

Kinetics for Chlorination of Maleic Anhydride Grafted Polypropylene

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ABSTRACT: Preparation of Chlorinated maleic anhydride grafted polypropylene (Cl-PP-g-MAH) by free radical process was carried out using carbon tetrachloride (CCl_4) as the solvent and benzoperoxide (BPO) as the initiator. Effects of reaction temperature, concentrations of PP-g-MAH and BPO on the rate of chlorination were studied. The experimental results showed the actual rate constant for chlorination of maleic anhydride grafted polypropylene followed the Arrhenius law and the total apparent activation energy was 19.7 kJ mol^{-1} . The kinetic model for

chlorination of maleic anhydride grafted polypropylene was found to be $R = K[\text{BPO}]^{0.53}[\text{C}]^{0.93}$. The properties of chlorination of maleic anhydride grafted polypropylene were better than those of maleic anhydride grafted polypropylene. The products were characterized by Fourier transform infrared spectroscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 117–121, 2007

Key words: chlorine; polypropylene; degree of chlorination; rate of chlorination; kinetics model

INTRODUCTION

Because of the low cost and versatile properties, polypropylene is one of the most important polymers, which are widely used in the household and industrial fields. However, lack of chemical functionalities, dyeing difficulty, poor compatibility with other polymers, poor adhesion strength, and nonpolarity have restricted its further use in fiber, adhesive, printing ink, coating, and plastic etc. The grafting copolymerization offers an effective way of increasing the polarity of polypropylene. Research activities have concentrated on grafting of maleic anhydride and acrylates onto PP.^{1–12} Fu et al.¹³ studied the melt-grafting for maleic anhydride onto polypropylene with the assistant added. Li et al.³ studied the styrene-assisted melt free radical grafting of maleic anhydride onto polypropylene. Sun et al.⁴ studied the free radical grafting of glycidyl methacrylate onto polypropylene in a corotating twin screw extruder. Grafting of various vinyl monomers onto PP had been reviewed by Xu and Lin¹⁴ and Singh.¹⁰

The chlorination modification of polypropylene has been studied by several investigators.^{15,16} Ma et al.¹⁷ studied the preparation of chlorinated polypropylene by solid phase method, Yang¹⁸ studied the chlorinated polypropylene adhesive.

However the properties of the polypropylene modified only by maleic anhydride or chlorine can

not suit for the needs in fiber, adhesive, printing ink, and coating.

In this article, PP-g-MAH was chlorinated to improve its properties and make it suitable for the special needs such as in fiber, adhesive, printing ink, and coating.

On the other hand, there was no report about the kinetics for the chlorination of maleic anhydride grafted polypropylene. The present work finds a kinetic model for the chlorination of maleic anhydride grafted polypropylene. The model may be useful for the theory research on the chlorination of polypropylene.

EXPERIMENTAL

Raw materials

PP-g-MAH was synthesized by our research group in National Engineering Research Center of Novel Equipment for Polymer Processing, South China University of Technology, Guangzhou.¹³ Carbon tetrachloride (CCl_4) (CP grade), BPO (CP grade), deuterium oxide (H_2O_2) (CP grade), sodium hydroxide (NaOH) (AR grade), potassium chromate ($\text{K}_2\text{Cr}_2\text{O}_4$) (AR grade), and silver nitrate (AgNO_3) (AR grade) were purchased from Guangzhou Dongfang Chemical Agent Factory, Hengyang Chemical Agent Factory, Guangzhou Xingang Chemical, Guangzhou Jinzhuijiang Chemical, Guangzhou Donghong Chemical Agent Factory, Guangzhou Chemical Agent Factory, and Tianjing Chemical Agent Factory, respectively.

Experimental procedure

PP-g-MAH (100 g) was dissolved in carbon tetrachloride in a four-necked flask equipped with a mechanical

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stirrer, thermometer, dropping funnel and condenser, and chlorinated with chlorine. The initiator BPO was dissolved in carbon tetrachloride and was added dropwise to the reaction mixture. The reaction temperature was varied from 70 to 90°C. The reaction time was varied from 1 to 6 h. Upon the chlorination, the reaction mixture was added slowly to methanol. The precipitates were filtered and washed with methanol to remove hydrogen chloride. The final product was dried in a vacuum oven at 60°C.

Analysis of the degree of chlorination

About 20 mg purified chlorinated maleic anhydride grafted polypropylene was burned in a flask, in which there was 10 mL of 5% H₂O₂ solution and was full of oxygen. Then the flask was shaken until the smoke disappeared. Two drop of bromcresol green-methyl red reagent was added into the solution in the flask. The solution was neutralized by 0.5% NaOH solution until the solution became brilliant green. At last 1 mL of 5% K₂Cr₂O₄ solution as the tracer agent was added. The solution was titrated by 0.1N of AgNO₃ solution until it became red.¹⁷

The degree of chlorination (Cl%) was calculated by the following equation:

$$\text{Cl}\% = \frac{c \times V \times 35.45 \times 10^{-3} \times 100\%}{W}$$

where *c* is the equivalent concentration of AgNO₃ solution, *V* is the used volume of AgNO₃ solution, *W* is the weight of the purified chlorinated maleic anhydride grafted polypropylene, 35.45×10^{-3} is the mole mass of chlorine.

Analysis of the properties

The viscosity is measured by a NDJ-79 viscometer at 20°C. The transmission light is analyzed by a DR-

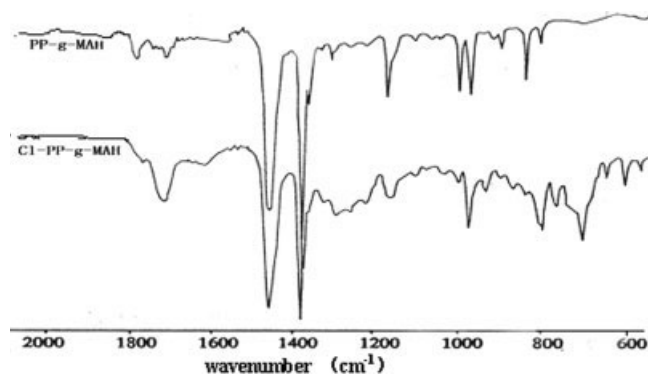


Figure 1 FTIR spectra of the PP-g-MAH and the Cl-PP-g-MAH. B: 3×10^{-3} mol L⁻¹; C: 2.5×10^{-3} mol L⁻¹; D: 2×10^{-3} mol L⁻¹; E: 1×10^{-3} mol L⁻¹; F: 5×10^{-4} mol L⁻¹.

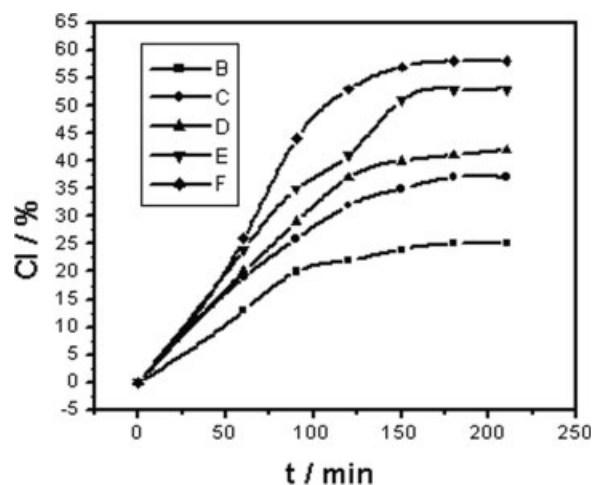


Figure 2 The degree of chlorination versus time at different PP-g-MAH concentrations.

890 chromometer. The fineness is measured by a fineness meter. The adhesion property was analyzed by a United Data System tension meter according to ASTM D 1876 01.

RESULTS AND DISCUSSION

Characterization

Cl-PP-g-MAH and PP-g-MAH were characterized by Fourier transform infrared spectroscopy (FTIR). Figure 1 is the FTIR spectroscopy of PP-g-MAH and Cl-PP-g-MAH. Comparison with FTIR spectroscopy of PP-g-MAH, new bands appeared in the figure of Cl-PP-g-MAH at the several bands from 550 to 800 cm⁻¹, which are assigned to C—Cl stretching vibration. Thus, chlorine has been grafted onto PP-g-MAH.

Effect of PP-g-MAH

PP-g-MAH was chlorinated in CCl₄ at 353.15 K for different time using 1.65×10^{-3} mol L⁻¹ BPO, 0.16 L min⁻¹ flow rate of chlorine, and 3×10^{-3} , 2.5×10^{-3} , 2×10^{-3} , 1×10^{-3} , and 5×10^{-4} mol L⁻¹ PP-g-MAH, respectively.

Figure 2 shows the effect of time at different PP-g-MAH concentrations on the degree of chlorination. As the time increases, the degree of chlorination increases firstly, then the rates start leveling off. As the concentration of PP-g-MAH decreases, there is an increase in the degree of chlorination with the increasing time period. As the PP-g-MAH concentration decreases, the amount of PP-g-MAH per unit volume decreases, which leads to the reduction in the interchain interaction. Second, in the reaction, the chlorine atoms on the polymer backbone become integrated onto a part of the chain. Thus, the stiffness of

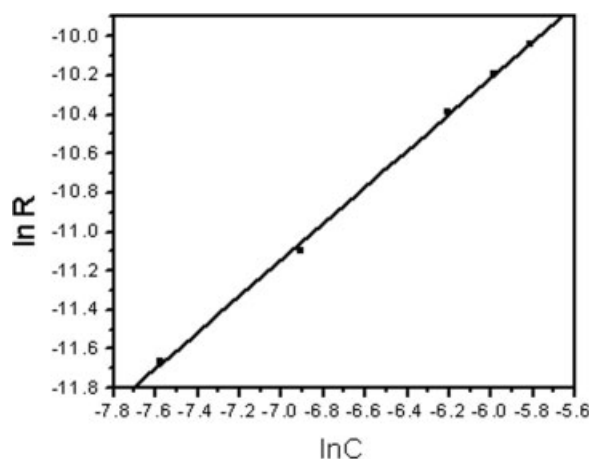


Figure 3 Effect of concentration of PP-g-MAH on rate of chlorination. B: 343.15 K; C: 348.15 K; D: 353.15 K; E: 358.15 K; F: 363.15 K.

the chain was increased. For these reasons, the polymeric chain can open up more and a great number of reaction sites become available to the attacking chlorine. As the reaction progresses, the substitution of replaceable H-atom by chlorine increases, which reduces the number of available H-atom for chlorination. Hence, there is an increase in the rate of chlorination followed by a decrease in it.

Figure 3 presents the effect of chlorination rate versus PP-g-MAH concentration. It is a linear and the slope value is 0.93, so the rate equation for chlorination follows the relationship $R = KC^{0.93}$.

Effect of temperature

PP-g-MAH was chlorinated in CCl_4 at 343.15, 348.15, 353.15, 358.15, and 363.15 K for different time using

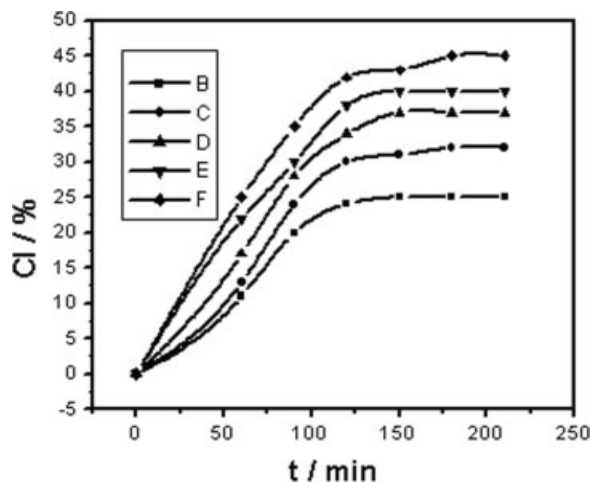


Figure 4 The degree of chlorination versus time at different temperatures.

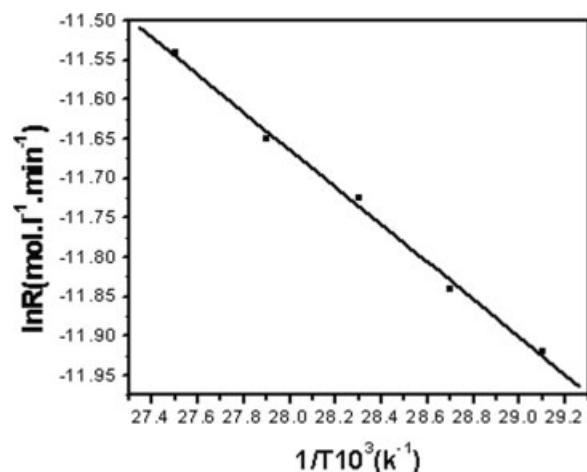


Figure 5 Effect of temperature on rate of chlorination. B: $4.13 \times 10^{-4} \text{ mol L}^{-1}$; C: $8.26 \times 10^{-4} \text{ mol L}^{-1}$; D: $1.24 \times 10^{-3} \text{ mol L}^{-1}$; E: $1.65 \times 10^{-3} \text{ mol L}^{-1}$; F: $2.06 \times 10^{-3} \text{ mol L}^{-1}$.

$2.5 \times 10^{-3} \text{ mol L}^{-1}$ PP-g-MAH, $1.65 \times 10^{-3} \text{ mol L}^{-1}$ BPO, and 0.16 L min^{-1} flow rate.

Figure 4 shows that with the increase in temperature, the degree of chlorination increases fast firstly, then it increases slowly. Because with the increase in temperature, more chlorine grafts onto the PP-g-MAH and the degree of chlorination increases. After a period of time, H-atoms of PP-g-MAH chlorinated by chlorine is saturable, the chlorine can not graft on the PP-g-MAH and the degree of chlorination does not increase.

Figure 5 shows the dependence of rate of chlorination on temperature, it shows an Arrhenius plot and the energy of activation E value is 19.7 kJ mol^{-1} .

Effect of BPO initiator

PP-g-MAH was chlorinated in CCl_4 at 353.15 K for different time using $2.5 \times 10^{-3} \text{ mol L}^{-1}$ PP-g-MAH,

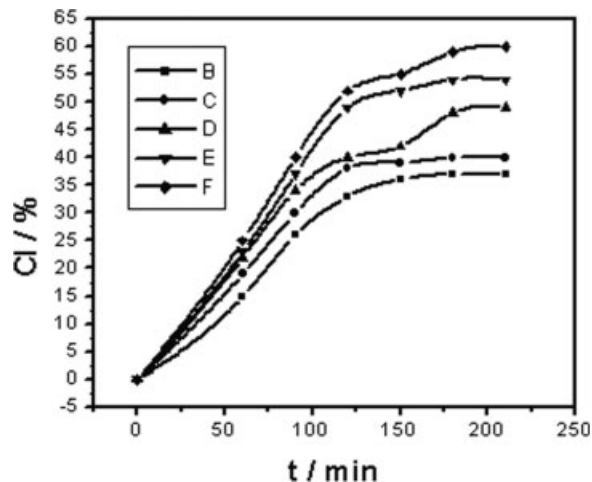


Figure 6 The degree of chlorination versus time at different initiator concentrations.

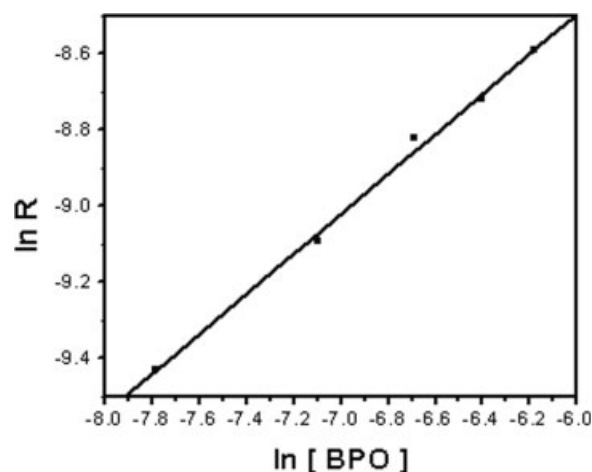


Figure 7 Effect of initiator concentration on rate of chlorination. B: 0.04 L min⁻¹; C: 0.08 L min⁻¹; D: 0.12 L min⁻¹; E: 0.16 L min⁻¹; F: 0.20 L min⁻¹.

0.16 L min⁻¹ flow rate of chlorine, 4.13×10^{-4} , 8.26×10^{-4} , 1.24×10^{-3} , 1.65×10^{-3} , and 2.06×10^{-3} mol L⁻¹ BPO.

Effect of the initiator concentration on the degree of chlorination is given in Figure 6. With the increasing concentration of BPO, the degree of chlorination initially increases fast and then increases slowly and finally does not increase. The initial increase in the degree of chlorination is due to the increased availability of chlorine free radicals for chlorination of PP-g-MAH. Then the concentration of initiator exceeds a certain limit, the chlorine free radicals increase slowly. Finally, the chlorine free radicals increase little.

Figure 7 presents effect of initiator concentration on chlorination rate yielding a slope value of 0.53, so the

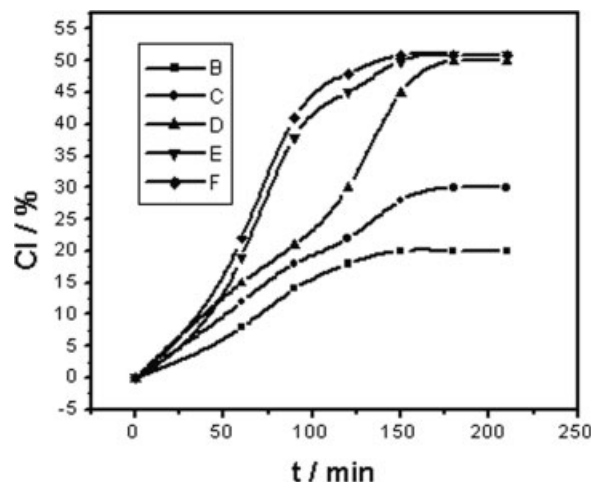


Figure 8 The degree of chlorination versus time at chlorine flow rate.

TABLE I
Properties of MAH-g-PP and Cl-MAH-g-PP

| Properties | Viscosity (mP s) | Transmission light | Fineness (μm) | Adhesion strength (kgf cm ⁻²) |
|-------------|------------------|--------------------|---------------|---|
| PP-g-MAH | 359 | 0.17 | 40 | 1.5 |
| Cl-PP-g-MAH | 330 | 0.05 | 20 | 8.2 |

reaction equation for chlorination follows the equation: $R = k[\text{BPO}]^{0.53}$.

Effect of chlorine flow rate

PP-g-MAH was chlorinated in CCl₄ at 353.15 K for different time using 2.5×10^{-3} mol L⁻¹ PP-g-MAH, 1.65×10^{-3} mol L⁻¹ BPO, 0.04 L min⁻¹, 0.08 L min⁻¹, 0.12 L min⁻¹, 0.16 L min⁻¹, 0.20 L min⁻¹ chlorine flow rates, respectively. The results were presented in Figure 8.

From the Figure 8 it can be seen that with the increase in flow rate of chlorine, the degree of chlorination increase initially. Then, it starts leveling off. This is because with the increase of the flow rate, more chlorine is available for the reaction and the reaction can proceed at a faster rate. Then, when the chlorine is fully saturated, the degree of chlorination is leveling off.

Properties of PP-g-MAH and Cl-MAH-g-PP

The degree of Cl-PP-g-MAH is 40% and its molecular weight is 5000. Table I shows that the properties of viscosity, transmission light, fineness, and adhesion strength of the Cl-PP-g-MAH are better than those of the PP-g-MAH.

The reason is that when the chlorine has grafted onto PP-g-MAH, the polar and activity of Cl-PP-g-MAH were improved, which causes the transmission light increases, the fineness decreases, and the adhesive strength increases. On the other hand, when the chlorine has grafted onto PP-g-MAH, Cl-PP-g-MAH is dissolved more readily than the PP-g-MAH. The viscosity of Cl-PP-g-MAH decreases.

CONCLUSIONS

The properties of the chlorinated of maleic anhydride grafted polypropylene were better than those of the maleic anhydride grafted polypropylene. The kinetic model for chlorination of maleic anhydride grafted polypropylene was found to be $R = K[\text{BPO}]^{0.53}[\text{C}]^{0.93}$.

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