

Supercritical Carbon Dioxide Assisted Grafting of Polyacrylamide to Polypropylene

Qun Xu, Zhenzhong Hou, Guangfa Zhang, Haijuan Fan, Jianbo Li, Shijun Zheng

College of Materials Engineering, Zhengzhou University, Zhengzhou 450052, People's Republic of China

Received 29 September 2005; accepted 5 January 2006

DOI 10.1002/app.24220

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The grafting of polyacrylamide to polypropylene was realized with supercritical carbon dioxide as a substrate-swelling agent and monomer/initiator carrier. The effects of supercritical carbon dioxide assisted impregnation and graft polymerization conditions on the grafting ratio were studied. The original polypropylene and grafting products were characterized with infrared spectroscopy, dif-

ferential scanning calorimetry, and scanning electron microscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2614–2618, 2006

Key words: poly(propylene) (PP); graft copolymers; modification

INTRODUCTION

Recently, there has been increasing interest in using supercritical carbon dioxide (CO₂) as a solvent/processing aid in polymer processing and polymer chemistry.^{1–5} The advantages of using supercritical CO₂ include its high diffusivity, low viscosity, nearly zero surface tension, mild critical parameters (critical temperature = 31.1°C, critical pressure = 73.8 bar), non-toxicity, nonflammability, and low cost. Moreover, it can be easily removed from the system after the reaction. Although supercritical CO₂ is a poor solvent for most polymers, it is a desirable swelling agent for polymers and can dissolve many small molecules.^{6–9} One of the most intriguing features of supercritical CO₂ is that its density and solvent strength can be adjusted by changes in the pressure and temperature of the system. As a result, the use of supercritical CO₂ has been applied to impregnating polymer matrices with different organic molecules, and chemical^{10–13} and physical^{14–16} modifications of the polymers have been carried out. McCarthy and coworkers^{14,15,17} first developed a new route for producing polymer composites by the impregnation of a monomer and a thermal initiator into matrices, followed by thermal free-radical polymerization.

Polypropylene (PP) is one of the most important general-purpose polymers widely used in various fields, but its lack of chemical functionalities, nonpolarity, and poor compatibility with other polymers restrict its application. Therefore, graft copolymerization offers an effective approach to introducing some desirable properties and expands its application.^{18–20} Conventional methods, such as solution and extrusion processes, often require high temperatures or organic solvents. Presently, researchers have used supercritical CO₂ to perform the grafting of polymers with various monomers, such as the maleation of PP.²¹

In this work, we used supercritical CO₂ as a solvent for the monomer acrylamide and the initiator azobisisobutyronitrile (AIBN) and as a swelling agent for PP to obtain grafted PP. The effects of various factors, such as the pressure of CO₂, the impregnation temperature, and reaction time on the grafting ratio were studied. The grafted and ungrafted products were characterized with Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

PP was provided by the State Key Laboratory of Chemical Engineering at East China University of Science & Technology (Guangzhou, China). PP was Soxhlet-extracted from acetone for 5 h and dried in a vacuum oven at 60°C. AIBN (analytical-reagent-grade) was purchased from Shanghai Sanpu Chemical Co., Ltd. (Shanghai, China). Ethanol (analytical-reagent-grade) was supplied by Kaifeng Chemical Reagent Factory (Kaifeng, China). Acrylamide (analytical-grade) was produced by Tianjin

Correspondence to: Q. Xu (qunxu@zzu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20404012.

Contract grant sponsor: Prominent Youth Science Foundation of Henan Province; contract grant number: 0512001200.

Contract grant sponsor: Natural Science Foundation of Henan Province; contract grant number: 0411020900.

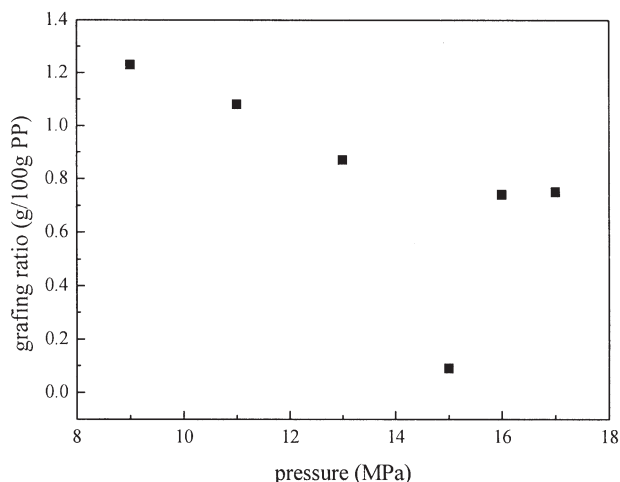


Figure 1 Effect of the impregnation pressure on the grafting at 40°C with 3 h of impregnation (the graft reaction took place at 65°C for 3 h).

Fuchen Chemical Reagent Factory (Tianjin, China). CO₂ with a purity of 99.9% was obtained from Zhengzhou Shuangyang Gas Co. (Zhengzhou, China) and was used as received.

Grafting procedure

The pure PP film, acrylamide, and AIBN were placed in a 50-mL, high-pressure, stainless steel vessel together with a magnetic stirrer. In this vessel, the pure PP film and acrylamide/AIBN were separated by a stainless steel cage. The vessel was put into a heating jacket. The air in the vessel was replaced by CO₂, and then CO₂ was compressed into the vessel to a desired pressure with a high-pressure pump. After a desired impregnation time, the temperature of the vessel was increased to a suitable grafting reaction temperature. The pressure of supercritical CO₂ in the vessel also increased along with the temperature. After a reaction time of 3 h, the fluid in the system was released, and the sample was taken out and weighed on an analytical balance with a sensitivity of 0.1 mg. Then, the sample was Soxhlet-extracted for 6 h with ethanol and dried at 60°C *in vacuo* to remove unreacted reagents and homopolymer.

The grafting ratio was calculated as follows:

$$\text{Grafting ratio} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the weight of the original PP and W_2 is the weight of the grafted PP.

Characterization

Infrared (IR) spectroscopy experiments were performed with a Nicolet 460 FTIR instrument (Netzsch-

Gerätebau GmbH, Bavaria, Germany) under standard operating conditions. An Amray 1000B scanning electron microscope at an accelerating voltage of 20 kV was used to observe the changes in the morphology of the samples. DSC measurements were conducted on a Netzsch 204 DSC under an atmosphere of N₂ with a heating rate of 10°C/min in the temperature range of 80–210°C.

RESULTS AND DISCUSSION

Effect of the impregnation pressure

Figure 1 shows the effect of the impregnation pressure in the range of 9–17 MPa. The original concentration of acrylamide was 0.1 mol/L with 5 wt % AIBN, the impregnation time was 3 h, and the impregnation temperature was 40°C. The graft reaction took place at 65°C for 3 h. Figure 1 shows that the grafting ratio decreases with the impregnation pressure at first, and there is a minimum at 15 MPa. Then, it increases with the pressure. There are two factors affecting the impregnation and grafting. First, an increase in the pressure results in increased solvent power of CO₂, which is not favorable to the partitioning of acrylamide in the PP matrix. Second, increasing the pressure of CO₂ results in an increase in the swelling or plasticization of the PP substrate, which makes the diffusion of the monomer and initiator in PP easier, and this is favorable to the grafting reaction. The first factor is predominant in the pressure range of 9–15 MPa, so the grafting ratio decreases. However, at higher pressures, the second factor becomes much decisive, so the grafting ratio increases after 15 MPa.

Effect of the impregnation temperature

Figure 2 shows the effect of the impregnation temperature in the range of 35–45°C. The original concentra-

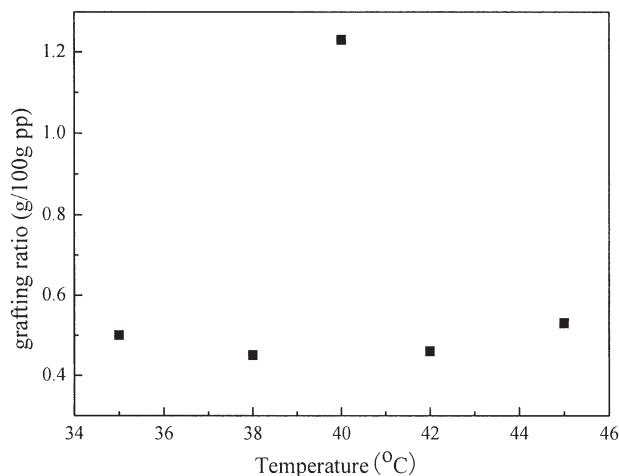


Figure 2 Effect of the impregnation temperature on the grafting at 9 MPa with 3 h of impregnation (the grafting reaction took place at 65°C for 3 h).

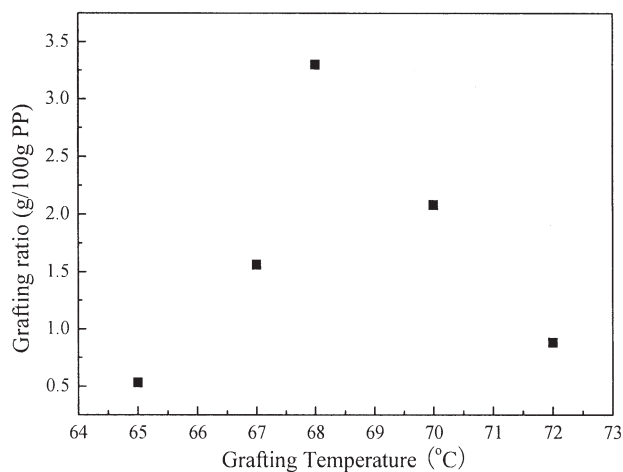


Figure 3 Effect of the grafting temperature on the grafting at 9 MPa and 40°C with 3 h of impregnation.

tion of acrylamide was 0.1 mol/L with 5 wt % AIBN, and the impregnation time was 3 h. The grafting reaction took place at 65°C for 3 h. According to Figure 2, there is a maximum point at 40°C for the grafting ratio. Therefore, this experimental condition at a su-

percritical impregnation pressure of 9 MPa, an impregnation temperature of 40°C, is a optimal experimental impregnation condition to obtain a high grafting rate of polyacrylamide to PP. However, the detailed mechanism is very complex, and it will be mentioned in the next step of the grafting polymerization of acrylamide in supercritical CO₂.

Effect of the grafting temperature

On the basis of the aforementioned study, the effect of the grafting temperature on the grafting rate was studied. A series of experiments were conducted at 40°C and 9 MPa during the impregnation process, with the acrylamide containing 5 wt % AIBN. Figure 3 shows the effect of the grafting temperature on the ratio of grafting. The grafting ratio increases initially and then decreases with the temperature. An increase in the temperature, on the one hand, improves the decomposition speed of the initiator, and this makes many free-radical sites available on the PP backbone, so the grafting amount increases. On the other hand, it results in decreased solution power of CO₂, which cannot dissolve enough acrylamide, so the grafting

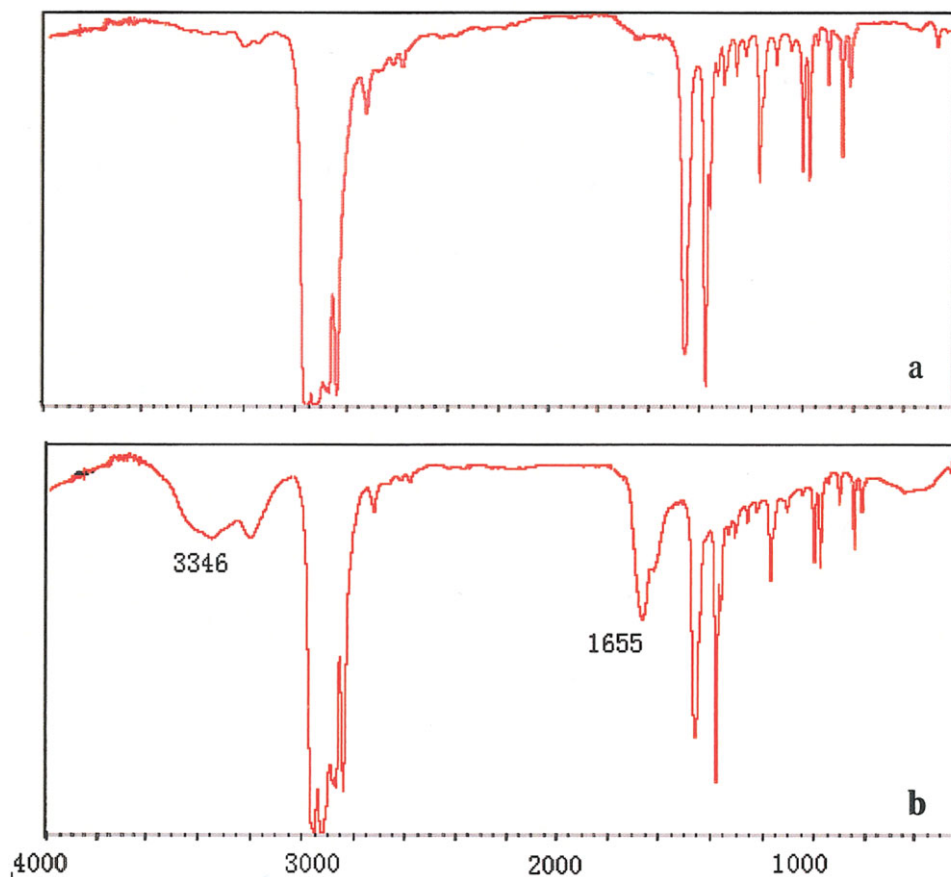


Figure 4 FTIR spectra of (a) virgin PP and (b) grafted polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

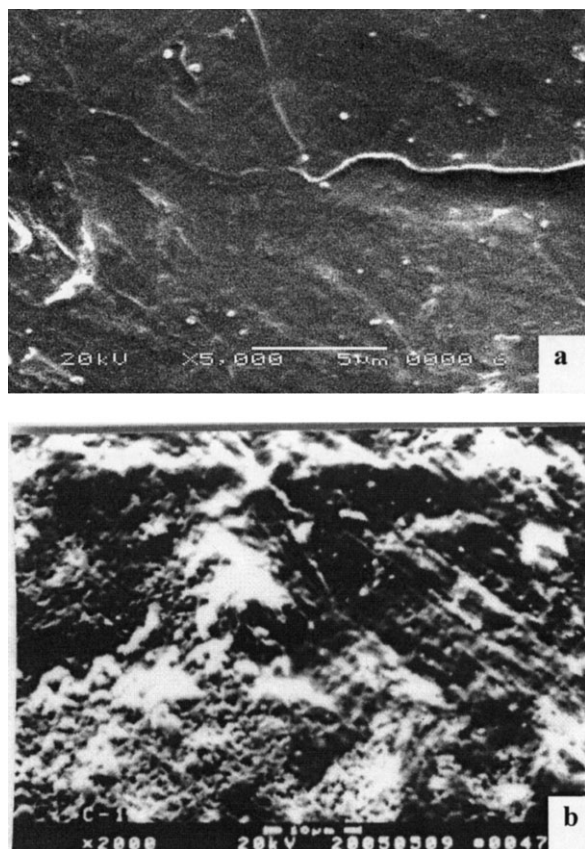


Figure 5 SEM images of (a) virgin PP and (b) grafted PP.

amount decreases. In addition, the high temperature makes the initiator decompose so quickly that it cannot form effective free-radical sites. This is another important reason for the decrease in the grafting ratio. Therefore, at the grafting temperature of 68°C, there is a balance point that shows the maximum grafting rate of polyacrylamide onto PP.

Characterization

IR spectroscopy measurements

The FTIR spectra of pure PP and a grafted sample in the wave-number range of 4000–400 cm^{-1} are shown in Figure 4. There is some new absorption at 1655, 3346, and 3198 cm^{-1} for C=N, O—H, and N—H, indicating that acrylamide has been grafted onto PP.

SEM measurements

SEM studies of pure and grafted PP allow the assessment of the effect of grafting on the morphology. The results are shown in Figure 5. After the treatment with supercritical CO_2 and grafting reaction, the surface morphology of grafted PP is no longer even and homogeneous as that of the virgin PP film. As shown in

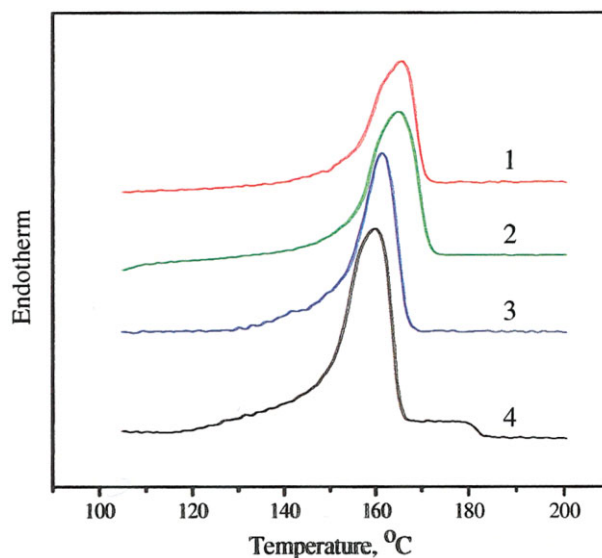


Figure 6 DSC curves for (1) virgin PP, (2) a 1.56% grafted PP specimen, (3) a 2.15% grafted specimen, and (4) a 3.23% grafted specimen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5, the grafted surface of PP is very rough, and this indicates the existence of polyacrylamide.

DSC measurements

Figure 6 shows the DSC thermograms of pure PP and grafted samples with different grafting ratios of 1.56, 2.15, and 3.23 wt %, respectively. The melting point (T_m) and enthalpy of melting (ΔH_m) obtained from the DSC curves in Figure 6 are listed in Table I. In this work, all runs were conducted in a nitrogen atmosphere, and the temperature of the samples was raised from 80 to 210°C at a rate of 10°C/min. Table I shows that ΔH_m of the composites decreases as the grafting ratio increase.

The apparent crystallinity (C_a) of isotactic polypropylene (iPP) and grafted iPP was calculated with the following equation:

$$C_a(\%) = \Delta H_m / \Delta H^0 \quad (2)$$

TABLE I
Parameters of PP and Its Composites

Sample ^a	T_m (°C)	ΔH_m (J/g)	C_a (%)
Pure PP	165.7	96.10	46.0
Sample A	165.0	78.36	37.5
Sample B	161.4	76.54	36.6
Sample C	159.8	73.72	35.3

^a The grafting ratios of sample A, sample B, and sample C were 1.56, 2.15, and 3.23%, respectively.

where ΔH_m is the apparent enthalpy of melting and ΔH^0 is the heat of fusion per gram of 100% crystalline iPP (209 J/g).²² Table I shows that C_a of the composites decreases as the grafting degree increase. This is probably due to the grafted branches, which disrupt the regularity of the chain structure and increase the spaces between the chains.

CONCLUSIONS

Acrylamide was polymerized and grafted onto PP substrates with the aid of supercritical CO₂. Different experimental conditions, such as the impregnation temperature, pressure, and grafting temperature, affected the grafting ratio. FTIR spectra of virgin PP and grafted PP indicated that polyacrylamide had indeed grafted onto PP. DSC measurements were performed, and the results showed that T_m of the grafted sample was lower than that of pure PP and decreased with an increasing grafting ratio. SEM studies of pure PP and grafted PP allowed an assessment of the effect of grafting on the morphology.

References

1. Kazarian, S. G. *Polym Sci Ser C* 2000, 42, 78.
2. Cooper, A. I.; Holmes, A. B. *Adv Mater* 1999, 11, 1270.
3. Li, D.; Han, B. X. *Macromolecules* 2000, 33, 4555.
4. Siripurapu, S.; Gay, Y. J.; Royer, J. R. *Polymer* 2002, 43, 5511.
5. Zhang, J.; Busby, A. J.; Roberts, C. J. *Macromolecules* 2002, 35, 8869.
6. Wissinger, R. G.; Paulaitis, M. E. *J Polym Sci, J Polym Phys Ed* 1987, 25, 2497.
7. Berens, A. R.; Huvard, G. S.; Kormeyer, R. W. *J Appl Polym Sci* 1992, 46, 231.
8. Berens, A. R.; Huvard, G. S. In *Supercritical Fluid Science and Technology*; Johnston, K. P.; Penniger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989.
9. Shine, A. D. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics: Woodbury, NY, 1996.
10. Dispenza, C.; Filardo, G.; Silvestri, G. *Colloid Polym Sci* 1997, 275, 390.
11. Jobling, M.; Howdle, S. M.; Poliakoff, M. *J Chem Soc Chem Commun* 1990, 1762.
12. Yalpani, M. *Polymer* 1993, 34, 1102.
13. Dong, Z.; Liu, Z.; Han, B. X. *J Mater Chem* 2002, 12, 3565.
14. Watkins, J. J.; McCarthy, T. J. *Macromolecules* 1994, 27, 4845.
15. Watkins, J. J.; McCarthy, T. J. *Macromolecules* 1995, 28, 4067.
16. Watkins, J. J.; McCarthy, T. J. *Chem Mater* 1995, 7, 1991.
17. Kung, E.; Lesser, A. J.; McCarthy, T. J. *Macromolecules* 1998, 31, 4160.
18. Pan, Y. K.; Ruan, J. M.; Zhou, D. F. *J Appl Polym Sci* 1997, 65, 1905.
19. D'Orazio, L.; Guarino, R.; Mancarella, C. *J Appl Polym Sci* 2000, 75, 553.
20. Gatenholm, P.; Ashida, T.; Hoffman, A. S. *J Polym Sci Part A: Polym Chem* 1997, 35, 1461.
21. Galia, A.; De Gregorio, R.; Spadaro, G.; Scialdone, O.; Filardo, G. *Macromolecules* 2004, 37, 4580.
22. *Polymer Handbook*; Bandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1975.