Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Yu-Zhong Wang[a]; Xiao-Xia Zheng[a]; Ze-Fang Chen[a]; Chang-Yi Zheng[a]
[a] Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, Sichuan University, Chengdu, P.R. China

Online publication date: 05 December 2003

To cite this Article Wang, Yu-Zhong , Zheng, Xiao-Xia , Chen, Ze-Fang and Zheng, Chang-Yi(2003) 'Microwave Assisted Radical Grafting of Maleic Anhydride onto Polyethylene in Solution', Journal of Macromolecular Science, Part A, 40: 7, 739 — 745
To link to this Article: DOI: 10.1081/MA-120021423
URL: http://dx.doi.org/10.1081/MA-120021423

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JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 7, pp. 739–745, 2003

NOTE

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Yu-Zhong Wang,* Xiao-Xia Zheng, Ze-Fang Chen, and Chang-Yi Zheng

Center for Degradable and Flame-Retardant Polymeric Materials,
College of Chemistry, Sichuan University, Chengdu, P.R. China

ABSTRACT

The reaction of maleic anhydride (MAH) grafted onto low density polyethylene (LDPE) in nylene solvents in the presence of benzoyl peroxide (BPO) as an initiator by microwave irradiation has been investigated. The influence of reaction conditions such as initiator content, monomer content and irradiation time have been examined. In the weight composition of xylene/LDPE/MAH/BPO = 10/1/1/0.07, the grafting degree reaches 56.5 mmol MAH/100 g PE within only 8 min of microwave irradiation. The grafting reaction time of microwave irradiation shortens over 40 times than in the conventional grafting reaction.

Key Words: Microwave; Grafting; Polyethylene; Maleic anhydride.

INTRODUCTION

Polyethylene (PE) has been widely used in many fields because of its excellent physical and mechanical behaviors. The modification of PE can widen its application fields and has brought researchers' additional attention. However, there is no polar group

*Correspondence: Yu-Zhong Wang, Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, Sichuan University, Chengdu 610064, P.R. China; E-mail: yzwang@mail.sc.cninfo.net.

DOI: 10.1081/MA-120021423 1060-1325 (Print); 1520-5738 (Online)

on the macromolecules of PE, which makes its chemical reactions difficult, so the introduction of polar groups onto the main chains of PE is an important route. Irradiation grafting and chemical reaction grafting are often used. Those studies have obtained definite effects, and some of them have been applied in industry. However ordinary grafting methods have some shortcomings because of long reaction time, complicated process and limited effect.[1]

Maleic anhydride (MAH) is one of very useful monomers. It is been well known that the chemical reactions can be completed by microwave techniques.[2–6] However, there has not been a report on the solution grafting of maleic anhydride (MAH) onto PE by means of microwave. In this investigation, we studied the solution grafting of MAH onto PE by microwave irradiation. The results of IR and DSC showed that the grafting could be completed successfully by means of microwave irradiation, which performs with a much higher grafting reaction efficiency than the conventional methods.

EXPERIMENTAL

Microwave Applicator

The microwave applicator used for this study is special equipment, which is manufactured by us. The flow chart of the microwave processing system is shown in Fig. 1. The entire system consists of five units. The signal generated by the microwave source excites the magnitude field in a cavity through the directional coupler, circulator source. The energy in the cavity can reach the maximum by adjusting the tune-shorter, and the power meter 2 can test it. However, the power meter 1 indicates the power of the microwave source.

Materials

Low density PE (1F7B) powders having a melt index of 7 were manufactured by Yanshan Petroleum Chemical Co. (Yanshan, China). Benzoyl peroxide (BPO) (A.R.), was recrystallized twice from chloroform before use, and MAH (A.R.) was provided by the Shanghai Chemicals Plant (Shanghai, China).

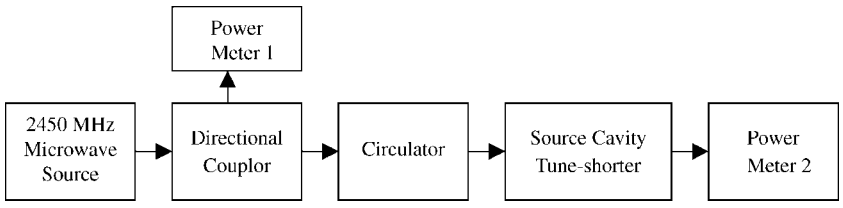


Figure 1. Microwave processing system.

Grafting Procedure

Maleation was carried out at 138°C with 100 W microwave input power. Dissolved PE in xylene then was mixed together with BPO and MAH in a certain proportion. In the total experiments, the weight ratio of xylene to PE is always 10:1. The mixtures are put into the cavity, irradiated for the expected time, then removed. The samples were purified by dissolving in xylene and precipitating in methyl alcohol three times, and then dried in vacuum at 60°C. The products were used to determine the grafting degree (GD) and to test IR and DSC.

Measurement

The grafting degree was analyzed by adding a standard methyl alcohol KOH solution to a xylene solution of the samples and after refluxing to dissolve and cooling, back-titrating the excess KOH with a standard isopropylol HCl solution. The grafting degree (GD) was calculated as following:

$$GD\,(\text{mmol MAH}/100\,\text{g}) = (N_{\text{KOH}}V_{\text{KOH}} - N_{\text{HCl}}V_{\text{HCl}}) \times 98.02/(2 \times 1000) \times 1000/\text{W}$$

where N_{KOH} and N_{HCl} are the concentrations of KOH and HCl solutions, respectively, and V_{KOH} and V_{HCl} volumes, respectively. W is the weight of PE samples.

IR spectra were recorded with Niolet FT-IR 170SX and DSC graph was made with DSC-7 of PE Co.

RESULTS AND DISCUSSION

Figure 2 is the IR spectra of PE (curve I) and PE-g-MAH (curve II). It shows that the grafting sample exhibits a characteristic vibration band of the carboxyl group.[7]

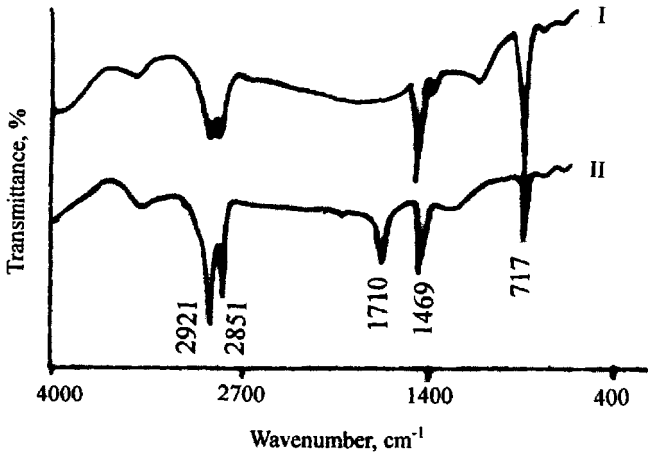


Figure 2. IR Spectra of PE (I) and PE-g-MAH (II) (DG = 56.4 mmol MAH/100 g PE).

The sample certainly has gotten rid of the unreacted MAH from PE-g-MAH according to the literature.[8] The new bands verify that MAH is really grafted on the PE in a xylene solution by means of microwave.

Figure 3 is the DSC graph of PE (curve I) and PE-g-MAH (curve II). We can see that the curve II in Fig. 3 has an obvious difference from curve I, that is, the melting temperature of PE-g-MAH is lower than that of PE, but the melting enthalpy of PE-g-MAH higher than that of PE.

The initiator is one of the important factors that influence the grafting of MAH onto PE. Figure 4 shows the influence of BPO content on the grafting degree. It can be seen that the grafting degree increases significantly with the increase of BPO weight ratio to PE within the range of 0.01–0.07, whereas it falls down above 0.07. So, under the condition selected in this study, the best BPO content is the weight ratio of 0.07.

The mechanism of MAH and PE in the presence of BPO by microwave irradiation is considered a radical one as shown in Sch. 1 .

The decomposition of peroxide generates radicals (process 1, Sch. 1) due to microwave irradiation, then, they attack the PE to generate PE macroradicals (process 2, Sch. 1) which are disproportionate in the absence of MAH, and make additional reactions with MAH when MAH is present (processes 3 and 4, Sch. 1). The initiator content is related to the amount of radicals. When the other conditions are certain, the more the initiator, the more the macroradicals, but too many macroradicals will couple with each other (process 5, Sch. 1). So the initiator content must be proper.

Figure 5 shows the influence of the MAH content on the grafting degree. Results show that the grafting degree increases with the increase of MAH content, but the percent conversion decreases. Because the MAH molecule has a symmetric structure, in general, it will not produce an inductive or conjugate effect, and its homopolymerization is very difficult.

From Sch. 1 we may see that one macromolecular radical only initiates one MAH molecule, so the MAH content determines whether the radical reacts fully with MAH.

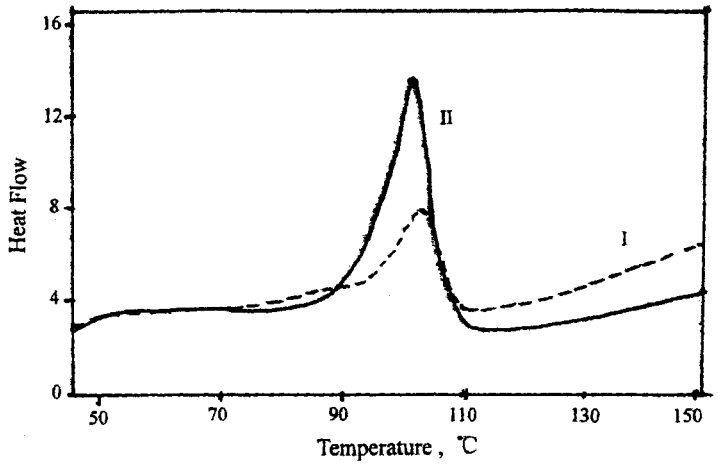


Figure 3. DSC curves of PE (I) and PE-g-MAH (II) (DG = 56.4 mmol MAH/100 g PE).

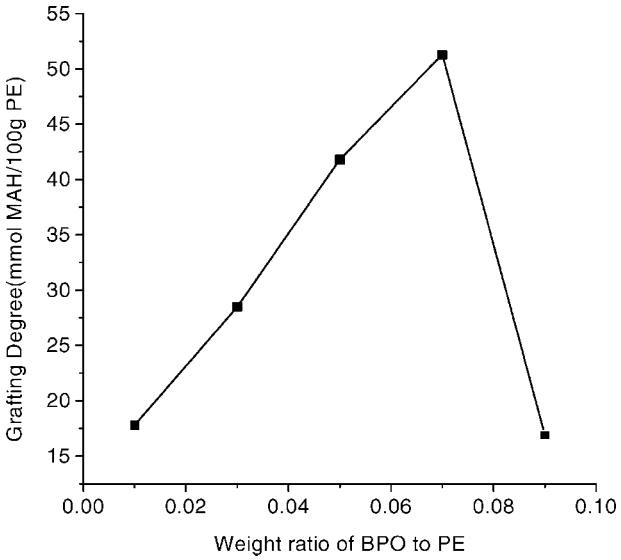
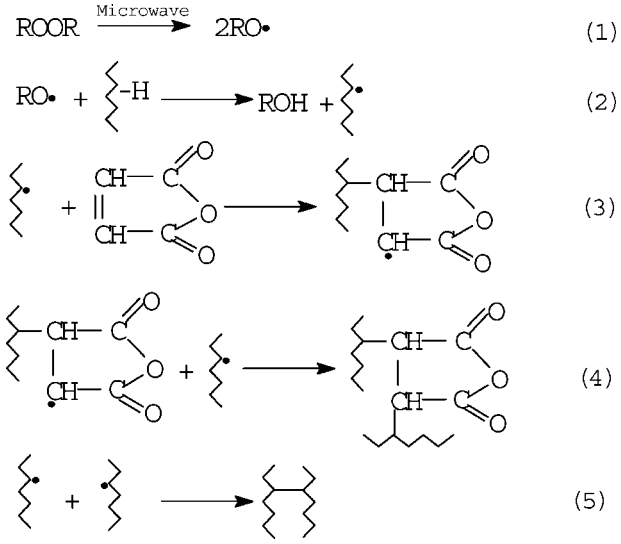


Figure 4. Relationship between grafting degree and initiator BPO concentration. Reaction conditions: xylene/PE/MAH = 10/1/0.7, temperature 138°C, input power 70 W, irradiation time 8 min.

When the radical concentration is certain, the collision chance of MAH and macromolecule increases with the increase of MAH content, leading to the increase of the grafting degree. However, too much of MAH causes its decomposition or volatilization in a great amount, leading to the decrease of percent conversion. From the economic



Scheme 1.

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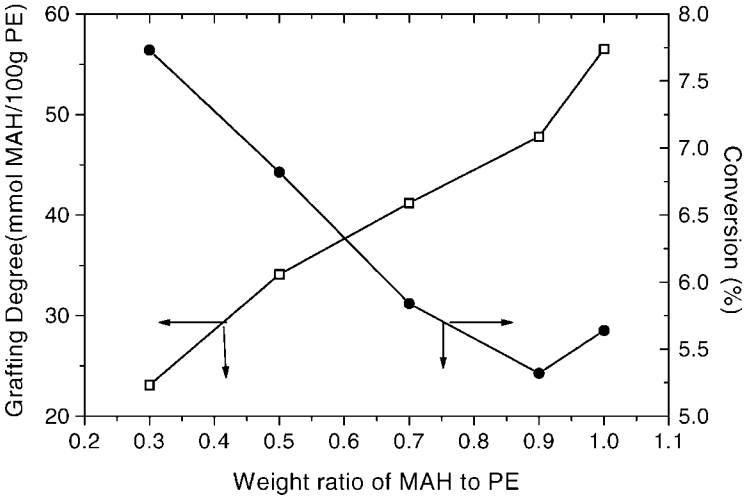

Figure 5. Influence of MAH concentration on grafting degree and the conversion of MAH. Reaction conditions: xylene/PE/BPO = 10/1/0.05, temperature 138°C, input power 100 W, irradiation time 8 min.

consideration, therefore, the grafting degree already reaches our expectation when the weight ratio of MAH to PE is 1, which is chosen as an optimum experiment content.

The relationship between irradiation time and the grafting degree is shown in Fig. 6. It can be seen that the grafting degree increases significantly with prolonging the irradiation time within the time range of 3–8 min, whereas it falls after 8 min. One of reasons for this is

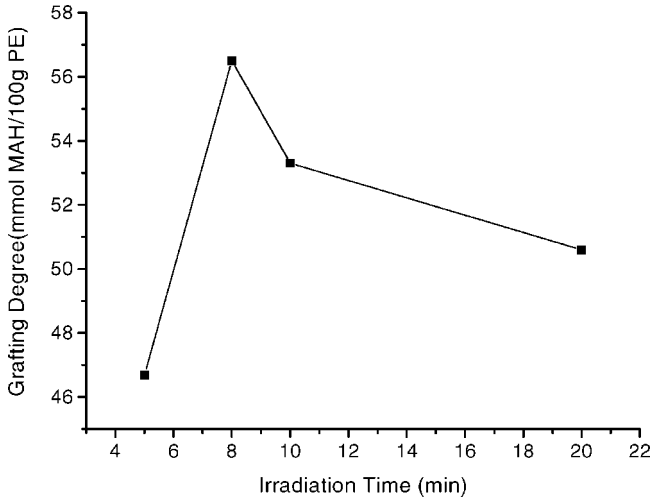

Figure 6. Relationship between grafting degree and irradiation time. Reaction conditions: xylene/PE/MAH/BPO = 10/1/1/0.05, temperature 138°C, input power 100 W.

that the longer the irradiation time, the higher the temperature, which causes MAH to decompose or volatilize faster. So the proper irradiation time in this study is 8 min.

According to the literature,[8,9] the reaction of PE and MAH by the conventional method usually takes 5–6 h to reach the highest grafting degree, but it only costs 8 min by microwave irradiation in our study, which means that the microwave irradiation has much higher grafting efficiency than the conventional reaction.

CONCLUSION

The grafting of MAH onto PE in xylene solution by microwave irradiation can be successfully completed. Based on the above research, we obtained the grafting degree of 56.5 mmol MAH/100 g PE in the following reaction conditions: the temperature is 138°C, the microwave input power 100 W, the irradiation time 8 min and the weight composition of xylene/PE/MAH/BPO = 10/1/1/0.07.

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Received August 2002
Revised February 2003