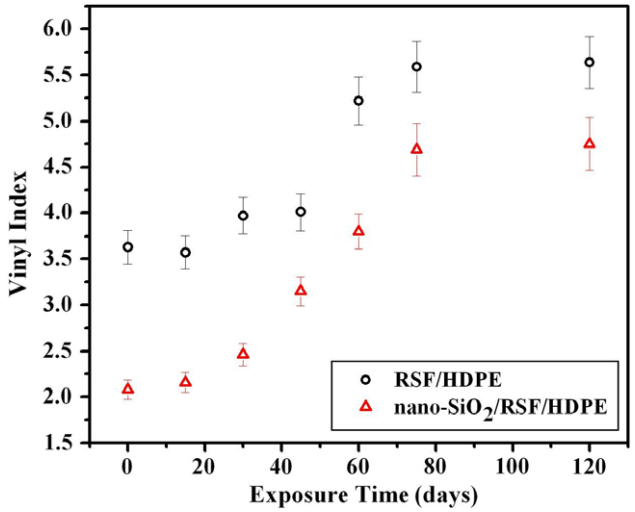

Fig. 4. Vinyl group formation as a function of exposure time for RSF/HDPE and nano-SiO_2/RSF/HDPE composites.

of exposure, then this increased in concentration through 75 days. Again, the concentration appeared to remain leveled between 75 days and 120 days of exposure. The change in vinyl group concentration is thought to be mainly due to the degradation of the HDPE matrix as a component of the RSF/HDPE and nano-SiO_2/RSF/HDPE composites.

3.2. FTIR analysis of the nano-SiO_2/RSF/HDPE composites at various aging depths

The nano-SiO_2/RSF/HDPE composites spectra at aging depths of 100, 200, 300, 400, 500, and 600 μm are shown in Fig. 5. The carbonyl index (calculated from Eq. (1)) and vinyl index (calculated from Eq. (2)) of the samples can be determined as shown in Fig. 6. From the same figure,

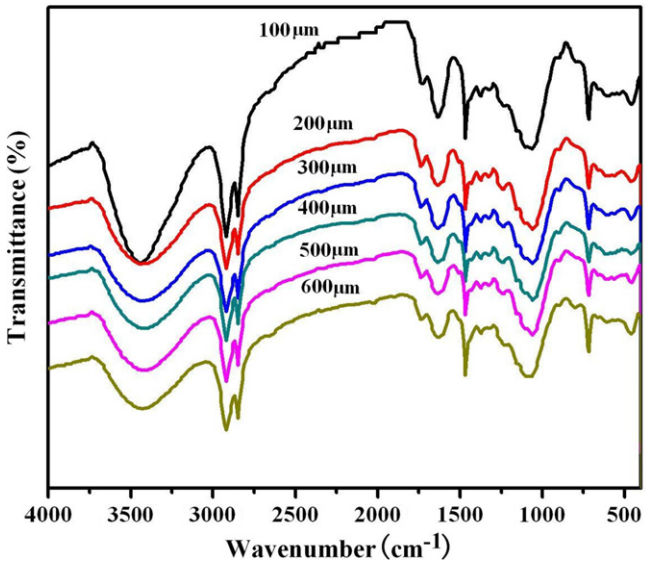

Fig. 5. FTIR spectra of nano-SiO_2/RSF/HDPE composites at different aging depth.

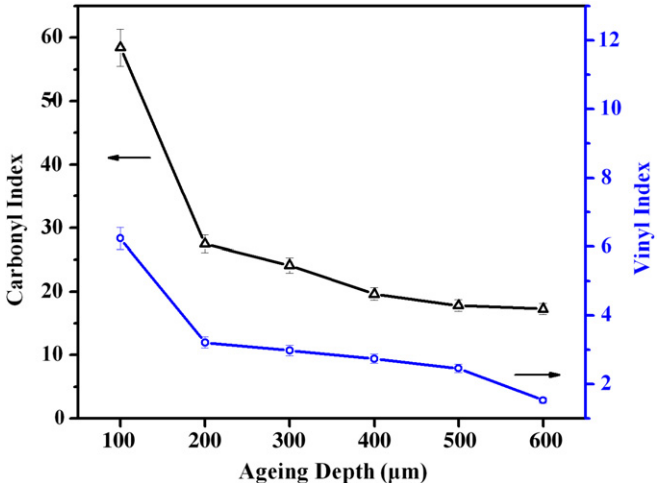

Fig. 6. Carbonyl and vinyl group formation as a function of aging depth for nano-SiO_2/RSF/HDPE composites.

it can be seen that the carbonyl index and vinyl index decrease with an increase in depth of the composites, that is, strongly decreasing from 100 to 200 μm. This indicates that the aging of the nano-SiO_2/RSF/HDPE composites occurs on the surface of the samples, with aging particularly being stronger at a smaller depth of the samples. The reason can be that there is a larger effect on the surface by accelerating weather factors such as oxygen, ultraviolet radiation, water, temperature, and pressure.

3.3. Crystallinity changes of the RSF/HDPE and nano-SiO_2/RSF/HDPE composites by FTIR

Zerbi et al. (Zerbi, Gallino, Del Fanti, & Baini, 1989) described that the crystallinity of HDPE was determined using the method. The doublet peaks roughly observed at 1474–1464 cm^{-1} and 729–717 cm^{-1} correspond to polyethylene crystalline content (1474 and 729 cm^{-1}) and amorphous content (1464 and 717 cm^{-1}). The percentage of the crystalline content, X_c, can be calculated using Eq. (3):

$$X_c = 100 - \frac{(1 - I_a/I_b)/1.233}{1 + I_a/I_b} \times 100 \quad (3)$$

where I_a and I_b can be derived from the bands at either 1474 and 1464 cm^{-1} or 729 and 717 cm^{-1}, respectively (Zerbi et al., 1989). In relation to this, Colom et al. determined that the bands at 729 and 717 cm^{-1} were the most appropriate to study because a peak from cellulose fibers at 1430 cm^{-1} interferes with the 1474 and 1464 cm^{-1} peaks (Colom, Canavate, Pagès, Saurina, & Carrasco, 2000). Using the bands at 1474 and 1464 cm^{-1} to determine crystallinity leads to unreliable results because these bands are asymmetric. In our work, the Fit-Gaussion of FTIR of 680–800 cm^{-1} was determined (Fig. 7). Crystallinity was calculated using the doublet peaks at 729 and 717 cm^{-1} as shown in Fig. 8.

As the samples underwent aging, the differences in the crystallinity of the RSF/HDPE and nano-SiO_2/RSF/

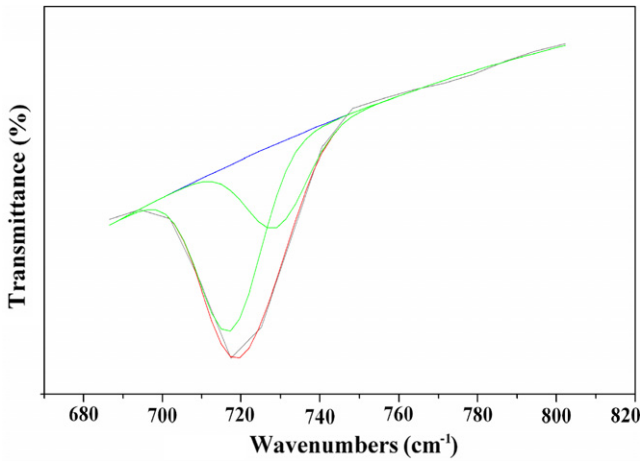

Fig. 7. Fit-Gaussion of FTIR at 680–800 cm^{-1} of RSF/HDPE composite (aging time: 75 days).

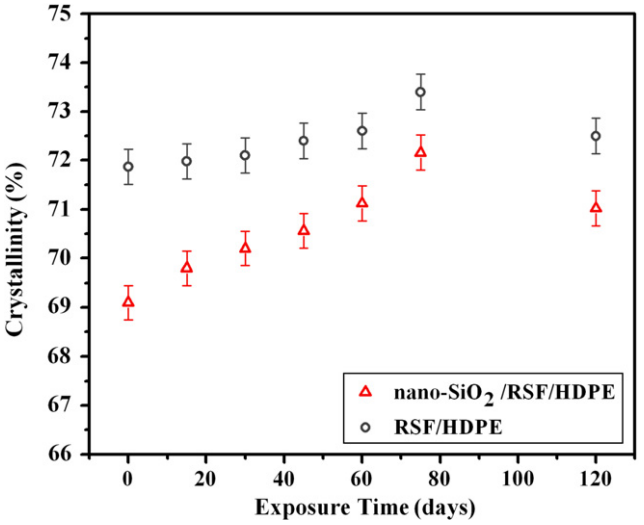

Fig. 8. Crystallinity as a function of exposure time for RSF/HDPE and nano-SiO_2/ RSF/HDPE composites.

HDPE composites became apparent. The crystallinity of the samples appeared to increase through 75 days of exposure, at which point they then began to decrease, resulting in a significant decrease at 120 days (Fig. 8). An increase in crystallinity can be used as an indicator of polyethylene chain scission during photodegradation. Chain scissions resulting from degradation via Norrish I and II reactions reduce the density of the entanglements in the amorphous phase, allowing shorter molecules to crystallize because of their higher mobility (Jabarin & Lofgren, 1994). Therefore, secondary crystallization takes place in the amorphous phase of polyethylene. Because chain scission occurs during exposure as evidenced by the growth of carbonyl and vinyl groups, we expected that the crystallinity would increase. Indeed, others have found increases in crystallinity after weathering. For instance, Kaci et al. (Kaci et al., 2001) used FTIR to determine the crystallinity of low-density polyethylene after natural weathering. Crystallinity increased with an increase in exposure time until a plateau was reached after 400 days. The authors attributed this trend to secondary crystallization in the amorphous phase (Colom et al., 2000). Hamid and Amin (Hamid & Amin, 1995) studied natural weathering of low-density polyethylene (LDPE). They concluded that crosslinking and chain scission reactions take place simultaneously. Tidjani (Tidjani, 2000) adds that under accelerated weathering, crosslinking reactions reduce the concentration of free radicals taking part in the oxidation process. As with the RSF/HDPE and nano-SiO_2/RSF/HDPE composites, oxidation damage can also occur at the tie molecule region. Tie molecules are polymer molecules that form a part of a folded crystalline region and extend through an amorphous region into another crystalline region. A small amount of oxidation products in polyethylene can cause great damage to the tie molecules, resulting in a breakdown of crystallization. Chain scission in the HDPE matrix of the composites eventually affected the tie molecules and the crystallinity was decreased at 120 days.

3.4. Crystallinity changes of the RSF/HDPE composites by DSC

Fig. 9 shows the DSC curves of unweathered and weathered RSF/HDPE composites (120 days). The crystallinity of the RSF/HDPE composites was investigated by means of differential scanning calorimetry (DSC). Crystallinity was calculated using the following equations:

$$X_c = \frac{\Delta H_m}{\phi \Delta H_m^0} \times 100 \quad (4)$$

where ΔH_m is the experimental heat of fusion or crystallization determined from DSC, $\Delta H_m{}^0$ is the assumed heat of fusion or crystallization of fully crystalline HDPE(293 J/g) (Liang, Xu, Bao, & Xu, 2004), and φ is the weight fraction

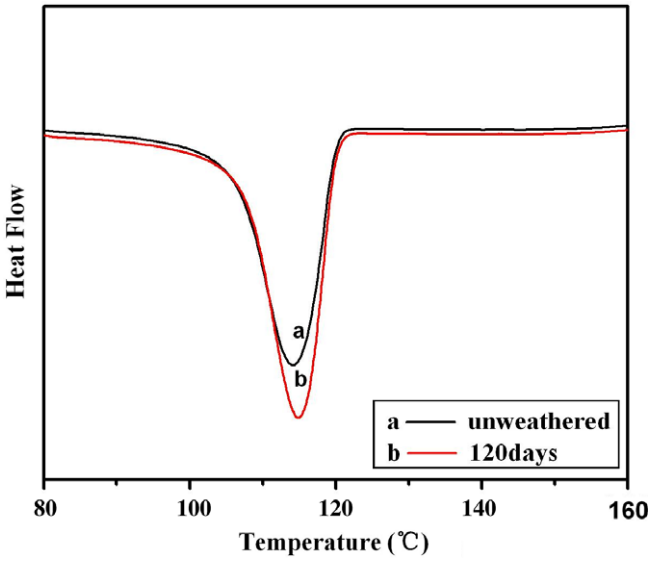

Fig. 9. DSC curves of unweathered and weathered RSF/HDPE composites.

of HDPE in the composites. Calculating from Eq. (4), it can be derived that the crystallinity of the unweathered RSF/HDPE composites is 39.3 and that of weathered RSF/HDPE composites (120 days) is 45.3. This result indicates that the crystallinity of the samples increases because of natural aging, and the values of crystallinity derived by DSC are smaller than those derived by FTIR.

4. Conclusions

FTIR spectroscopy was used to determine carbonyl group formation, vinyl group formation, and crystallinity changes during weathering. An increase in the calculated carbonyl index indicates an increase in polymer chain scission. The carbonyl index was roughly lower for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites. The calculated vinyl index can also be used to indicate polymer chain scission. The concentration of vinyl groups was generally much larger for the RSF/HDPE composites than for the nano-SiO_2/RSF/HDPE composites. At the same time, carbonyl index and vinyl index decrease with an increase in depth of the composites, particularly decreasing strongly from 100 to 200 μm. This indicates that the aging of the nano-SiO_2/RSF/HDPE composites occur on the surface of the samples, and that aging is stronger at a smaller depth of the samples. Increases in matrix crystallinity can occur if chain scission occurs. The shorter, more mobile chains recrystallize in the amorphous phase of the polymer. Our data show differences between crystallinity changes for RSF/HDPE and nano-SiO_2/RSF/HDPE composites. However, the crystallinity of the samples increase because of natural aging, and the values of crystallinity derived by DSC are smaller than those derived by FTIR.

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