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Chlorinated and anhydride modified low density polyethylene by solid-phase chlorinating and grafting----Improving the adhesion of film-forming polymer

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Abstract

This paper is mainly focused on the modification of low density polyethylene (LDPE) by chlorinating and grafting simultaneously in gas-solid phase. There are two key problems to the success of the process. The first is the feasibility of chlorination and grafting occurring simultaneously on LDPE chains, and the second is how to gain the control of high chlorinated polyethylene (HCPE, Cl%wt>60%) preparation with LDPE as raw material, which is a heterogeneous reaction. The feasibility of the process is discussed by FTIR and ^{1}H-NMR, in which LDPE is chlorinated to high chlorine content (Cl%wt=64%) while maleic anhydride (MAH) is being grafted onto backbone chain (LDPE). This is a novel modification method patented by us, called as in-situ chlorinating graft copolymerization (ISCGC).The products molecular weight and distribution, thermal properties, and the factors affecting the modification process are analyzed by gel permeation chromatography (GPC)， differential scanning calorimetry (DSC), stereoscopic microscope and the curve of chlorine content versus time, respectively. Graft degree (GD) of the graft copolymer achieved about 2% which has a broad practical significance. The adhesion and impact strength tests of the product as film-forming polymer in coating indicate that it could effectively increase the adhesion when MAH is being grafted onto LDPE by ISCGC.

Keyword: High chlorinated polyethylene, Grafting, Performance, Adhesion

1 Introduction

The modified polyethylene (PE) prepared by chlorination is of great importance for various applications, of which the performance depends on chlorination methods, degree of chlorination and reaction conditions. Previous studies have been carried out on chlorination of PE which is synthesized by either suspension polymerization or solid-state chlorination conducted below the melting temperature.[1] Particularly when the degree of chlorination reached 60%wt, the high chlorinated polyethylene (HCPE) will have excellent physical-chemical properties. HCPE is commonly used in corrosion-resistant paints[2] and many relevant patents[3-6] have been issued in recent years.

The raw material of HCPE is usually high density polyethylene (HDPE). As corrosion-resistant paint, the main drawback of HCPE made of HDPE is the high viscosity of the product which makes it difficult to paint. The problem can be addressed by using LDPE instead of HDPE as raw material of HCPE. However, it leads to a bad adhesion for painting. In order to make the HCPE with low viscosity to possess good adhesion, we proposed to chlorinate LDPE and simultaneously graft MAH onto it via in-situ chlorinating graft copolymerization (ISCGC). This is achieved by gas-solid phase preparation. So this paper is mainly concerned with two key problems to the success of the process. The first is the feasibility of chlorination and grafting occurring simultaneously on LDPE chains, and the second is how to gain the control of HCPE reaction with LDPE as raw material, which is a heterogeneous reaction.

Graft modification is the most commonly polymer modifications methods, in which maleic anhydride (MAH) is often used as graft monomer due to its high polarity and reactivity. Of course, a lot of work can be found in this field where backbones polymers are not only constraint to PE[7-9] but also include others, e.g., grafting of MAH onto polypropylene[10-12] and chlorinated polyvinyl chloride[13]. But in these methods modification is generally carried out by free radical reaction with peroxide as initiators, which is unlikely to achieve high grafting degree and requires two steps to get chlorinated graft copolymer, the preparation of HCPE and the grafting on HCPE. In contrast, ISCGC only requires one step to get chlorinated graft copolymer.

In ISCGC, the homolysis of the chlorine molecule produces the Cl free radicals under heating. Following closely, the free radicals deprive H from LDPE chains to form macromolecular radicals. The MAH monomers are grafted onto LDPE chains as long as contacting with macromolecular radicals effectively. Otherwise, LDPE macromolecules radicals would react with chlorine molecules to be chlorinated, finally producing functionalized graft copolymer (LHCPE-cg-MAH) with low viscosity. With polyolefin as raw material and ISCGC as modified method, we have done a lot of work[14-16] including using MAH as monomer grafted onto HDPE with low chlorine content (about 3%

chlorine content), of which the product can be used as adhesive of plywood[17]. Besides the two key points mentioned above, whether HCPE-cg-MAH is desirable for painting is also discussed in this paper.

To the best of our knowledge, no work being similar to this has been reported before. Both the melting point and molecular weight of LDPE are lower than that of HDPE which makes it difficult to control the process of ISCGC in gas-solid phase. Therefore, the main focus of this paper, to be exact, is on whether the reaction process can ensure that MAH being grafted onto the polymer skeleton effectively and whether the graft product can obviously improve the adhesion. The product of grafting MAH onto LDPE by ISCGC is referred as LHCPE-cg-MAH.

2 Experimental

2.1 Preparation and characterizations of LHCPE-cg-MAH

2.1.1 Preparation of LHCPE-cg-MAH

LDPE was supplied by Shidai Hongye industry & trade co., LTD (Wuhan, China); HDPE was supplied by Korean LG Chemical Ltd., LG 6040; MAH, acetone, dioctyl-phthalate (DOP), xylene, anhydrous ethanol, methanol, sodium hydroxide (NaOH) were AR grade reagents. Chlorine gas (Cl_2) and white carbon black was an industrial product.

The preparation of LHCPE-cg-MAH by ISCGC was as follow: The reaction was in a three-necked round-bottomed flask with mixing plant, a thermometer, and a Cl_2 inlet. 30 g of LDPE (drying at 60℃ before using) was put in 500-ml flask. 1.8 g of MAH was dissolved in same quality of acetone, and then poured the solution into the reactor and stirred evenly. It could make the LDPE and MAH fully mixed and at the same time acetone would be volatilized before the reaction. Before the start of the experiment, adding an appropriate amount SiO_2 as release agent to prevent polyethylene powder caking. Then Cl_2 continued to pass into the reactor for 15 minutes to exclude of air. In the next step, regulated the reactive temperature to the desired temperature (variation within ±2℃) and adjusted Cl_2 flow rate to meet the reaction condition. In initial stage of the reaction the temperature was maintained below 80℃. The by-product hydrogen chloride (HCl) was absorbed by water in reaction process and the weighting of by-product HCl determined the chlorine content of the products. With the improvement of the chlorine content, the reaction temperature constantly increased and the maximum temperature could not exceed 140℃. After the balance reaching the expected weight, Cl_2 was shut off. When the temperature of system dropped to 100℃, residual Cl_2 in the flask was removed by vacuum pumping. During this process, the flask was evacuated and backfilled with atmosphere many times to completely clear the residual chlorine. The experimental apparatus is as follow(Fig.1).

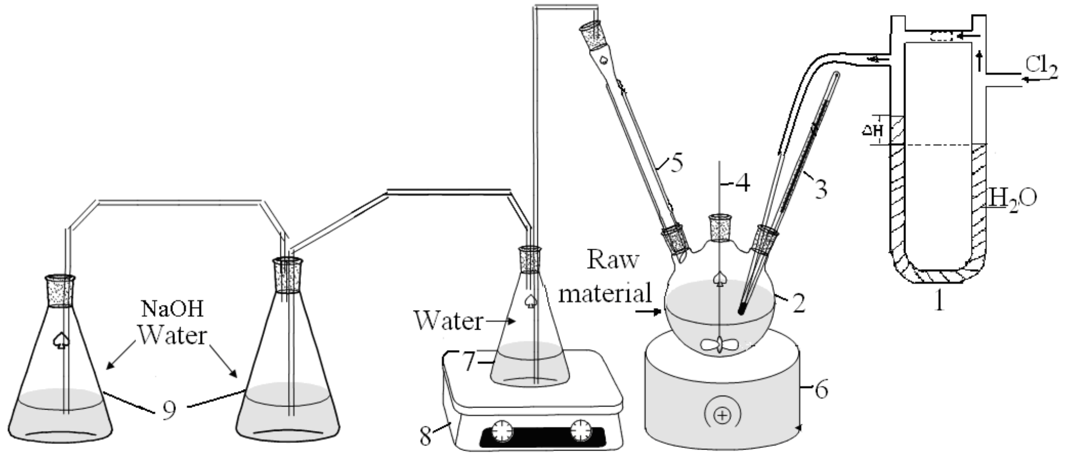


Fig. 1 Schematic representation of the experimental apparatus

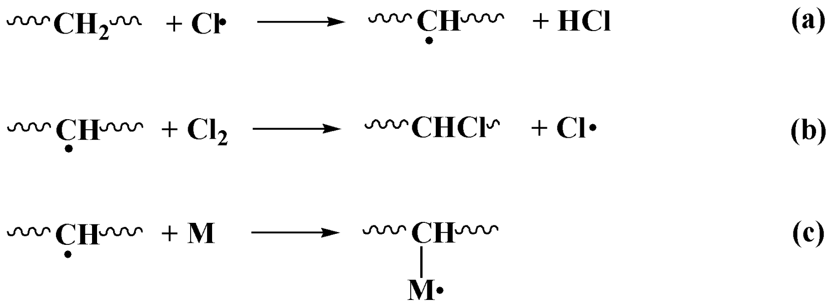
1- U flow meter; 2- three-necked flask; 3- thermometer; 4- vane stirrer; 5-buffer tube;

6- temperature controller; 7- water bottle; 8- balance; 9- NaOH solution bottle.

The chlorine content of the products may be calculated by absorbed HCl in Eq. (1):

$$\text{Chlorine content}(\%) = \frac{\Delta W_{\mathrm{HCl}}+69\Delta W_{\mathrm{HCl}}/2}{m_{\mathrm{LDPE}}+\Delta W_{\mathrm{HCl}}+m_{\mathrm{MAH}}} \times 100\% \qquad (1)$$

Where $\triangle W_{HCl}$ is the mass (g) of HCl released from the reaction system, m_{LDPE} and m_{MAH} are the initial weight of polymer and graft monomer in the reaction system, respectively. The calculation formula is based on the following reaction formula:



$$\sim\!\sim CH_2 \sim\!\sim + Cl\bullet \longrightarrow \sim\!\sim \dot{C}H \sim\!\sim + HCl \qquad \text{(a)}$$

$$\sim\!\sim \dot{C}H \sim\!\sim + Cl_2 \longrightarrow \sim\!\sim CHCl \sim + Cl\bullet \qquad \text{(b)}$$

$$\sim\!\sim \dot{C}H \sim\!\sim + M \longrightarrow \sim\!\sim \underset{\substack{|\\ M\bullet}}{CH} \sim\!\sim \qquad \text{(c)}$$

In the course of the chlorination reaction, a hydrogen atom was substituted by a chlorine atom and the change of weight of this reaction process was 34.5. The 34.5 was obtained from reaction formula (a) in the above formula. “M” in the formula represented the graft monomer.

2.1.2 Purification of products

About 1.5g of graft sample was dissolved in xylene (40mL), and then the solution was heated until the sample completely dissolved in the reflow temperature. The solution was pulled slowly into another flask which contained 75mL anhydrous ethanol under stirring condition, which made the polymer completely separated. The deposition was filtered through Buchner funnel, and repeated the process twice. Finally the deposition was shredded and then put them into vacuum oven at 50℃~60℃ in order to dry to constant weight.

2.1.3 Characterizations

GPC was carried out in THF on Waters 1515 gel permeation chromatography. Polystyrene (PS) was used as standard, sample concentration was 5mg/ml and flow rate was 1ml/min at room temperature.

DSC was taken using DSC204F1 differential scanning calorimetry (German NETZSCH company). The sample was approximately 5mg and the heating rate was 10℃/ min in nitrogen. The range of temperature was -50 ~ 200℃.

The surface of raw materials was observed by stereomicroscope (Olympus SMZ1500).

The structure of the graft copolymer was analyzed through Fourier-transform infrared spectrometer (VERTEX70, Brooke company).

Nuclear magnetic resonance spectrometer (NBR) were recorded in $CDCl_3$ using a Varin Associates Unity 500 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ =7.27).

The viscosity of samples was tested by 4# cup viscometer at room temperature. The same elution volume but different efflux time could judge the viscosity.

2.2 Grafting degree (GD) measurement

Determination of GD of purified samples: About 0.5 g of purified LHCPE-cg -MAH was dissolved in hot xylene (75mL). After being mixed, 3 droplets of water and 3 droplets of N, N dimethyl formamide (DMF) which would accelerate the hydrolysis of MAH were added into the solution. The mixture was heated to keep the solution boiling for 15 min, and then the indicator , Phenolphthalein/methanol solution, was added. The titration was carried out at high temperature (110℃~120℃) with KOH/methanol solution (0.012299 mol/L), which is necessary so that there was no deposition occurred during the titration process. It was the end point of titration when the solution turned into stable light pink. The following equation (Eq.(2))was used to calculate GD:

$$\mathrm{GD} = \frac{N \times (V - V_0) \times M}{2W} \times 100\% \qquad (2)$$

Where N is the concentration of the standard solution of KOH/methanol (mol/L), V and V_0 is consumption volume (ml) of the KOH/methanol solution for specimen titrating (ml) and blank titrating (ml), respectively. M is the molecular weight of MAH (98.06) and W (mg) is the weight of the polymer sample. The factor '2' in Eq. (2-2) represents the fact that one MAH can form two carboxyl groups after complete hydrolysis.

2.3 Preparation of coating sample

The coating sample preparation of LHCPE-cg-MAH was as follow: The sample is dissolved into xylene to prepare a solid content of 20% solution. The solution in appropriate amount is paved in tin plate (50×1000×0.50mm), and then dried to constant weight at 50~60℃ within a vacuum oven.

2.4 Adhesion measurement

The adhesion of the polymer was tested according to GB/T 1720-1989 and all the reported data of film properties were the average values of 5 tests. The level of the standard is divided into seven according to the integrity and testing part (I-VII) of film. If the integrity of part I is more than 80%, it will be judged to be 1 grade, and so on.

The film impact strength of samples was tested according to GB/T 1732-1993 and the good test results should be free of cracks, wrinkles and spalling in the 50kg·cm.

3 Results and discussion

3.1 Feasibility of preparing LHCPE-cg-MAH by ISCGC

3.1.1 Feasibility analysis

Compared with HDPE/MAH (HHCPE-cg-MAH), we found that when using LDPE /MAH as raw material, the process of preparing LHCPE-cg-MAH by ISCGC is more difficult to control. Therefore we infer that HDPE and LDPE are totally different when they are used as raw materials of grafted MAH. The measuring results of LDPE and HDPE by GPC are shown in Fig. 2 and table 1.

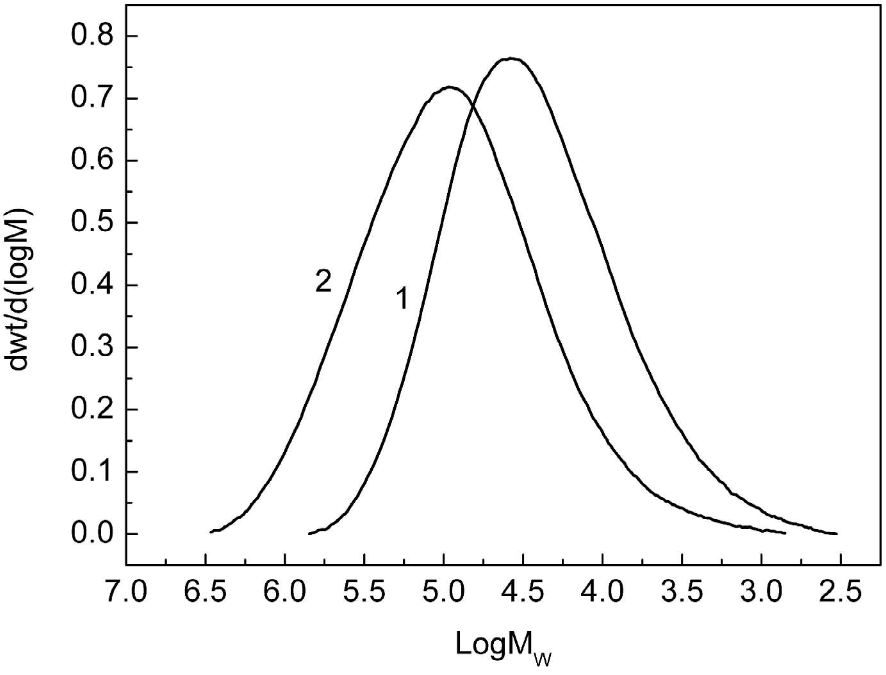


Fig. 2 GPC curves of LDPE (1) and HDPE (2)

Table 1 Molecular mass and distribution index of two kinds of PE

Sample	Mn	Mw	MP	Mz	M_{Z+1}	Mv	MWD
LDPE	1.2×10^4	5.2×10^4	3.8×10^4	1.3×10^5	2.2×10^5	4.5×10^4	4.36
HDPE	3.4×10^4	1.9×10^5	9.2×10^4	5.7×10^5	1.0×10^6	1.6×10^5	5.49

Conditions: All the data came from the GPC, polystyrene (PS) was used as standard, sample concentration was 5mg/ml, flow rate was 1ml/min in THF at room temperature.

As Fig. 2 and Table 1 show, number average molecular weight (Mn) of LDPE is about 1.2×10^4 and weight average molecular weight (Mw) is 5.2×10^4, and molecular weight distribution (MWD) is 4.36. Meanwhile, the Mn of HDPE is 3.4×10^4, Mw is 18.7×10^4, and MWD is 5.49. Clearly, the average molecular weight of LDPE is much lower than that of HDPE. The effects of lower average molecular weight on the preparing process are in two aspects. The solubility of the polymer increases after been chlorinated, however, the temperature control in preparation process will be more difficult.

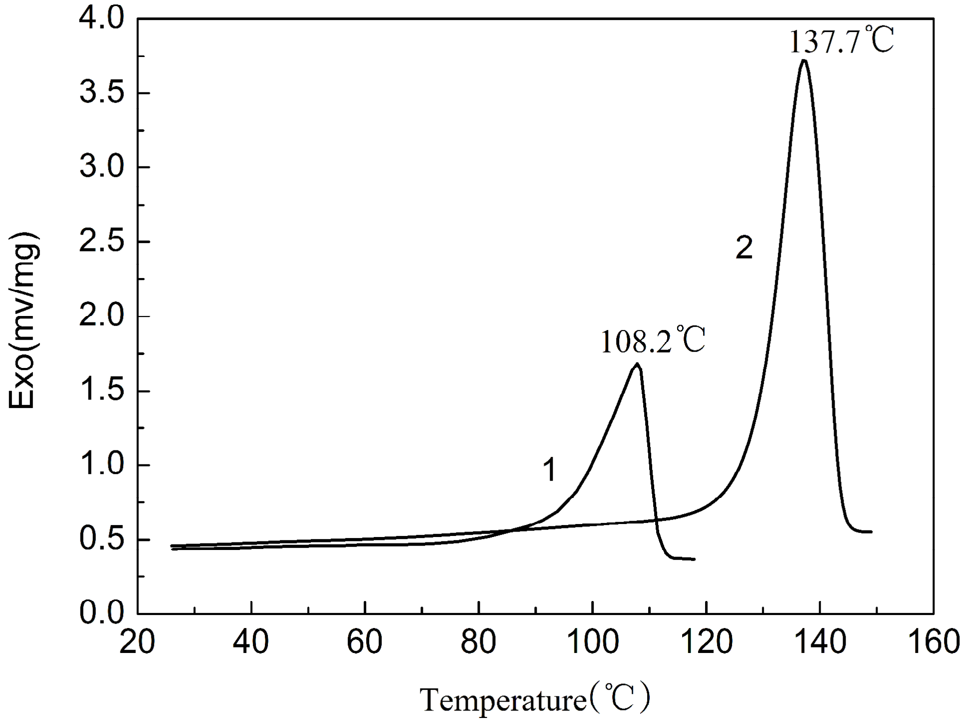


Fig. 3 DSC curves of LDPE (1) and HDPE (2)

Table 2 The DSC data of polymers

Sample No.	Tm/□	△ Hf*/Jg^{-1}	Crystallinity /%
HDPE	137.7	223.6	81.9
LDPE	108.2	90.8	33.3

Conditions: The sample was approximately 5mg and the heating rate was 10□/ min in nitrogen, the range of temperature was -50 ~ 200□.

Fig. 3 and Table 2 show the DSC test results of the raw material. The DSC results indicate that the melting point of LDPE is 108.2℃ while the melting point of HDPE is as high as 137.7℃; the degree of crystallinity of the former is 33.3%, and that of the latter is 81.9%. All these results show many differences between the two materials.

Lower melting point and degree of crystallinity of LDPE suggest that LDPE which serve as raw material has to react in lower temperature, making it difficult to control the exothermic process. Additionally, it is also a problem deserving special concern whether MAH can be effectively grafted onto the main chain under low temperature. This is because that MAH may prefer addition reaction to grafting in low temperature; moreover, lower melting point with raw material makes it easier to melt in the reactive process. In the reaction process, melting of surface of LDPE granule will reduce the porosity of the surface, so that Cl_2 is blocked from diffusing throughout the surface, which is to the disadvantage of further grafting reaction..

Gas-solid phase reaction is a kind of heterogeneous reaction and the structure and morphology of the solid granule surface also has significant effect on reaction process. For further discussion about feasibility and possible problem of solid-phase ISCGC, we observed the surface of the two kinds of PE granules using stereomicroscope.

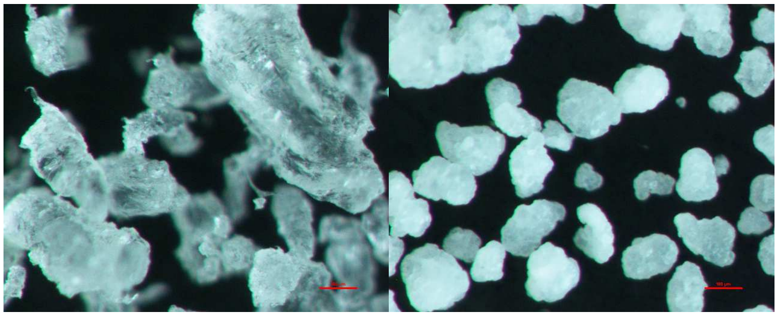


Fig. 4 Displays the photographs of LDPE (left) and HDPE (right)

Note: The image magnification of 100 times. The scale bars are all 100 μm.

It can be seen from the Fig.4 that granules of LDPE (on left) are with different sizes, irregular shapes and lower specific surface area. In comparison, the granules of HDPE (on right) are with uniform size and shape, and the granularity is small therefore the specific surface is higher. According to above, it can be inferred that in the heterogeneous gas-solid phase ISCGC, the irregular granules of LDPE would lead to smaller surface contacting with chlorine, which should affect the reaction rate and, particularly, lead to the sharp decline of the reaction rate in the late stage when the initial reaction rate is fast. Furthermore, the surface of LDPE granules is flat and smooth, while the surface of HDPE granules is loose, porous, and abundant in inner pore, which facilitates diffusion of chlorine molecule to take part in deep reaction from surface to inside. This suggests that the reaction rate of LDPE would be much lower than HDPE in the late phase of chlorination.

As a conclusion of all the analysis above, we think that the ISCGC of LDPE/MAH should go in low temperature and the reaction rate could be controlled. More specifically, the phase-wise chlorination can be employed to achieve this goal.

In the first stage (Cl%wt≤30%), the temperature was maintained at 80℃. Then in the second stage (30%≤Cl%wt≤50%). the temperature was raised to 120℃ for further reaction. Finally in the third stage, the temperature was below 140℃ and the reaction went on until being terminated. It is a totally different to the chlorinated reaction of HDPE.

To lower reactive temperature and increase reaction rate in early stage, adding radical initiator is optional, and it is also alternative to use UV to facilitate low temperature reaction.

3.1.2 Feasibility validation

The reactive scheme of LDPE and MAH by ISCGC is following(Fig.5):

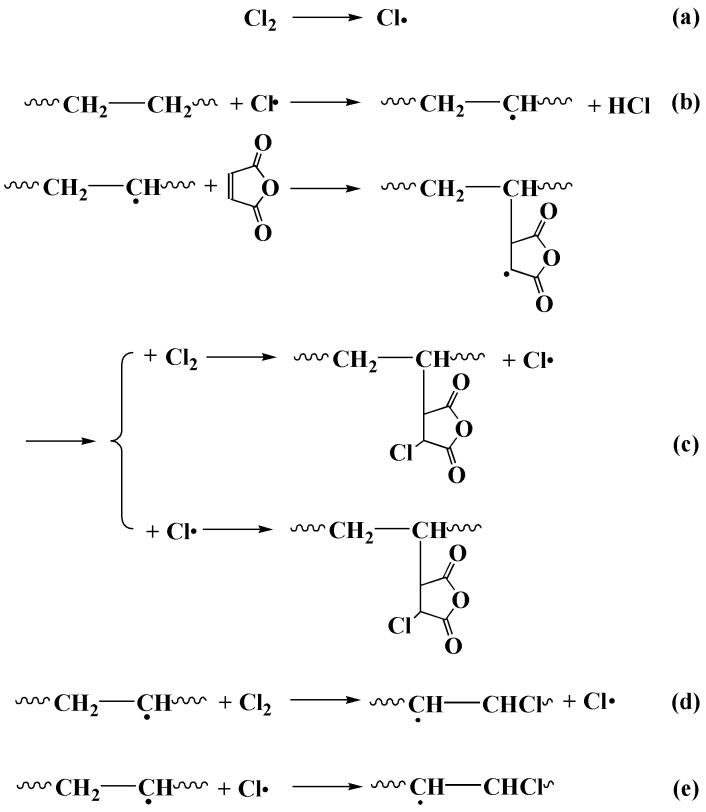
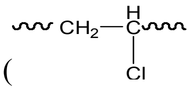
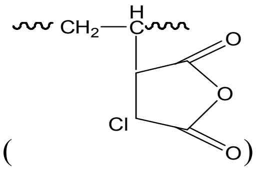


Fig. 5 Reaction process of LHCPE-cg-MAH and the chlorination of LDPE

To demonstrate the feasibility of the process, we carried out FTIR, ^{1}H-NMR and graft degree (GD) analysis on the graft product.

As Fig.6 shows, comparing spectra of LHCPE-cg-MAH and LHCPE, we can conclude the following:

(1) New absorption peaks of LHCPE-cg-MAH appear at 1743cm^{-1} and 1779cm^{-1}, corresponding to stretching vibration of C=O and the coupling of the two C=O stretching vibration, respectively.

(2) The CH bending vibration peak of LHCPE ( $\sim CH_2-\underset{Cl}{\overset{H}{C}}\sim$) is at 1269cm^{-1} and the CH bending vibration peak of LHCPE-cg-MAH () is toward 1264cm^{-1}. It can be explained that the inductive effect results the changes of the dipolar distance. This also supports that MAH has been grafted on the product.

(3) Peaks appear at 1606-1650cm^{-1} in both the spectra, indicating existence of conjugated double bond structure in LHCPE-cg-MAH and LHCPE.

(4) Both the spectra have peaks at 746-798cm^{-1}, suggesting vinylidene chlorine structure is presented in both LHCPE-cg-MAH and LHCPE.

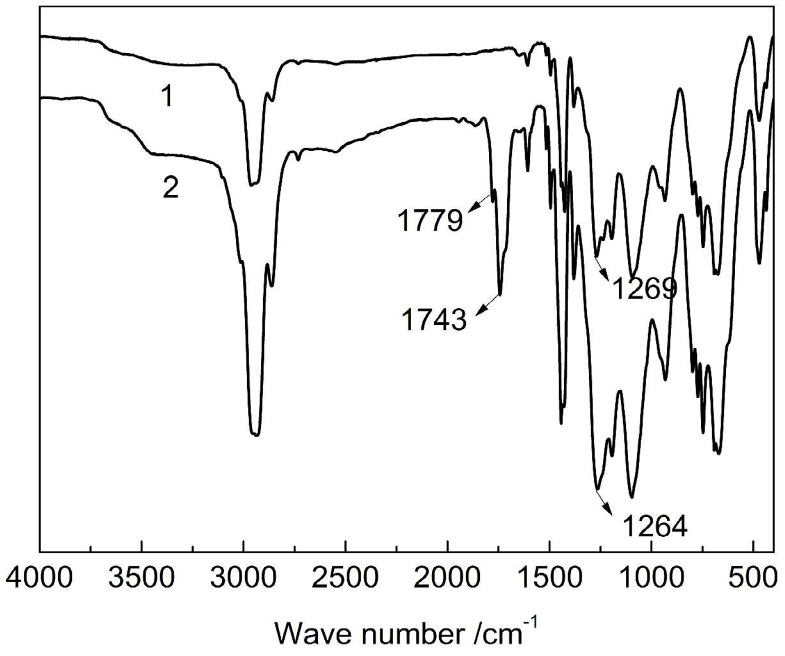


Fig. 6 FTIR spectra of LHCPE (1) and LHCPE-cg-MAH (2)

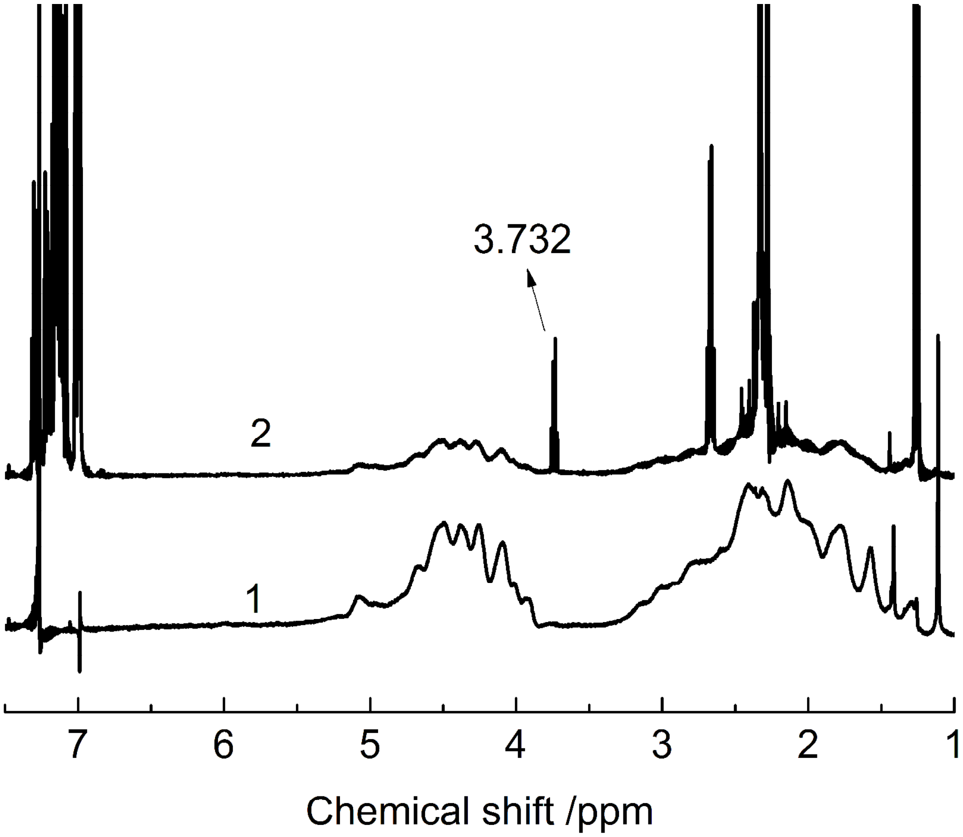


Fig. 7 ^{1}H-NMR spectra of LHCPE (1) and LHCPE-cg-MAH (2)

Conditions: Testing in $CDCl_3$ at room temperature.

The above results are sufficient to prove that the MAH monomer has been successfully grafted onto molecular chain of LHCPE, producing the graft copolymer LHCPE-cg-MAH.

The above result was confirmed again by ^{1}H-NMR spectra. Figure 7 is the ^{1}H-NMR spectra of LHCPE and LHCPE-cg-MAH. Compared with the spectrum of LHCPE, we saw a new chemical shift peak at d=3.732ppm in LHCPE-cg-MAH spectrum, confirming that MAH group had been successfully grafted onto the main chain. With combination of FTIR and H-NMR spectrum analysis, it could be proved that with LDPE as raw material, we can obtain chlorinated polyethylene with high chlorine content as well as graft MAH onto main chain by ISCGC to produce anhydride modified LHCPE.

Furthermore, the product was subjected to the analysis of GD through anhydrous titration method, and the result is shown in Table 3.

Table 3 The GD of LHCPE-cg-MAH*

samples	1	2	3
GD (%)	3.44	1.67	1.65

*The samples are all reached the same chloride contents.

The test results show that the average GD of LHCPE-cg-MAH is up to 2%. This not only indicates that MAH has been grafted onto the backbone polymer, but also is high enough to make practical sense of the graft product.

Accordingly, we took the experiments by controlling the reaction temperature (T). The control process is as follows: Cl%wt<30%, T<80℃; 30%<Cl%wt<50%, T<120℃; Cl%wt>50%, T<140℃ (Cl%wt is the chlorine content). All of the experiments were in accordance with the conditions. The curve of chlorine content versus time was shown in Fig.8. By comparing the three products, the grafting system reacted relatively slowly in the latter stage.

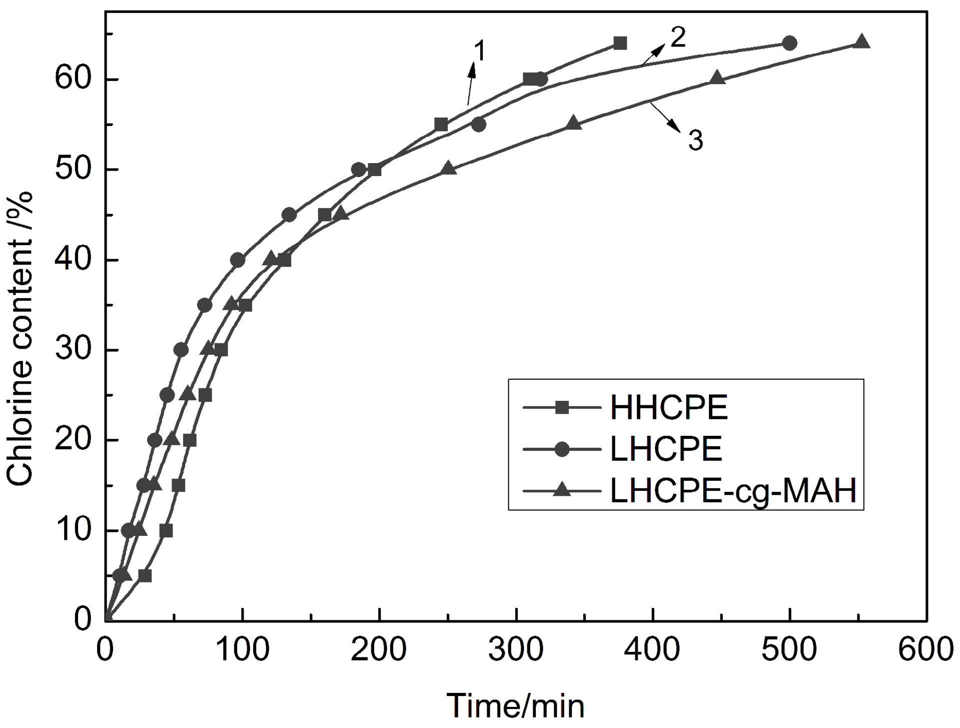


Fig. 8 The curve of chlorine content (Cl%) versus time

Note: HHCPE (1), LHCPE (2) and LHCPE-cg-MAH (3).

3.2 Adhesion and impact strength of LHCPE-cg-MAH film

While HHCPE made of HDPE has a wide range of application, but the adhesion of LHCPE made of LDPE is much lower than the former. The adhesion and impact strength of LHCPE, HHCPE and LHCPE-cg-MAH as a film-forming polymer (all the chlorine content is 64% and GD is 1.69%) was tested and the results are shown in Table 4.

Table 4 The test results* of film impact strength and film adhesion

Samples	Adhesion test results(grade)	Impact strength test results(50kg·cm)
LHCPE	20% or less of various parts of coating intact (7grade)	No cracks, wrinkles and flaking
HHCPE	More than 80% of part I of coating intact (1grade)	Minor cracks, wrinkles and flaking
LHCPE-cg-MAH	More than 80% of part I of coating intact (1grade)	No cracks, wrinkles and flaking

*All the reported data of film properties were the average values of 5 tests.

The test results show that grafting of MAH significantly improves adhesion which increased from 7 to 1 and is as high as of HHCPE. LHCPE with LDPE as raw material was dissolved in xylene to prepare a solid content of 20% solution. Although its viscosity was low, the adhesion was poor. However, LHCPE grafted MAH, LHCPE-cg-MAH, had almost the same viscosity and its film was excellent. The LHCPE-cg-MAH's viscosity tested by 4# cup was between 40 to 60s and was much lower than HHCPE's which was more than 20 minutes.

Obviously, the grafting of MAH onto backbone polymer plays an important role for the improvement of adhesion. Grafting of MAH onto macromolecular chain strongly improves the adhesive force between the polymer and the metal specimens. Additionally, this also demonstrates that the achieved degree of grafting generates high adhesion which is enough for the product to serve as film-forming polymer.

The impact strength data in Table 3 indicates that grafted MAH doesn't increase the brittleness of LHCPE-cg-MAH. There are two conflicting effects caused by grafting of MAH. On one hand, it increases polarity of the polymer. On the other hand, due to the high steric hindrance and random distribution of MAH group, the regularity of macromolecule was broken and distance between molecules was enlarged, which made the flexibility of molecular chain improved. The experimental results show that the latter effect is superior, which is to the advantage of coating film toughness. This is also supported by the DSC curves of LHCPE and LHCPE-cg-MAH shown in Fig. 8.

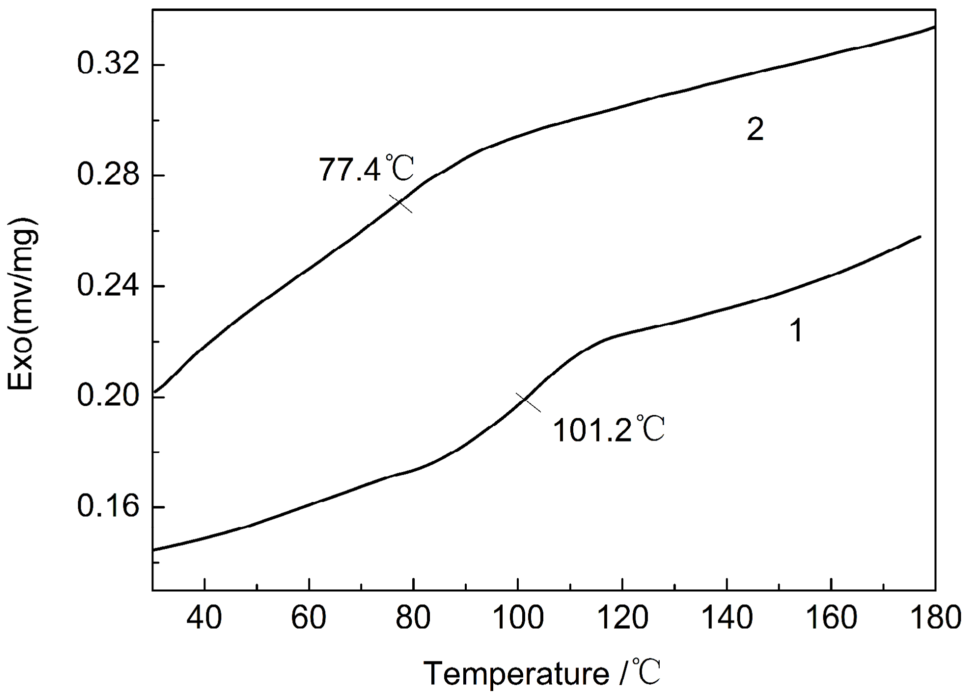


Fig. 9 DSC curves of LHCPE (1) and LHCPE-cg-MAH (2)

Conditions: The sample was approximately 5mg and the heating rate was 10□/ min in nitrogen, the range of temperature was -50 ~ 200□.

From Fig. 9 we can find that the grass transition temperature (T_g) of LHCPE-cg-MAH (77.4℃) is lower than LHCPE (101.2℃). We believe that it is the very result of improved flexibility of polymer backbone caused by random distribution of MAH.

4 conclusions

According to the results of FTIR and ^{1}H-NMR spectrum, it is feasible that MAH could be grafted onto LHCPE molecular chain via ISCGC, and the grafting degree could reach 2. Compared to LHCPE, the adhesion of grafting products is improved significantly and could attain 1 grade. In addition, the coating film of grafting products has good toughness and its impact strength can meet the performance requirements for coating.

Acknowledgements

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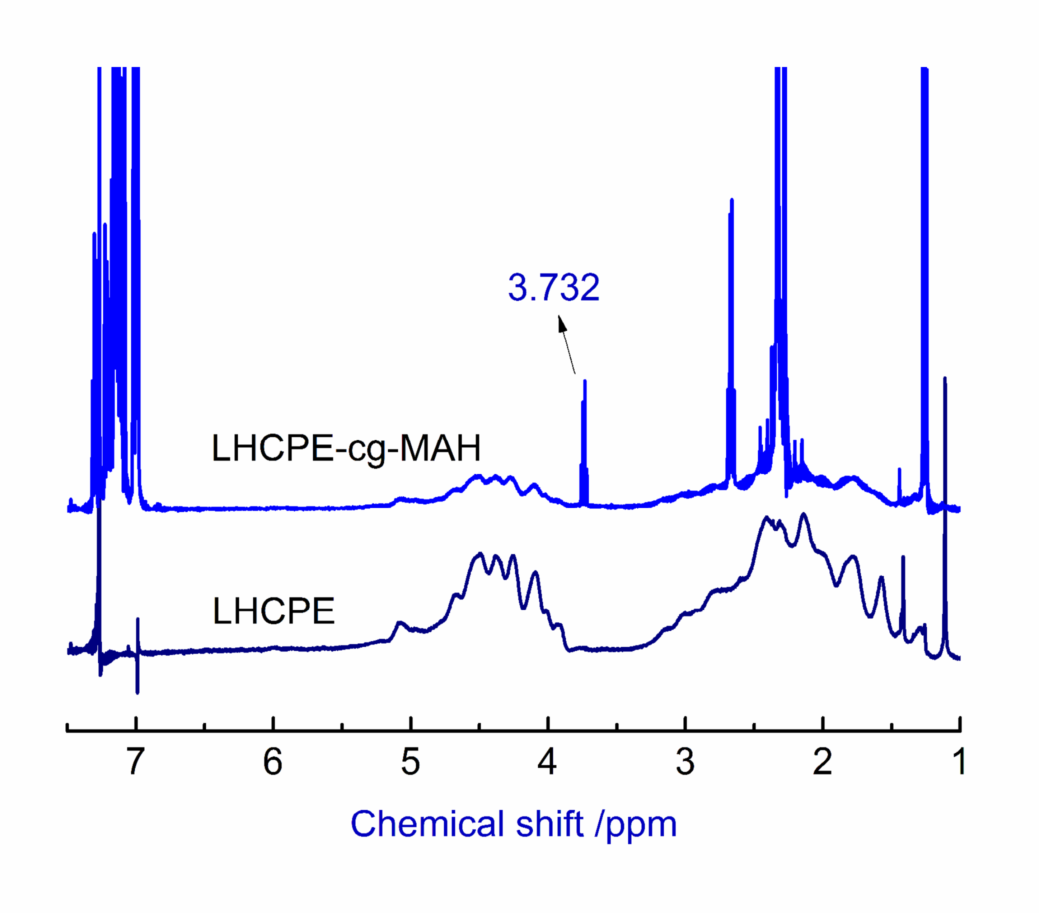

Text:

MAH was grafted onto LHCPE prepared from LDPE by in-situ Chlorinating Graft Copolymerization to improve the adhesion.