Polym. Bull. (2012) 68:2089–2096
DOI 10.1007/s00289-011-0666-x

ORIGINAL PAPER

Studies on fast functionalization of HDPE by ultraviolet irradiation and functionalized HDPE/$CaCO_3$ composites

Yue Lu · Pei-Pei Ma · Shi-Shan Wu · Jian Shen

Received: 26 August 2011 / Revised: 30 October 2011 / Accepted: 3 November 2011 /

Abstract High density polyethylene (HDPE) was functionalized quickly by ultraviolet irradiated in ozone atmosphere. The oxygen-containing groups in the functionalized HDPE were C=O and C–O, and their content increased with increasing the irradiation time. The molecular weight of the functionalized HDPE decreased and its distribution became wider with increasing the irradiation time. The gel was not found in the functionalized HDPE. Compared with those of HDPE, the melting temperature and crystallinity of the functionalized HDPE decreased. With increasing the irradiation time, the hydrophilicity of the functionalized HDPE was enhanced, while its temperature of thermal decomposition decreased. The functionalized HDPE/$CaCO_3$ composites were prepared. Compared with those of HDPE/$CaCO_3$ composites, the compatibility and dispersion of the functionalized HDPE/$CaCO_3$ composites were enhanced observably. The tensile strength and notch impact strength of the functionalized HDPE/$CaCO_3$ composites increased with increasing the irradiation time.

Keywords Ultraviolet irradiation · HDPE · Blends · Mechanical properties · HDPE/$CaCO_3$ composites

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Y. Lu · P.-P. Ma · S.-S. Wu (✉) · J. Shen
Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
e-mail: shishanwu@yahoo.com.cn

J. Shen
College of Chemistry and Environment Science, Nanjing Normal University,
Nanjing 210097, China

Introduction

Polyolefin is a kind of general polymeric material with low cost and simple processing. Through blending and filling, it is possible to prepare high performance polyolefin composites. But the compatibility between polyolefin and inorganic fillers or engineering plastics is usually poor because polyolefin is hydrophobic and inert, and their composites often have worse mechanical properties than the parent polymers. Functionalizing polyolefin to improve its compatibility with inorganic fillers or engineering plastics is one of the ways to prepare high performance polyolefin composites.

The oxygen-containing groups, such as C=O, C–O and C(=O)O, were introduced onto the molecular chains of polyolefin through irradiation in certain atmosphere without adding additional monomers and additives. These treatments were usually used to modify the surface tension and the adhesive properties of polyolefin [1, 2]. Lei et al. [3–17] functionalized polyolefin through ultraviolet irradiation in air and O_2 atmosphere to enhance the compatibility of polyolefin with the inorganic fillers or engineering plastics significantly, and stiffened and toughened polyolefin materials were obtained. However, the disadvantage of ultraviolet irradiation in air and O_2 atmosphere is time-consuming [7, 10, 12, 15]. Because of its hydrophilic and compatibility, the ultraviolet irradiated HDPE could be used directly in printing and as a type of macromolecular compatibilizer.

In this article, high-density polyethylene (HDPE) was quickly functionalized by ultraviolet irradiation in ozone atmosphere and the functionalized HDPE/$CaCO_3$ composites were prepared. Compared to those of HDPE/$CaCO_3$ composites, it was glad to see that the dispersion and compatibility of the functionalized HDPE/$CaCO_3$ composites were both improved and thus their mechanical properties were increased.

Experimental

Materials

High density polyethylene (DGDA 6098, powder) with a melt index (MI) of 0.1 g/10 min was manufactured by Qilu petrochemical Company (China). $CaCO_3$ treated with silane coupling agent with average size of 1.2 μm was provided by Nanjing University of Technology (China).

Functionalization of HDPE

The functionalization of HDPE was performed at environmental temperature of 40 °C and light intensity of 78 W/m^2 in ozone atmosphere under a Ga-I lamp with the wavelength in the range of 365–450 nm manufactured by Chengdu Lamp Factory (China). The functionalized HDPE by ultraviolet irradiation was denoted as uvHDPE.

HDPE/$CaCO_3$ and uvHDPE/$CaCO_3$ composites

The HDPE (or uvHDPE) and $CaCO_3$ were blended in a two-roll mill at 165 °C for 10 min. The blends were processed at 190 °C and 15 MPa for 10 min using hot hydraulic press and then cooled down at room temperature and 10 MPa for 10 min using cold hydraulic press to produce 1- or 4-mm thick sheets.

Measurement and characterization

X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALB MK II spectrometer (UK) with AlKα source (1486.6 eV). The C_{1S} peak was fittingly decomposed into component peaks according to Gaussian distribution.

Gel permeation chromatography (GPC) analysis was performed using a Waters Alliance 2000GPC/V instrument (USA; the solvent of mobile phase: o-dichlorobenzene, temperature: 135 °C, flow rate: 1.0 mL/min).

Gel contents testing were determined by means of a soxhlet extractor. The samples were exposed to refluxing xylene for 72 h.

X-ray diffraction (XRD) analysis was performed with a D/Max II diffractometer (Japan). The sample was scanned from 10° to 50° at a scan rate of 4°/min.

Differential scanning calorimetry (DSC) analysis was performed on a pyres 1 thermal analyzer (USA). The samples were heated from room temperature to 180 °C at a heating rate of 10 °C/min. The crystallinity (C) was determined from $C = \Delta H_m/\Delta H_m^o \times 100\%$, where ΔH_m is melt enthalpy of the HDPE sample; ΔH_m^o is melt enthalpy at 100% crystallinity of polyethylene (286 J/g).

The samples were compression-molded into a 30–50 μm thick films. Contact angle testing of the film with distilled water was carried out on a RAMEHART 100 instrument (USA) at room temperature.

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

Tensile test was carried out on an Instron 4466 all-purpose tester (USA) according to ASTM D268. Izod notched impact measurement was made on notched samples using an XJ-40A apparatus (China) according to ISO 180-1993E.

Scanning electron microscopy (SEM) analysis was performed using a LEO-15300VP Scanning Electron Microscope (Germany).

Results and discussion

XPS analysis of uvHDPE

In order to know how oxygen actually bonded with carbon in uvHDPE, the sample was investigated by XPS. The C_{1S} peak of the uvHDPE was resolved into three component peaks at binding energy of 285.0, 286.3, and 287.6 eV, corresponding to carbons in C–H, C–O, and C=O, respectively, the introduced oxygen-containing were thus C–O and C=O. Their contents are listed in Table 1. The contents of the C–O and C=O were increased with increasing the irradiation time. Compared with that of the uvHDPE in air and O_2 atmosphere, the functionalization of HDPE in ozone atmosphere was accelerated remarkably, and the fast functionalization of HDPE was thus actualized.

GPC and gel analysis of uvHDPE

The number average molecular weight ($\overline{M}_n$), the weight average molecular weight ($\overline{M}_w$) and the distribution of uvHDPE are listed in Table 2. Compared with those of HDPE, the $\overline{M}_n$ and $\overline{M}_w$ of the uvHDPE decreased, respectively, and the distribution of the molecular weight became wider. The decreases of the molecular weight indicated that the HDPE chains were partly degraded in the process of the functionalization of HDPE by ultraviolet irradiation. The wider distribution of the molecular weight was because of different degradation degree of the HDPE chains on the surface and inner part of the uvHDPE particles.

The gel was found in the functionalized HDPE by ultraviolet irradiation in air and O_2 atmosphere. But there was no gel formed in the functionalized HDPE by ultraviolet irradiation in ozone atmosphere, and that was advantaged for subsequently blend process.

XRD analysis of uvHDPE

The cell parameter and the face space of the uvHDPE are listed in Table 3. The HDPE and uvHDPE were both orthorhombic lattice, and their cell parameters (a, b, and c) and face space were almost the same.

DSC analysis of uvHDPE

The melting temperature (T_{onset} and T_{peak}) and crystallinity (C) of uvHDPE are listed in Table 4. Compared with those of HDPE, the T_{onset} and T_{peak} of the

Table 1 XPS analysis data of uvHDPE

Irradiation time (min)	C–H (%)	C–O (%)	C=O (%)
0	100	0	0
10	97.54	1.88	0.58
15	96.18	3.09	0.73

Table 2 GPC and gel analysis data of uvHDPE

Irradiation time (min)	$\overline{M}_n(\times 10^4)$	$\overline{M}_w(\times 10^5)$	$\overline{M}_n/\overline{M}_w$	Gel content (%)
0	8.12	5.76	7.09	0
10	7.63	5.70	7.47	0
15	7.15	5.66	7.92	0

Table 3 XRD analysis data of uvHDPE

Irradiation time (min)	*a* (Å)	*b* (Å)	*c* (Å)	Face space (Å)				
				110	200	210	020	011
0	7.38	4.93	2.54	4.09	3.69	2.95	2.47	2.26
10	7.37	4.92	2.54	4.10	3.70	2.94	2.47	2.25
15	7.38	4.94	2.54	4.09	3.69	2.95	2.47	2.26

Table 4 DSC analysis data of uvHDPE

Irradiation time (min)	T_{onset} (°C)	T_{peak} (°C)	ΔH_{m} (J/g)	*C* (%)
0	122.8	133.2	174.7	61.1
10	122.6	132.9	173.9	60.8
15	122.3	132.6	173.0	60.5

Table 5 Water contact angle of uvHDPE

Irradiation time (min)	0	10	15	20
Water contact angle (°)	95	90	86	80

Table 6 TG analysis data of uvHDPE

Irradiation time (min)	T_{i} (°C)	T_{max} (°C)
0	443.5	476.8
15	438.7	475.6

uvHDPE decreased because of entity of the crystal lattice defects formed in process of the functionalization of HDPE [18]. With increasing the irradiation time, the crystallinity of the uvHDPE decreased because of the breakage of crystals in process of the functionalization.

Contact angle analysis of uvHDPE

The water contact angle of uvHDPE is listed in Table 5. The water contact angle of the uvHDPE decreased markedly with increasing the irradiation time, which indicated that the hydrophilicity of the uvHDPE was increased with increasing the irradiation time. We thought that the compatibility between the components in the uvHDPE/inorganic fillers composites might be improved.

TG analysis of uvHDPE

The T_{i} and T_{max} of uvHDPE were reported in Table 6. Compared with those of HDPE, the T_{i} and T_{max} of the uvHDPE decreased, indicating that its thermal stability became worse. Owing to that its T_{i} reached to 439.7 °C, the succeeding process might be accomplished successfully.

Mechanical properties of uvHDPE/$CaCO_3$ composites

The mechanical properties of HDPE/$CaCO_3$ and uvHDPE/$CaCO_3$ composites are listed in Table 7. The tensile strength and impact strength of the HDPE/$CaCO_3$ composites were lower than those of the HDPE because of the agglomeration of the $CaCO_3$ particles induced by poor compatibility between the $CaCO_3$ and the HDPE matrix.

Owing to strong interfacial interaction between the $CaCO_3$ and the uvHDPE matrix and improvement of the dispersion of the $CaCO_3$ particles, the tensile strength and impact strength of the uvHDPE/$CaCO_3$ composites were higher than those of the HDPE/$CaCO_3$ composites. With increasing the irradiation time, the mechanical properties of the uvHDPE/$CaCO_3$ composites were further increased because of the increase of the compatibility of the uvHDPE/$CaCO_3$ composites.

SEM of uvHDPE/$CaCO_3$ composites

The SEM photographs of liquid nitrogen frozen fractured surface of HDPE/$CaCO_3$ and uvHDPE/$CaCO_3$ composites were shown in Fig. 1. For the HDPE/$CaCO_3$

Table 7 Mechanical properties of HDPE, HDPE/$CaCO_3$ (60/40) and uvHDPE/$CaCO_3$ (60/40) composites

Sample	Tensile strength (MPa)	Notched impact strength (J/m)
HDPE/$CaCO_3$ composites	25.9	72
uvHDPE (10 min)/$CaCO_3$ composites	30.1	350
uvHDPE (15 min)/$CaCO_3$ composites	30.3	405

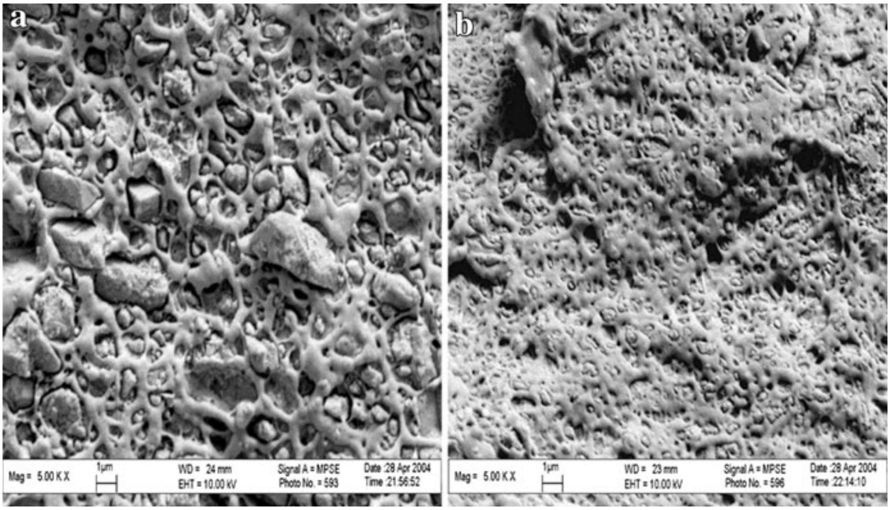

Fig. 1 SEM photographs of liquid nitrogen frozen fractured surface of HDPE/$CaCO_3$ (60/40) (**a**) and uvHDPE (15 min)/$CaCO_3$ (60/40) composites (**b**)

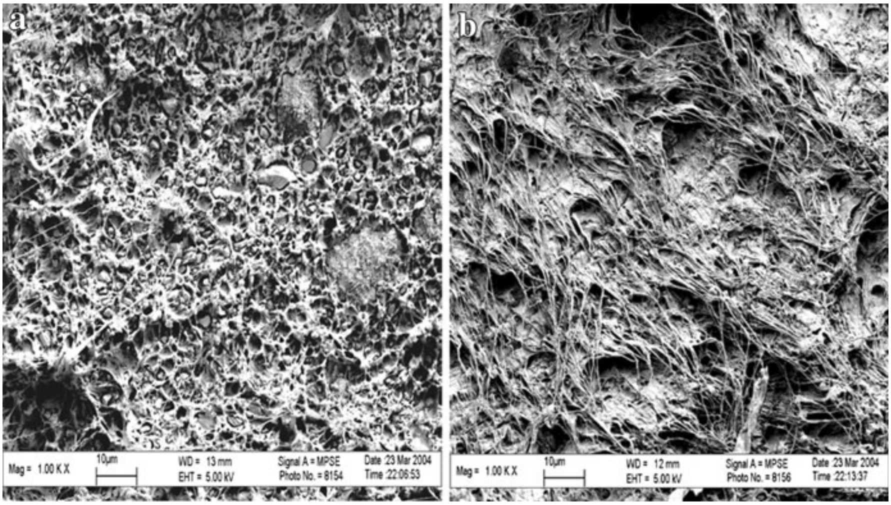

Fig. 2 SEM photographs of impact fractured surface of HDPE/$CaCO_3$ (60/40) (**a**) and uvHDPE (15 min)/$CaCO_3$ (60/40) composites (**b**)

composites, some agglomerated $CaCO_3$ particles emerged on the fractured surface, and their distribution of the size were wide (Fig. 1a), indicating that the dispersion of $CaCO_3$ particles in the HDPE/$CaCO_3$ composites was poor. For the uvHDPE/$CaCO_3$ composites, big agglomerated $CaCO_3$ particles were not found on the frozen fractured surface (Fig. 1b), and the agglomeration of the $CaCO_3$ particles in the uvHDPE/$CaCO_3$ composites was improved effectively because of the increase of compatibility of the composites.

The impact fractured surface of the HDPE/$CaCO_3$ composites displayed a character of brittle fracture, and some $CaCO_3$ particles were exposed on the fractured surface (Fig. 2a). The impact fractured surface of the uvHDPE/$CaCO_3$ composites displayed toughness fracture, indicating that some HDPE matrix was drawn out to fibrous HDPE, and no $CaCO_3$ particles were exposed on the impact fractured surface (Fig. 2b). The results above were due to that the dispersion of $CaCO_3$ particles and interfacial interaction between components in the uvHDPE/$CaCO_3$ composites were both enhanced.

Conclusions

In this work, HDPE was functionalized quickly by ultraviolet irradiation in ozone atmosphere. The molecular weight of the functionalized HDPE decreased and its distribution became wider with increasing the irradiation time. The gels were not found in the functionalized HDPE. Compared with those of HDPE, the melting temperature and crystallinity of the functionalized HDPE decreased. With increasing the irradiation time, its water contact angle and thermal stability decreased. Compared with those of HDPE/$CaCO_3$ composites, the compatibility between components and dispersion of $CaCO_3$ particles in the functionalized HDPE/$CaCO_3$ composites were both improved, and their mechanical properties were thus increased.

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