

SUPERCRITICAL CARBON DIOXIDE ASSISTED FREE-RADICAL GRAFTING OF ACRYLIC ACID AND GLYCIDYL METHACRYLATE ONTO POLYPROPYLENE

LiuTao, Tong Gang-Sheng, Wu Yin-Lin, Zhao Ling* and Yuan Wei-Kang
State Key Laboratory of Chemical Engineering, East China University of Science and Technology,
Shanghai 200237, Peoples Republic of China. Email: zhaoling@ecust.edu.cn

Abstract

The work reported in this paper aimed at exploring the advantages of using supercritical carbon dioxide as an environmentally benign solvent and swelling agent for carrying out the grafting process of acrylic acid and glycidyl methacrylate onto isotactic polypropylene in the solid state. The effects of various factors on the grafted content and gel content were investigated. Those factors included the reaction time, CO₂ pressure, monomer and initiator concentrations. Results showed that the CO₂ pressure could regulate both the grafted content and gel content with ease. With CO₂ assisted, we can produce grafted iPP with a much higher grafted content and lower gel content than those produced by the melt or conventional solid-state processes.

1. Introduction

Owing to its intrinsic properties such as low cost, versatility and growing application, isotactic polypropylene (PP) has become one of the largest and fastest growing thermoplastic. However, being lack of polar sites, PP has a hydrophobic nature that restricts its application such as being dyed and printed. Polar monomers including maleic anhydride (MAH), acrylic acid (AA), methyl methacrylate (MMA) and glycidyl methacrylate (GMA) have been grafted onto polypropylene (PP) by conventional solution, melt and solid-state grafting processes, which has been proved to be a promising method for functionalizing PP and thus extending its range of application. [1] However, these conventional processes suffered from their own drawbacks such as use of solvent, severe decrease in molar mass and heterogeneity in quality, respectively. Supercritical carbon dioxide (scCO₂) assisted solid-state grafting process is supposed to be able to overcome the drawbacks while retaining its advantages. Besides environmental benignity, scCO₂ assisted solid-state grafting process has the advantages of being capable of easily regulating the CO₂ pressure to control the grafted content of polar monomer and producing grafted PP much more uniform in grafted content. [2] In our previous work, both MAH and MMA were grafted onto PP by using a scCO₂ assisted solid-state process [2, 3]. For PP grafted MAH, the scCO₂ process produced more uniform in anhydride content than the classical solid-state process did. For PP grafted MMA, the scCO₂ process produced much higher MMA grafting contents and longer MMA grafts than the conventional processes did. Moreover, during the grafting process, no gel was produced indicating that PP was not crosslinked during the grafting process.

In this work, grafting of another two polar monomers, AA and GMA onto PP were studied

using the scCO₂ assisted solid-state process. It aimed at exploring the advantages of scCO₂ as an environmentally benign solvent and swelling agent for carrying out the grafting process of AA and GMA onto PP in the solid state. The effects of various factors on the grafted content and gel content were investigated. Those factors included the reaction time, CO₂ pressure, monomer and initiator concentrations.

2. Experimental

Materials. PP (M_w = 188 700, M_n = 37 000) pellets with an average diameter of 3 to 4 mm were supplied by Shanghai Petrochemical Company. IPP powder (average diameter < 0.15 mm) used in this study was prepared from the above pellets by grinding with liquid nitrogen as the coolant. The purity of CO₂ obtained from Air Product Co. was 99.9% and was used as received. Dicumyl peroxide (DCP) (chemical-grade) was commercially available from Shanghai Chemical Co. and purified twice from chloroform before use. AA (purity: 99.0%) was purchased from Shanghai Lingfeng Chemical Reagents Co. and was filtered through aluminum oxide neutral (200–300 mesh) twice to eliminate polymerization inhibitors before use. GMA (assay > 97.0%) was commercially available from Fluka Chemical Co. and was used as received.

Grafting Reactions Procedure. A schematic of the experimental setup has been described in detail elsewhere. [2, 3] A high-pressure vessel of about 20 ml made from stainless steel was used. The grafting process was carried out in the following manner. The PP powder, AA/GMA and DCP were charged into the vessel. The latter was then thoroughly flushed with low-pressure CO₂. Thereafter, a given amount of CO₂ was charged with a DZB-1A syringe pump of Beijing Satellite Instrument Co., China, at an accuracy of 0.01 cm³. The reaction vessel was immersed in the oil bath, heated to 80 °C and then kept at that temperature for 2 h so as for the PP powder to soak the monomer and the free radical initiator. After that, it was further heated up to the desired reaction temperatures, a temperature that was below the melting temperature of the PP over the whole CO₂ pressure range studied in this work. Prior to sampling, the vessel was quenched with cold and running water to stop the reaction. Samples were then taken out for subsequent characterization after purification.

Gel content of PP-g-AA and PP-g-GMA. PP might crosslink when a vinyl monomer is grafted onto it. If crosslinking occurs, the molecular architecture and properties of PP will be altered to a great extent, which is not desired for most of the time. Thus the crosslinking issue was addressed first in the work. The method and procedure were as follows: a prescribed amount of PP-g-AA or PP-g-GMA was placed in gauze with 200 mesh holes (the size of which is smaller than the smallest diameter of PP powder), and then put in excess boiling xylene. After keeping refluxing for 6 h, the gauze was taken out and dried in a vacuum oven at 80 °C for 24 h. The gauze was weighted at each step and the gel percent of PP-g-GMA or PP-g-AA was defined as:

$$Gel\% = \frac{w_3 - w_1}{w_2 - w_1} \times 100\% \quad (1)$$

where w_1 was the weight of gauze, w_2 and w_3 was the total weight of gauze and PP-g-GMA or

PP-g-AA before and after extraction, respectively.

Purification of PP-g-GMA and PP-g-AA. Before characterization, PP-g-GMA and PP-g-AA were purified in the following manner. About 4.0 g unpurified grafted PP was placed in gauze with 200 mesh holes, put in 100 ml xylene and kept refluxing for 2 h at 120 °C. The gel would be retained in the gauze. Excess acetone was added to the hot xylene with dissolved grafted PP, and the latter would be precipitated. The precipitate was then washed by acetone twice and dried in a vacuum oven at 80 °C for 24 h.

Quantitative infrared characterization of PP-g-GMA and PP-g-AA. Fourier Transform infrared spectroscopy (FTIR) of type EQUINOX 55 FTIR spectrometer system (Bruker Company, Germany) was used to study whether or not GMA and AA were grafted onto PP and to what extent. The use of FTIR to quantitatively determine of the grafted GMA or AA content required the calibration curves. The calibration curve for determining the grafted GMA content were built-up by the following method: Poly-GMA was first prepared by a solution polymerization process with diethylene oxide as the solvent and BPO as the initiator.[4] After that, excess acetone was added into the reaction solution to precipitate the poly-GMA. The filtered poly-GMA was then purified by Soxhlet extraction in acetone for 24 h and dried in a vacuum oven at 90 °C for 10 h in order to eliminate the unreacted GMA and other volatile molecules. Thereafter, a given amount of poly-GMA was mixed with PP in a Hakke Minilab (Therm. Elec. Co., Germany) at 220 °C. A uniform mixture of poly-GMA and PP with a known mass ratio was then obtained. Five poly-GMA/PP mixtures with different poly-GMA contents were prepared that way. The calibration curve was constructed as shown in Figure 1 which related the known mass ratio of poly-GMA/PP mixtures to those of FTIR ratio of the absorbance of the carbonyl bond of GMA at 1730 cm⁻¹ (A_{1730}) over that of the methyl group of the PP at 2722 cm⁻¹ (A_{2722}) as shown in Fig. 1. The calibration curve for determining the grafted AA content was based on the carboxylic acid content obtained by titration and the ration between the absorbance of the carbonyl bond of AA at 1716 cm⁻¹ (A_{1716}) and that of the methyl group of the PP at 2722 cm⁻¹ (A_{2722}) as shown in Fig. 2.

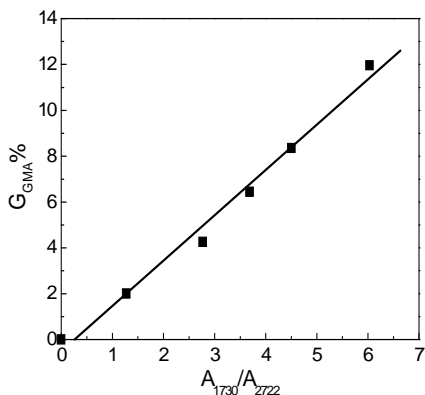


Fig. 1 Relationship between the grafted GMA content in PP-g-GMA and the ratio between the FTIR absorbance of the peak at 1730 cm⁻¹ and that at 2722 cm⁻¹. $G_{GMA} \% = -0.5167 + 1.9786 A_{1730}/A_{2722}$. $R = 0.99$

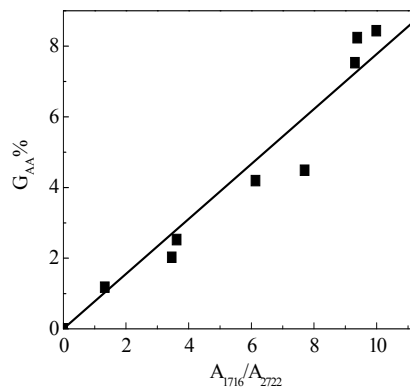


Fig.2 Relationship between the grafted AA content in PP-g-AA and the ratio between the FTIR absorbance of the peak at 1716 cm⁻¹ and that at 2722 cm⁻¹. $G_{AA} \% = 0.7776 \times A_{1716}/A_{2722}$, $R = 0.9734$.

3. Results and Dissusion

Determination of Reaction Time. Fig. 3 shows the grafted content of GMA and gel content as a function of the reaction time at 140 °C. The mass ratio of iPP/GMA/DCP was 100/10.75/0.5. The grafted content of GMA and gel content first increased with increasing reaction time and then reached an equilibrium after about 2 h at 140 °C. In Fig. 3 is also shown the amount of the primary radicals formed from the decomposition kinetics of DCP as a function of time in scCO₂ at 140 °C. [5] More than 85% DCP was decomposed after about 2 h at 140 °C indicating that 2 hour is enough long for the grafting of GMA under scCO₂. Fig. 4 shows the grafted content of AA and gel contents as a function of the reaction time at 130 °C. The mass ratio of iPP/AA/DCP was 100/10.5/0.5. The grafted content of AA increased with increasing reaction time and reached an equilibrium after about 4 h at 130 °C. However, the gel content increased with increasing reaction time which indicated that a redundant reaction time would result in a further crosslinking of PP.

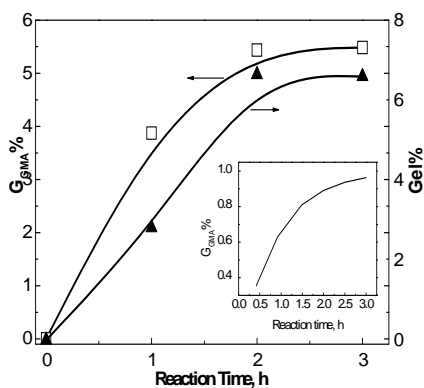


Fig. 3 Effect of reaction time on the grafted GMA content ($G_{GMA}\%$) and gel content (Gel%). GMA/DCP/PP mass ratio = 10.75/0.5/100, $p = 11.5$ MPa, $T = 140$ °C. (—) The decomposition of DCP in scCO₂.

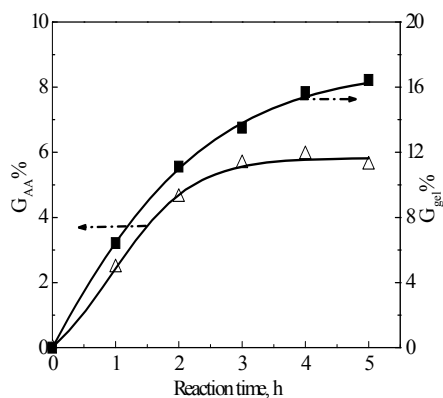


Fig. 4 Effect of reaction time on the grafted AA content ($G_{AA}\%$) and gel content (Gel%). AA/DCP/PP mass ratio = 10.5/0.5/100, $p = 13.0$ MPa, $T = 130$ °C.

Effects of the CO₂ pressure and initial monomer concentration on the grafted AA/GMA content and gel content. Fig. 5 and 6 show the grafted content and gel content in PP-g-AA as a function of the CO₂ pressure at three different initial AA/PP mass ratios: 5.25/100, 10.5/100 and 21.0/100, respectively. The grafting temperature was 130 °C, and the CO₂ pressure was varied between 7 and 24 MPa. The three grafted content and gel content versus CO₂ pressure curves obtained at the above initial AA/PP mass ratios all followed the same trend. At each initial AA/PP mass ratios, with increasing CO₂ pressure, the grafted content first increased, reached a maximum at a certain CO₂ pressure, and then decreased. However, with increasing CO₂ pressure, the gel content first decreased, reached a minimum at the certain CO₂ pressure at which a maximum grafted content reached, and then increased. The value of the CO₂ pressure corresponding to the maximum or minimum in CO₂ pressure depended on the initial AA/PP mass ratio. The results indicated the CO₂ pressure constituted an additional and important process parameter that could control both the grafted content and the gel content in PP-g-AA to a

significant extent and with ease. Moreover, there was an optimum in the initial AA/PP mass ratio below or above which the grafted MMA content rapidly decreased at the corresponding CO₂ pressure.

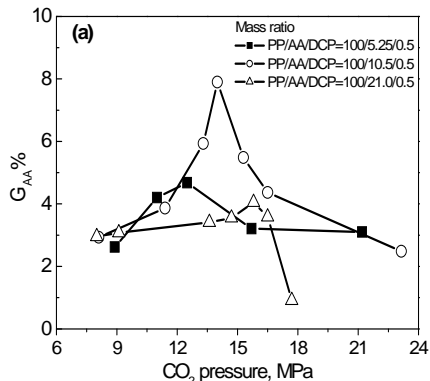


Fig. 5 Effect of CO₂ pressure and initial AA concentration on the grafted content in PP-g-AA. T=130 °C

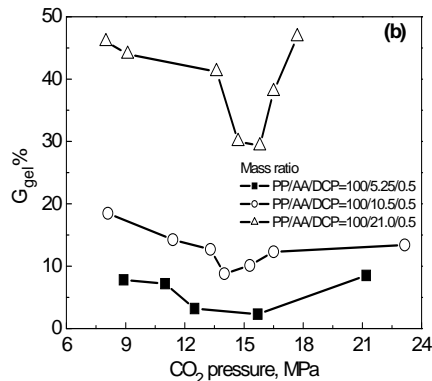


Fig. 6 Effect of CO₂ pressure and initial AA concentration on the gel percent in PP-g-AA. T=130 °C

Fig. 7 and 8 show the grafted content and gel content in PP-g-GMA as a function of the CO₂ pressure at two different initial GMA/PP mass ratios: 10.75/100 and 16.125/100, respectively. The grafting temperature was 140 °C, and the CO₂ pressure was varied between 8 and 24 MPa. The two grafted content and gel content versus CO₂ pressure curves obtained at the above initial GMA/PP mass ratios followed the same trend. At each initial GMA/PP mass ratios, with increasing CO₂ pressure, the grafted content first increased, reached a maximum at a certain CO₂ pressure, and then decreased. However, with increasing CO₂ pressure, the gel content decreased and reached a minimum. Moreover, both the maximum value in the grafted GMA content and the corresponding CO₂ pressure increased with increasing GMA/PP mass ratio. Gel content in the PP-g-GMA also increased with increasing GMA/PP mass ratio. The CO₂ pressure constituted an additional and important process parameter that could control both the grafted content and the gel content in PP-g-GMA to a significant extent and with ease. Results also indicated that a GMA grafts with high grafted content and low gel content could be produced by using the scCO₂-assisted solid-state process. For example, the grafted content of the GMA grafts is 9.8 % and the gel content is 0.9% at 140 °C, CO₂ pressure of 18.8 MPa and initial GMA/PP mass ratio of 16.125/100.

Effects of reaction temperature on the grafted AA content and gel content. Fig. 9 and 10 show the grafted and gel content in PP-g-AA as a function of the CO₂ pressure at three different reaction temperatures. The reaction time was 4 h. The three grafted content and gel content versus CO₂ pressure curves obtained at the above reaction temperatures followed the same trend as described above. With increasing the temperature, the grafted content in PP-g-AA increased at a certain CO₂ pressure. However, the PP-g-AA with the maximum grafted content was obtained at 130 °C. The gel content in PP-g-AA decreased with increasing the temperature at a certain CO₂ pressure.

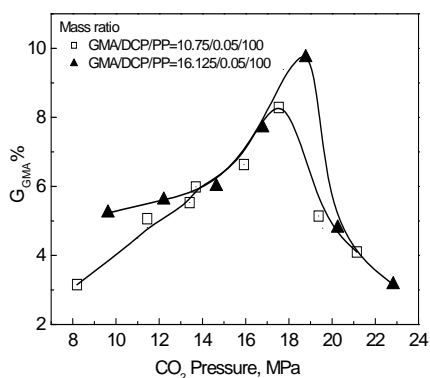


Fig. 7 Effect of CO₂ pressure and initial GMA concentration on the grafted content in PP-g-GMA. T=140 °C

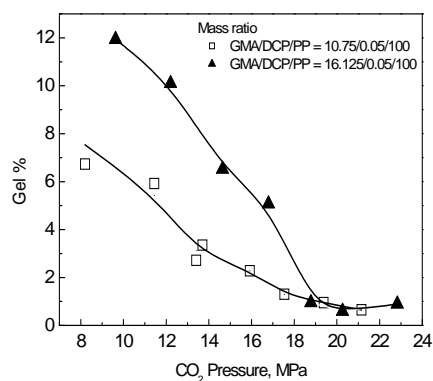


Fig. 8 Effect of CO₂ pressure and initial GMA concentration on the gel percent in PP-g-GMA. T=140 °C

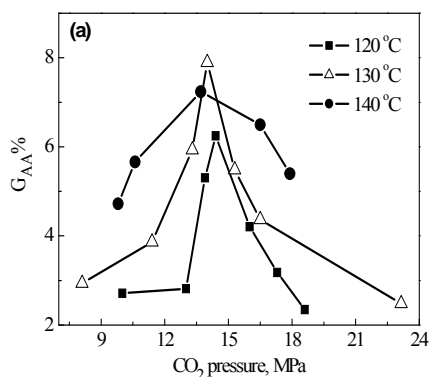


Fig. 9 Effect of reaction temperature on the grafted content in PP-g-AA. PP/AA/DCP mass ratio = 100/10.5/0.5.

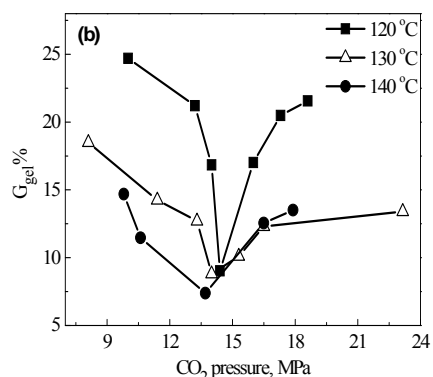


Fig. 10 Effect of reaction temperature on the gel content in PP-g-AA. PP/AA/DCP mass ratio = 100/10.5/0.5

4. Conclusion

Both AA and GMA were used as polar monomers for functionalizing isotactic polypropylene by using a scCO₂ assisted grafting process. Results showed that the CO₂ pressure could regulate both the grafted content and gel content with ease. With CO₂ assisted, we can produce PP-g-AA and PP-g-GMA with a high grafted content and low gel content.

References

- [1] S. Al-Malaika, *Reactive Modifiers for Polymers*, Blackie Academic & Professional, Chapman & Hall, London, 1997.
- [2] T. Liu, G. H. Hu, G. Sh. Tong, L. Zhao, G. P. Cao and W. K. Yuan, *Supercritical Carbon Dioxide Assisted Solid-State Grafting Process of Maleic Anhydride onto Polypropylene*. *Ind. Eng. Chem. Res.* 44, 4292-4299, 2005.
- [3] G. Sh. Tong, T. Liu, G. H. Hu, L. Zhao and W. K. Yuan. *Supercritical carbon dioxide-assisted solid-state free radical grafting of methyl methacrylate onto polypropylene*. *J. Supercritical Fluids*, 43, 64-73, 2007.
- [4] G Li, X L Zhu, J Zhu, et al. *Homogeneous reverse atom transfer radical polymerization of glycidyl methacrylate and ring-opening reaction of the pendant oxirane ring*. *Polymer*, 46(26): 12716~12721, 2005.
- [5] G. Sh. Tong, T. Liu, G. H. Hu, S. Hoppe, L. Zhao and W. K. Yuan. *Modelling of the kinetics of the supercritical CO₂ assisted grafting of maleic anhydride onto isotactic polypropylene in the solid state*. *Chem. Eng. Sci.*, 62, 5290-5294, 2007.