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Studies on quick functionalization of polyethylene through ultraviolet irradiation and its composites

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Abstract The oxygen-containing groups such as C–O, C=O, and C(=O)O were quickly introduced onto high-density polyethylene (HDPE) chains through ultraviolet irradiation in ozone atmosphere, and the functionalized HDPE was prepared. The content of the C–O, C=O, and C(=O)O groups increased with increasing the irradiation time. There was no gel in the functionalized HDPE. Compared with that of HDPE, the crystal form, cell parameters, and face space of the functionalized HDPE did not change, and its melting temperature and thermal stability decreased, while the crystallinity, hydrophilicity, and melt index increased. The functionalized HDPE/Sericite–Tridymite–Cristobalite (STC) (60/40) composite was prepared by melting blend. Compared with that of the HDPE/STC composite, the interfacial interaction and the dispersion of the STC particles in the functionalized HDPE/STC composite were improved markedly. With increasing the irradiation time, the tensile strength and notched impact strength of the functionalized HDPE/STC composite increased, while its melt index decreased.

Keywords Polyethylene · Quick functionalization · Ultraviolet irradiation · Composite

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Introduction

Polyolefin is a class of hydrophobic and inert polymer, and the compatibility between them and polar materials (such as inorganic fillers) is poor. Therefore, the mechanical properties of their blends are often poorer than those of the parent polymers. The most common approach to improve compatibilization is to introduce a third component as a compatibilizer, usually a polymer attached with some functional groups, which can promote interfacial interaction between the matrix and the dispersed phase. In general, the active functional groups can be introduced onto polymer chains through graft copolymerization with monomers containing desired functional groups. However, this approach has some disadvantages, such as complex processing and chemical pollution. Furthermore, the residue of graft monomers and other auxiliaries will then bring about negative effects on the thermal, electrical, and mechanical properties of the blends. Lei, Guan and Wu et al. [1–18] adopted ultraviolet light to irradiate polyethylene (PE) and polypropylene (PP) in air or oxygen (O_2) atmosphere without adding any monomers and auxiliaries, some oxygen-containing groups such as C–O, C=O, and C(=O)O were successfully introduced onto the molecular chains of PE and PP, and realized the functionalization of the PE and PP. The compatibility between the functionalized polyolefin and inorganic fillers or engineering plastics or polar polymer was improved, and the mechanical properties of the polyolefin composite increased. Obviously, the way above to functionalize polyolefin was environmental friendly. However, the functionalization of polyolefin by ultraviolet irradiation in air or O_2 atmosphere had disadvantages of time-consuming (24–48 h) and low efficient, furthermore the gels were found in the functionalized PE, which was bad for blending process.

In this article, through ultraviolet irradiation in ozone atmosphere, some oxygen-containing groups such as C=O, C–O, and C(=O)O were introduced onto HDPE chains in short time ($\leq$20 min), and HDPE was quickly functionalized, while there was no gel in the functionalized HDPE. Compared with those of HDPE/STC composite, the dispersion and interfacial adhesion of functionalized HDPE/STC composite were increased markedly, and its mechanical properties especially impact strength were thus increased.

Experimental

Materials

HDPE powder (grade 5000S) with a melt flow index of 1.0 g/10 min was manufactured by Yangzi Petrochemical Stock Co. Ltd (China). STC with an average particle size of 1.6 μm was manufactured by Sichuan Powder Engineering Center (China).

Functionalization of HDPE

The ultraviolet irradiation of HDPE was performed at 78 W/m^2 and 40 °C in ozone atmosphere under an ultraviolet lamp manufactured by Chengdu Lamp Factory (China).

Preparation of functionalized HDPE/STC composites

The HDPE/STC (60/40) composite and functionalized HDPE/STC (60/40) composite were prepared with a twin roller at 170 °C for 10 min, respectively. The composites were molded to 1 and 4-mm thick plates, respectively. The plates were then cut into the required specimens according to the test standards.

Measurement and characterization

FTIR analysis was carried out on a VECTOR22 spectrometer (Germany). HDPE and the functionalized HDPE were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}, respectively.

XPS analysis was performed using an ESCALAB MK-II spectrometer (UK) with AlKα source (1486.6 eV). The C_{1s} peak was fitly resolved according to Gauss distribution.

Gel content measurement was determined by means of a soxhelet extractor. The sample was exposed to refluxing xylene for 168 h.

XRD measurement was made using a XD-3A X-ray diffractometer (Japan) with CuKα irradiation source.

DSC analysis was carried out on a LABSYS thermal analyzer (France). HDPE and functionalized HDPE were heated from room temperature to 200 °C at a heating rate of 10 °C/min, respectively. The crystallinity was determined from $C = H_\text{m}/H_\text{m}^\text{o} \times 100\%$, where H_m is the melting enthalpy of the sample; H_m^o is the melting enthalpy at 100% crystallinity of PE, which is 285.9 J/g.

Water contact angle measurement was carried out with a RAMHAR-100 contact angle tester (USA) at room temperature.

Melt index measurement was carried out using an XNR-400A tester (China) under 190 °C and 2.16 kg load.

Thermogravimetry (TG) analysis was performed with a TA2100-SDT2926 (USA). The samples were heated from room temperature to 600 °C at heating rate of 10 °C/min in nitrogen atmosphere. The initial temperature of weight loss was denoted T_i and the corresponding temperature to the maximum rate of weight loss was denoted T_max.

Molau test: HDPE or functionalized HDPE/STC composites (1 g) were dissolved in hot xylene (19 g). The solution was laid for 72 h at 90 °C, and then the suspension of STC particles was carefully observed.

SEM was carried out using a HITACHI-X650 tester (Japan).

Tensile test was performed using an INSTRON-4466 all-purpose tester (USA) according to ASTM D268. Notched Izod impact test was performed using a XJ-40A impact tester (China) according to ISO 180-1993E.

Results and discussion

FTIR analysis of functionalized HDPE

As shown in Fig. 1, the absorption peak around 1725 and 1180 cm^{-1} of the functionalized HDPE was, respectively, increased compared with that of

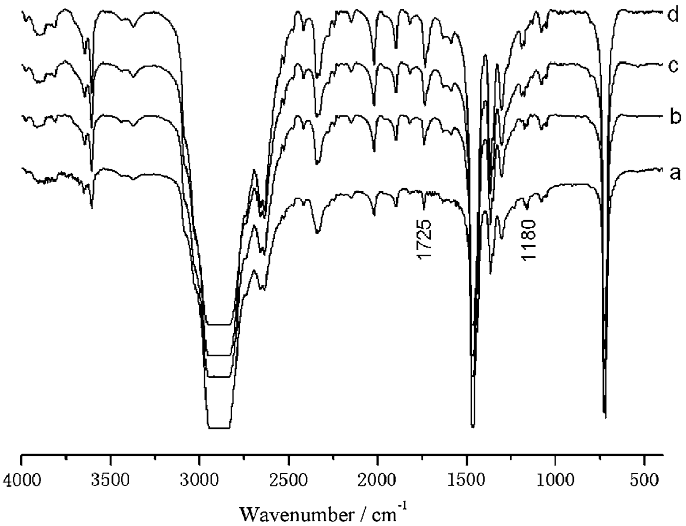

Fig. 1 FTIR spectra of HDPE (*a*) and functionalized HDPE for 10 min (*b*), 15 min (*c*), and 20 min (*d*)

Table 1 XPS data of functionalized HDPE

Irradiated time/min	C–H	C–O	C=O	C(=O)O	Gel content/%
0	97.02	2.18	0.75	0.05	0
10	93.62	5.48	0.83	0.07	0
15	93.29	5.78	0.85	0.08	0
20	92.53	6.41	0.94	0.12	0

unirradiated HDPE. This indicated that the functional groups of C=O and C–O were introduced onto HDPE chains through ultraviolet irradiation for short time in ozone atmosphere, and a sort of functionalized HDPE was obtained. The content of C=O and C–O increased with increasing irradiation time, and the functional degree of the functionalized HDPE was thus controlled by adjusting the irradiation time.

XPS analysis of functionalized HDPE

To know accurately the figure of the oxygen incorporation with carbon, the functionalized HDPE was investigated by XPS. The C_{1s} peak of the sample was resolved into component peaks at binding energy of 285.0, 286.2, 287.5, and 289.2 eV, corresponding to carbon in C–H, C–O, C=O, and C(=O)O groups. It was seen from Table 1 that the groups introduced through ultraviolet irradiation in ozone atmosphere were C–O, C=O, and C (=O) O, respectively, and the content of the groups was increased with increasing the irradiation time.

Compared with that of HDPE through ultraviolet irradiation in air or O_2 atmosphere [5–7, 9], the rate of functionalization of HDPE in ozone atmosphere was increased remarkably.

The gel was not found in the functionalized HDPE through ultraviolet irradiation for short time in ozone atmosphere (Table 1), which was different from the functionalized PE through ultraviolet irradiation for long time in air [4–8], and was advantaged for preparation of the functionalized HDPE/fillers composites.

XRD analysis of functionalized HDPE

The crystal form of the functionalized HDPE was the same orthorhombic lattice as HDPE. As shown in Table 2, the cell parameters (*a*, *b*, and *c*) and face space (d_{110}, d_{200}, and d_{020}) of functionalized HDPE were also not changed compared with that of HDPE.

DSC analysis of functionalized HDPE

As shown in Table 3, the melting temperature (T_{onset}) of the functionalized HDPE decreased compared with that of HDPE. This was due to the formation of crystal lattice defects in process of functionalization of HDPE [3]. The crystallinity (*C*) of functionalized HDPE was increased with increasing irradiation time (Table 3). These were due to scission of the HDPE chains in process of the functionalization followed by the subsequent recrystallization of the broken chains.

Hydrophilicity and liquidity of functionalized HDPE

As shown in Table 4, the melt index of functionalized HDPE increased with increasing irradiation time, indicating that the fluidity of functionalized HDPE was higher than that of HDPE because of the degradation of functionalized HDPE chains. The water contact angle of functionalized HDPE was lower than that of HDPE (Table 4), indicating that the hydrophilicity of functionalized HDPE was improved because of the introduction of polar functional groups of C–O, C=O, and C(=O)O.

Table 2 XRD data of functionalized HDPE

Irradiated time/min	Cell parameter/Å			Face space/Å				
	a	*b*	*c*	d_{110}	d_{200}	d_{210}	d_{020}	d_{011}
0	7.43	4.95	2.55	4.11	3.71	2.97	2.47	2.27
10	7.41	4.93	2.55	4.12	3.70	2.96	2.48	2.26
20	7.42	4.93	2.54	4.10	3.69	2.97	2.47	2.28

Table 3 DSC data of functionalized HDPE

Irradiation time/min	T_{onset}/°C	ΔH_{m}/J/g	*C*/%
0	125.2	169.8	59.4
10	125.0	171.1	59.9
20	124.7	174.9	61.2

Table 4 Water contact angle and melt index of functionalized HDPE

Irradiation time/min	0	10	15	20
Water contact angle/°	93	91	89	87
Melt index/g/10 min	1.0	1.0	1.1	1.2

Table 5 TG data of functionalized HDPE

Irradiation time/min	T_i/°C	T_{max}/°C
0	451.5	476.6
10	448.3	474.8
20	446.2	473.1

TG analysis of functionalized HDPE

As shown in Table 5, the T_i of the functionalized HDPE decreased with increasing irradiation time, indicating that the thermal stability of the functionalized HDPE felled down because of the formation of the degradation product in process of the functionalization. However, the blend of the functionalized HDPE with filler was not influenced because the initial temperature of weight loss was higher than the blending temperature of 170 °C.

XRD and DSC analysis of functionalized HDPE/STC composite

As shown in Fig. 2, the location of diffraction peak of the functionalized HDPE in functionalized HDPE/STC composite was not changed compared with that of HDPE, and the functionalized HDPE still kept orthorhombic structure.

As shown in Table 6, the crystallinity of the functionalized HDPE in the functionalized HDPE/STC composite decreased compared with that of the HDPE in HDPE/STC composite, and the decreased extent augmented with increasing the irradiation time. This was because the interfacial interaction between STC particles and functionalized HDPE matrix was strong, and it hampered the crystallizing of HDPE, and lead to the drop of crystallinity of the HDPE Table 7.

Molau test of functionalized HDPE/STC composite

The xylene solution of the HDPE/STC composite separated into two parts, the transparent xylene solution containing HDPE component was on the top in the test tube, and the STC particles deposited on the bottom in the test tube. These indicated that the interfacial interaction between the STC particles and the HDPE chains was weak, and resulted in abruption of the STC particles from the HDPE. Concerning functionalized HDPE/STC composite, the top in the test tube was a turbidity suspension containing STC particles and HDPE, and only a small amount of STC particles deposited on the bottom of the test tube, and the amount of deposited STC particles decreased with increasing the irradiation time of HDPE. These were due to strong interfacial interaction between the components and melioration of dispersion

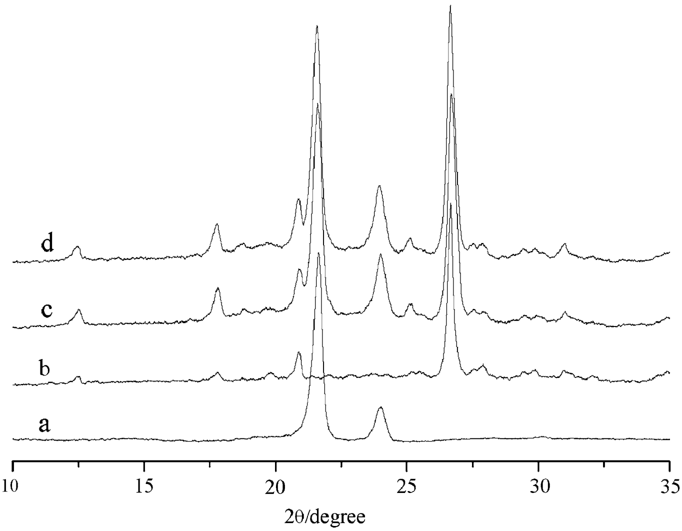

Fig. 2 XRD spectra of HDPE (*a*), STC (*b*), functionalized HDPE (10 min)/STC composite (*c*), and functionalized HDPE (20 min)/STC composite (*d*)

Table 6 DSC data of HDPE/STC and functionalized HDPE/STC composite

Samples	Melting temperature/°C	Melting enthalpy/J/g	Crystallinity/%
HDPE/STC	125.1	169.5	59.29
Functionalized HDPE (10 min)/STC	124.8	168.2	58.83
Functionalized HDPE (20 min)/STC	124.5	167.0	58.41

Table 7 Molau test results of HDPE/STC and functionalized HDPE/STC composite

Sample	Observed phenomenon
HDPE/STC	Transparent solution containing HDPE in the superstratum and STC particles deposit at the bottom of test tube
Functionalized HDPE (10 min)/STC	A persistent turbidity and a small amount of STC particles deposit at the bottom of test tube
Functionalized HDPE (15 min)/STC	A persistent turbidity and a smaller amount of STC particles deposit at the bottom of test tube
Functionalized HDPE (20 min)/STC	A persistent turbidity and a smallest amount of STC particles deposit at the bottom of test tube

of the STC particles in the functionalized HDPE/STC composite. The interfacial interaction and the dispersion were farther improved with increasing the irradiation time.

SEM of functionalized HDPE/STC composite

As shown in Fig. 3a, some STC particles emerged on liquid nitrogen frozen fractured surface of unirradiated HDPE/STC composite, and the agglomeration of the STC particles was found, while the size of the STC particles was asymmetric, indicating the poor dispersion of STC particles in unirradiated HDPE matrix. On the other hand, the STC particles emerged on liquid nitrogen frozen fractured surface of functionalized HDPE/STC composite were few, and the aggregated STC particles were not detected (Fig. 3b), indicating that the dispersion of the STC particles in the composite was increased markedly. This was attributed to improvement of compatibility of functionalized HDPE/STC composite.

As shown in Fig. 4a, the impact fractured surface of unirradiated HDPE/STC composite was smooth, which presented a brittle fracture surface. Therefore, the impact strength of HDPE/STC composite was low. The impact fractured surface of functionalized HDPE/STC composite was accidented, and some functionalized HDPE as matrix was drawn out to turn to fibrous structure (Fig. 4b), revealing a toughness fractured surface due to the increase of interfacial interaction between components in the composite. The impact strength of HDPE/STC composite was thus increased compared with that of unirradiated HDPE/STC composite.

Mechanical properties and liquidity of functionalized HDPE/STC composite

As shown in Table 8, the mechanical properties of the HDPE/STC composite were poor. This was because of weak interfacial interaction between the polar STC and the nonpolar HDPE and agglomeration of the STC particles in the HDPE/STC composite.

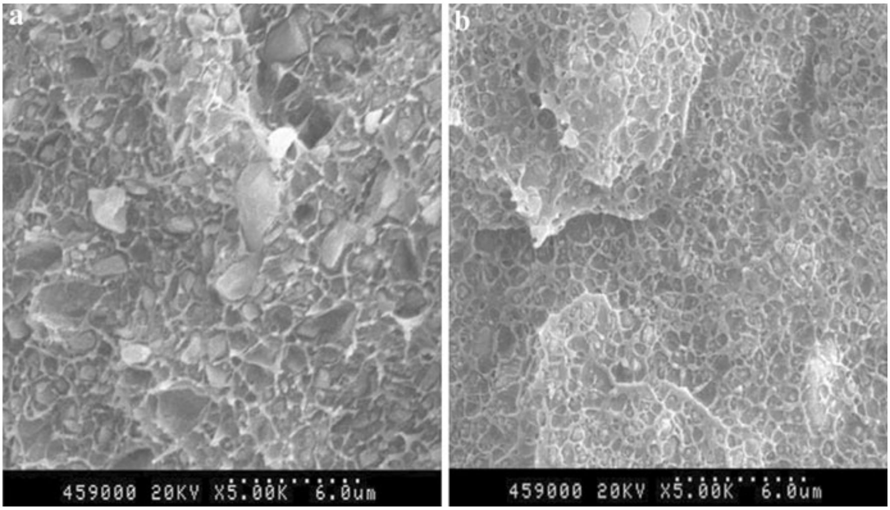

Fig. 3 SEM photographs of liquid nitrogen frozen fractured surface of HDPE/STC (60/40) composite (**a**) and functionalized (20 min) HDPE/STC (60/40) composite (**b**)

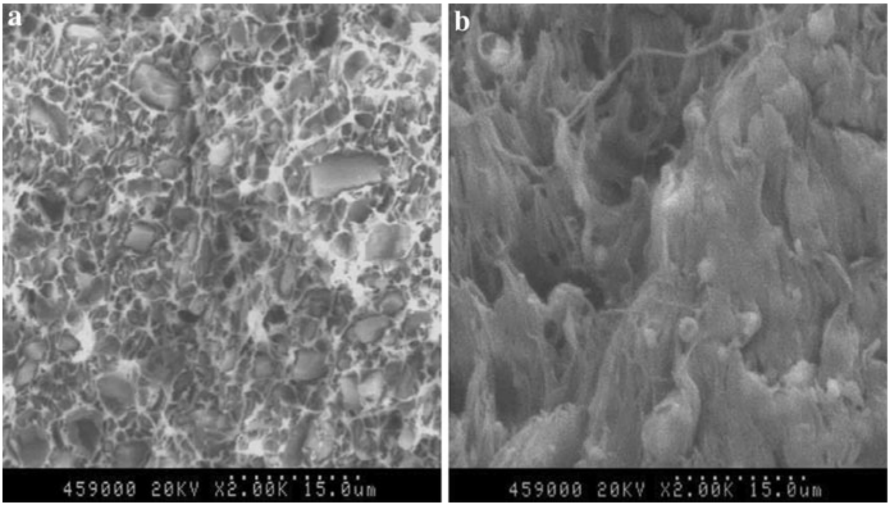

Fig. 4 SEM photographs of impact fractured surface of HDPE/STC (60/40) composite (**a**) and functionalized (20 min) HDPE/STC (60/40) composite (**b**)

Table 8 Mechanical properties and melt index of functionalized HDPE/STC composite

Irradiation time/min	Tensile strength/MPa	Impact strength/J/m	Melt index/g/10 min
0	24.2	48	0.25
10	27.5	130	0.20
15	28.0	210	0.18
20	28.4	316	0.16

Compared with that of the HDPE/STC composite, the tensile strength and the notched impact strength of the functionalized HDPE/STC composite were increased, and their enhanced extent increased with increasing the irradiation time (Table 8). This was due to strong interfacial interaction between the STC particles and the HDPE chains and fine dispersion of the STC particles in the functionalized HDPE/STC composite.

The melt index of the functionalized HDPE/STC composite decreased with increasing the irradiation time, also indicating that the interfacial interaction between the STC particles and the functionalized HDPE chains enhanced with increasing the irradiation time.

Conclusions

The functional groups of C–O, C=O, and C(=O)O were quickly introduced onto HDPE chains through ultraviolet irradiation in ozone atmosphere, and their content increased with increasing the irradiation time. Furthermore, the gel was not found in the functionalized HDPE. Compared with that of HDPE, the cell parameters and face space of the functionalized HDPE were not changed, while its melting temperature decreased, and the crystallinity increased. With increasing the irradiation time, the hydrophilicity and melt index of the functionalized HDPE were increased, respectively, while its temperature of weight loss was decreased appreciably.

The functionalized HDPE/STC (60/40) composite was prepared. Compared with those in the HDPE/STC (60/40) composite, the interfacial interaction between the STC particles and the HDPE chains and the dispersion of the STC particles in the functionalized HDPE/STC (60/40) composite were increased markedly, and its mechanical properties especially the notched impact strength were increased, while its melt index decreased.

References

1. Lei JX, Zhou R (2000) Mechanical properties and interfacial interaction of $CaCO_3$ filled HDPE compatibilized with HDPE functionalized by ultraviolet irradiation. Polym Eng Sci 40:1529–1533
2. Guan R (2000) Study on compatibility of PP-STC blends functionalized by ultraviolet irradiation. J Appl Polym Sci 77:96–103
3. Guan R, Xu X (2001) Structure and properties of isotactic polypropylene functionalized by ultraviolet irradiation. J Appl Polym Sci 79:1456–1466
4. Wu SS, Ji GD, Shen J (2003) A study on ultraviolet irradiation modification of high-density polyethylene and its effect in the compatibility of HDPE/PVA fibre composites. Mater Lett 57:2647–2650
5. Wu SS, Chen ZN, Xu X (2003) Study on structure and properties of HDPE functionalized by ultraviolet irradiation in air and O_2 atmosphere. Mater Lett 57:3495–3499
6. Wu SS, Xu X (2003) Structure and properties of ultraviolet-irradiated high density polyethylene at different environmental temperatures. J Appl Polym Sci 89:2966–2969
7. Wu SS, Zhang J, Xu X (2003) Studies on high density polyethylene (HDPE) functionalized by ultraviolet irradiation and its application. Polym Int 52:1527–1530
8. Wu SS, Xu X (2004) Effect of the reaction atmosphere on high-density polyethylene functionalized by ultraviolet irradiation. J Appl Polym Sci 91:2326–2329
9. Wu SS, Sang HB, Liu ZM, Shen J (2004) Effect of ultraviolet irradiation on structure and properties of HDPE and HDPE/STC blends. J Macromol Sci (Pure Appl Chem) 41:1311–1319
10. Wu SS, Sang HB, Liu ZM, Xu X (2005) Effect of reaction temperature on HDPE functionalized through ultraviolet irradiation. Polym Plast Tech Eng 44:381–390
11. Wu SS, Ran QP, Liu ZM, Shen J (2005) Studies on structure and properties of HDPE functionalized through ultraviolet irradiation and its blends with $CaCO_3$. Polym Plast Tech Eng 44:1467–1474
12. Wu SS, Chi B, Yan H, Shen J (2006) A study of LLDPE functionalized through ultraviolet irradiation and interfacial interaction of PA66/functionalized LLDPE blends. J Appl Polym Sci 99:2029–2032
13. Wu SS, Chen ZN, Ma QQ, Shen J (2006) Studies on linear low-density polyethylene functionalized by ultraviolet irradiation and its compatibilization. Polym Bull 57:595–602
14. Deng SS, Ran QP, Wu SS, Shen J (2008) Storage stability of ultraviolet irradiated HDPE. Polym Polym Compos 16:303–307
15. Deng SS, Ran QP, Wu SS, Shen J (2008) Fast functionalisation of polypropylene (PP) by ultraviolet irradiation and compatibilised PP/$CaCO_3$ composite. Polym Polym Compos 16:375–378
16. Wu SS, Ran QP, Shen J (2009) Effect of storage on ultraviolet irradiated HDPE. Plast Rubber Compos 38:219–221
17. Wu SS, Ran QP, Shen J (2010) Effect of light intensity on ultraviolet irradiated polypropylene and its compatibilization with $CaCO_3$. J Thermoplast Compos 23:149–159
18. Qiao M, Wu SS, Ran QP, Shen J (2010) Effect of environmental temperature on ultraviolet irradiated PP and its composite. J Thermoplast Compos 23:137–148