Improving Foamability of Polypropylene by Grafting Modification

Chunsheng Liu[1], Dafu Wei,[1] Anna Zheng,[1] Yong Li, Huining Xiao[2]

[1]*Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology, Shanghai 200237, People's Republic of China*
[2]*Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*

ABSTRACT: Polypropylene (PP) foam has been considered as a potential substitute for other thermoplastics foams in industrial applications. However, the key concern is the weak melt strength of PP, which leads to a high content of open-cell structure in PP foams; and, thus, unsatisfactory for a number of applications. In this work, PP was modified by grafting with unsaturated linear polyester (ULP) in a twin-screw extruder in attempt to improve the melt strength of PP. The grafting reaction on PP and the modified PP were characterized using FT-IR, DSC, and TGA. The improved foamability was verified by SEM observation. In addition, the rheological behavior of modified PP was investigated using a Hakke rheometer. The results indicated that the melt strength of grafted PP was significantly enhanced, facilitating the foam formation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4114–4123, 2006

Key words: polypropylene; foams; grafting modification; polyester

INTRODUCTION

Thermoplastic foam possesses a cellular structure created by the expansion of a blowing agent. Polystyrene (PS) and polyethylene (PE) foams are typical of such types. Because of inherent weakness, the applications of PS and PE foams are constrained.[1] For example, the foams cannot be used at the temperature above 100°C because of their low heat deflection temperatures.[2] Polypropylene (PP) has a number of superior properties over PS and PE in terms of mechanical properties. Relatively high thermal stability also allows PP to be used in a broader temperature range.[3] Therefore, PP foam has been considered as a potential substitute for other thermoplastics foams in various industrial applications. However, few cases have been reported on the production of PP foams in a commercial scale, which is attributed to the weak melt strength and melt elasticity of PP. During foaming processes, the weak melt strength of polymer tends to create cell walls, which are not sufficiently strong to bear the extension force and rupture readily. As a result, foamed PP products usually have a high open-cell content and, thus, are unsatisfactory for various applications.[4,5]

To improve the foamability, modifications on PP have been conducted[6–9]. Nojiri et al.[10] modified PP by mixing PP with crosslinking agent in an extruder, followed by γ-radiation to induce the crosslinking of PP to achieve the high melt strength (HMS). Secheve et al.[11] disclosed a process for preparing HMS-PP by high energy radiation in a reduced active oxygen environment. The process generated the modified PP containing some long chain branches with free-ends or formed a crosslinked polymer. Dang and Dong[12] also used the homopolymer or copolymer of PP to form HMS-PP by irradiation. However, the chain scission or degradation was often found during the irradiation.

In this work, we aimed at developing an improved approach for preparing a HMS-PP with better foamability. The modification was focused on melt-grafting PP in a twin-screw extruder with unsaturated linear polyester (ULP) as a functional macromonomer or modifier in the presence of diisopropylbenzene hydroperoxide (DCP) as an initiator. The key objective was to use this grafted PP as a foaming matrix to obtain an excellent foam material that has fine cell structure after extrusion process. Several influencing factors were investigated, and the mechanism of the grafting reaction was explored. The rheological behavior of modified PP was also revealed using a Hakke rheometer as well as a rotating rheometer.
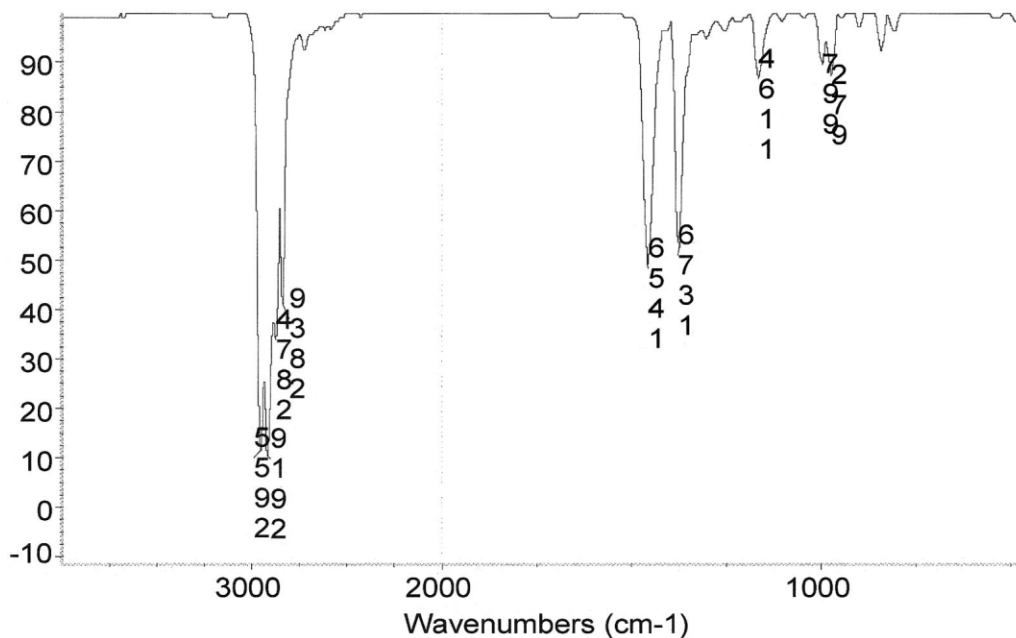
Figure 1 FT-IR Spectra of Original PP.

EXPERIMENTAL

Materials

A commercial grade Polypropylene (PP) resin, EPS30R (MFR = 1.0–2.5 g/10 min), was supplied by Qilu petrochemical Co. Ltd. (Shandong, China). The unsaturated linear polyester (ULP) as grafting macromonomer was self-prepared. Diisopropylbenzene hydroperoxide (DCP) and styrene were used as initiator and chain extender, respectively. 1,1,2-trichlorotrifluoroethane, CCl_2FCClF_2 (CFC-113), and talc were used as blowing agent and a nucleating agent, respectively. Reagent grade acetone and xylene, purchased from Shanghai Chemical Reagent Co. Ltd., were used as an extracting agent solvent for PP, respectively.
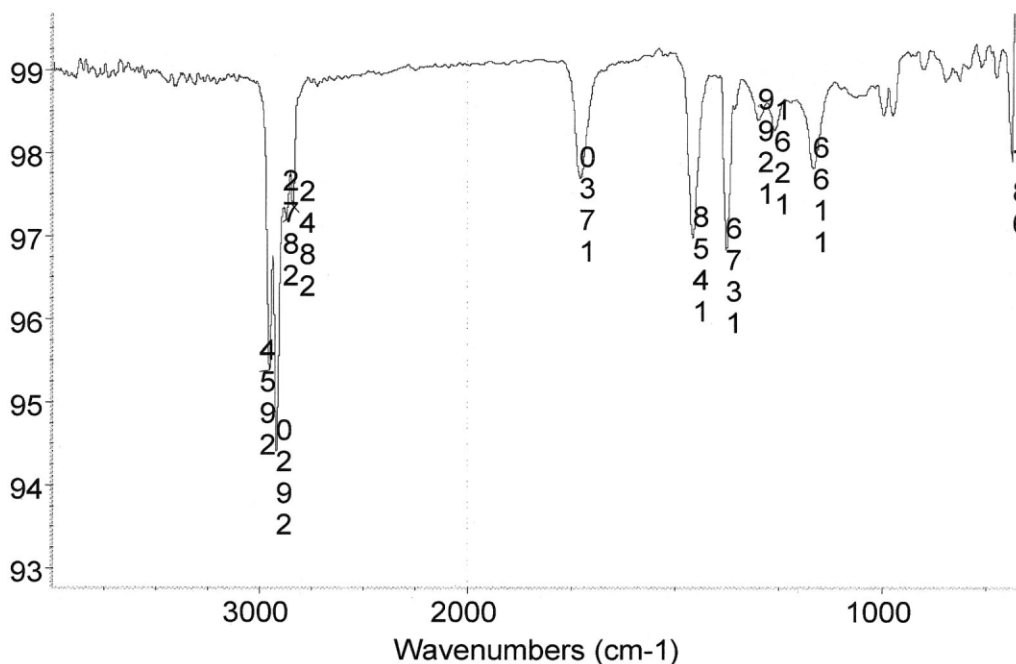

Figure 2 FT-IR Spectra of Grafted PP.

TABLE I
Gel Content of the Grafted PP

No.	Original PP	ULP	Styrene	Gel content (%)
1	100	5	2	0
2	100	10	2	0
3	100	15	2	0
4	100	20	2	0
5	100	5	4.5	0
6	100	5	6	0
7	100	5	8	0
8	100	5	10	0

Modification procedure and characterization

The PP pellets, mixed with ULP, styrene, diisopropyl-benzene hydroperoxide, and antioxidant agent 1010, were fed into the barrel through a hopper and processed at the screw speed of 50 rpm in a corotating twin-screw extruder. The temperature of extruder barrels was set at 185°C. The melt-grafting PP was extruded, and cut into pellets.

The grafting reaction was monitored using a FT-IR spectrometer (Nicolet Magna- IR550). The grafted PP sample was dissolved in xylene at 140°C and precipitated with acetone. The precipitated sample was filtrated out and extracted in acetone for 24 h, then dried at 110°C in vacuum. The gel content of grafted PP was measured by extracting the grafted PP in xylene for 24 h. The amount of crosslinked PP was calculated based on the mass extracted. The melt flow rates (MFR) of the resins were determined according to ASTM D-1238. The rheological behavior of the grafted

PP was characterized using a Dynamic Stress Rheometer 600 (Thermo Haake Co.). The thermal analysis of the resin was carried out with differential scanning calorimetry (DSC, TA MDSC-2910) and thermal gravimetric analysis (TGA). In both cases, the heating rate was 10°C/min, and the measurement was performed in nitrogen atmosphere. The mechanical properties of the resins were tested according to ASTM standard.

The extrusion and foaming of PP were carried out in the same extruder, where PP was mixed with talc and other auxiliary agents. The blowing agent was injected into the extrusion barrel at the preconcerted position by a positive displacement pump. The weight ratio of blowing agent to PP was varied by controlling the flow rates. The foamability was observed under a scanning electron microscope (SEM) (Japan JSM-6360LV Co.), which revealed the morphology of foams including the diameter of the cell. To determine the cell density, the foam samples were randomly chosen and dipped into the liquid nitrogen, then fractured to expose the cellular morphology.

The cell density of the foam was calculated by the following equation

$$(1 - \rho_f/\rho)/(\pi D^3/6)$$

Where ρ is the density of the original PP, while ρ_f is the apparent density of foam samples, and D is the diameter of the cell obtained from the SEM observation.[13]

RESULTS AND DISCUSSION

The grafting reaction of PP

Figures 1 and 2 shows the FT-IR spectra of the original PP and the grafted PP. The absorption peak at 1730
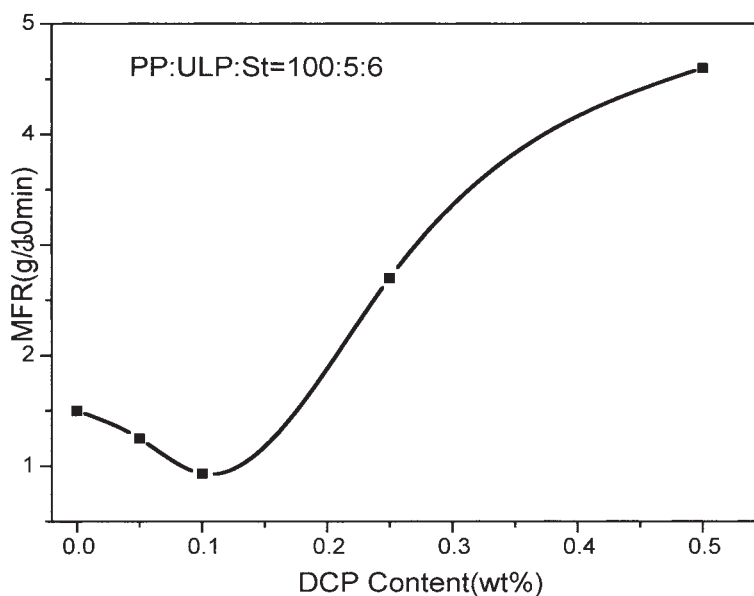

Figure 3   MFR of the grafted PP as a functional of the content of diisopropylbenzene hydroperoxide (DCP).
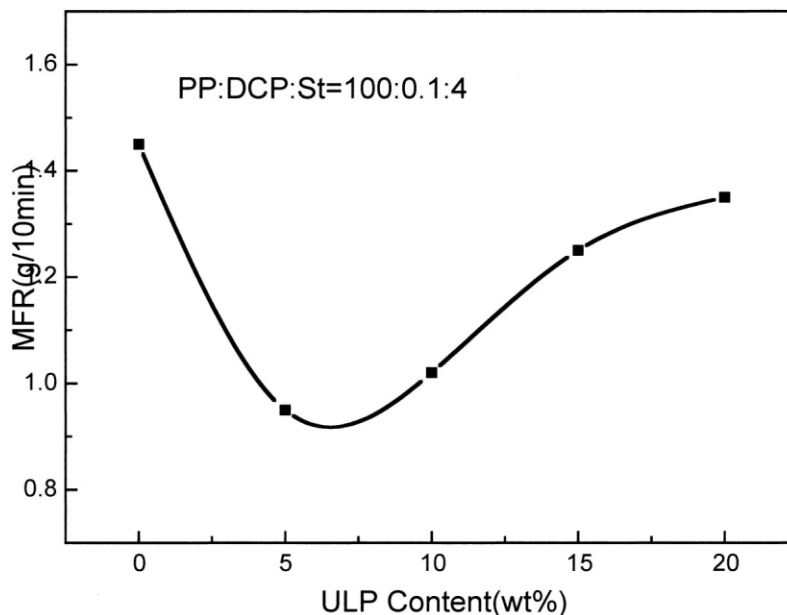
Figure 4 MFR of the grafted PP as a functional of the content of unsaturated linear polyester (ULP).

cm^{-1} in Figure 2 represents the carbonyl group originating from ULP. The detected carbonyl group is the evidence that ULP has been grafted onto PP.

In addition, the gel contents of the grafted PP prepared at various ULP/styrene levels were measured. The results are listed in Table I. Clearly, the zero gel content simply indicated that PP was only grafted or branched by the ULP and styrene, and did not form crosslinked or network structure. Therefore, the

grafted PP can be softened or melted in the foaming process.

Analysis of melt flow rate (MFR)

As shown in Figure 3, with the increasing diisopropyl-benzene hydroperoxide (DCP) content, the MFR of grafted PP decreases, and then rapidly increases after reaching a minimum point. This indicated that there
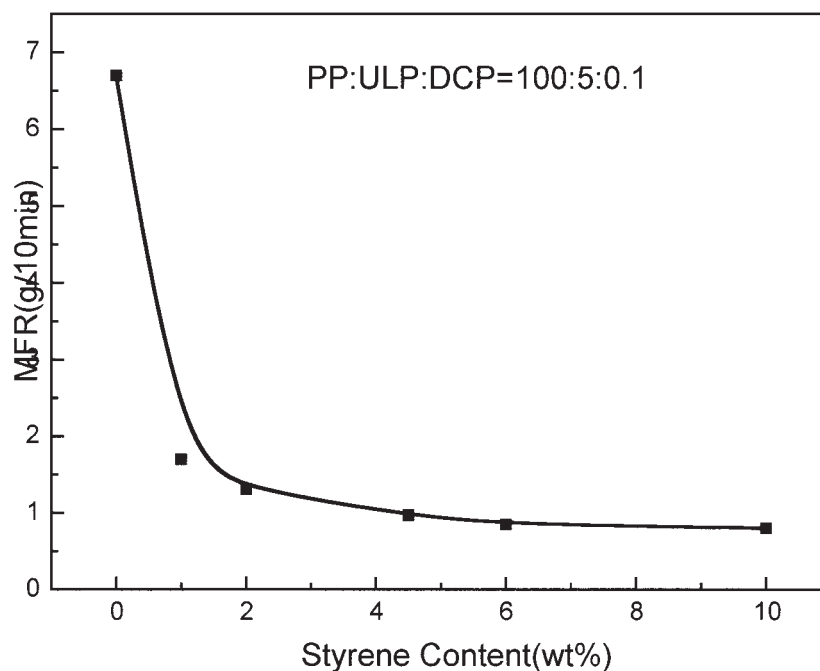

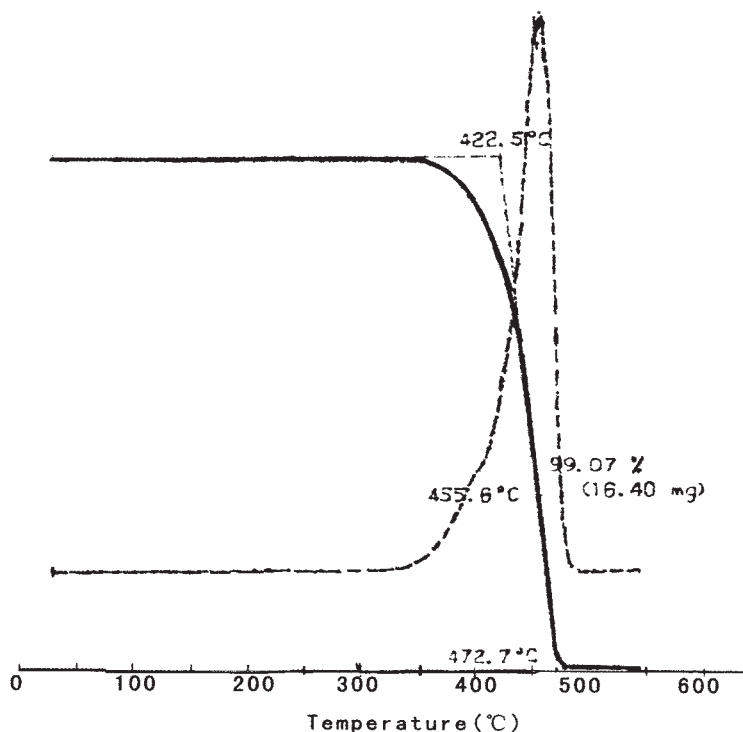**Figure 5** MFR of the grafted PP as a functional of the content of Styrene.

Figure 6 TGA curve of the original PP.

was an optimal dosage point of DCP at which the grafting reaction was initiated while the β-scission of PP seldom occurred. On the other hand, at a constant dosage of DCP (0.1%, i.e., the minimum point in Fig. 3), as the amount of ULP increases, the MFR of grafted PP drops sharply to a minimal value, then increases gradually, as shown in Figure 4. The above results suggested that the existence of DCP promoted the reaction between the ULP and PP. However, excessive ULP (under the same content of DCP) led to an incomplete reaction and increasing MFR because of the presence of the residual ULP. The effect of styrene content on MFR is shown in Figure 5. The MFR drops sharply and then slowly levels off at the content of styrene beyond 5%.

Thermal analysis of the grafted PP

TGA results for the original PP and grafted PP are illustrated in Figures 6 and 7. The results showed that the grafted PP had a higher decomposition temperature (433.1°C), compared with that of the original PP (422.5°C). This indicated that the polymer became more heat resistant after grafting modification. The improved thermal stability also ensures the applications of the grafted PP in various areas.

Table II lists the DSC results for the original PP and grafted PP, and the corresponding DSC curves are shown in Figures 8 and 9. Referring to Figure 9, the crystalline temperature (T_c) of grafted PP was 119°C,

about 10°C higher than that of the original PP, whereas the melt temperatures (T_m) were almost identical. These data suggested that grafting modification facilitated the crystallization of PP. The similar result was also reported by Guan et al.[14] The high T_c is beneficial to the foaming of PP. In the course of foaming, when the mixture of PP and gas is extruded out of the die, the pressure sharply decreases. Consequently
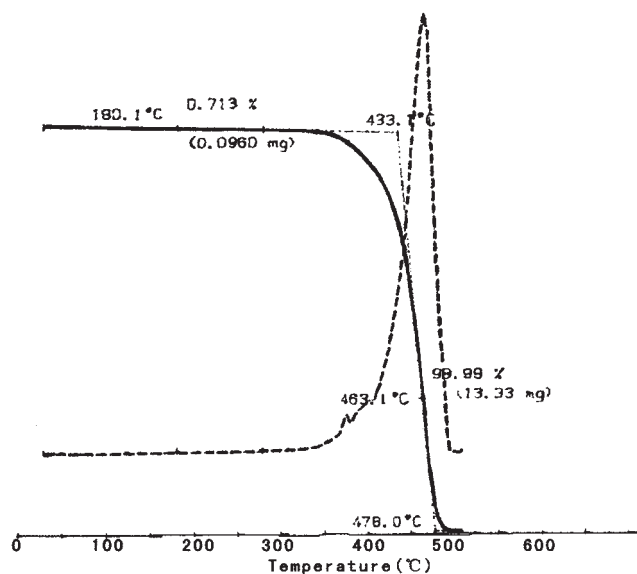

Figure 7 TGA curve of the grafted PP.

TABLE II
Parameters of DSC Curves of Original PP and Grafted PP

Sample	$T_{c(onset)}$ (°C)	$T_{c(peak)}$ (°C)	$T_{m(onset)}$ (°C)	$T_{m(peak)}$ (°C)	ΔH (J/g)
Original PP	116.08	109.85	154.98	167.43	70.15
Grafted PP	125.25	119.39	152.90	166.40	64.15

PP and gas will expand instantaneously, the gas in particular. At this time if the crystallization temperature of PP is higher, the crystallization of PP will proceed rapidly, thus benefiting the stability of foaming. The results also imply that the grafted PP could induce the rapid case-hardening of the foams. Therefore, the high crystalline temperature of the resin is propitious to the foaming in the twin-screw extruder. The crystallinity of the polymers, calculated through ΔH (enthalpy of melting), was 0.464 and 0.508 for the grafted PP and original PP, respectively. Obviously, the grafting reduced the crystallinity of PP, which could be due to the fact that the grafted ULP molecular chains retard the orderly arraying of PP molecular chains.

The rheological behavior of the resins

At the same shear rate but different temperatures, the variations of shear viscosity for the grafted PP and original PP are shown in Figures 10 and 11. As can be seen from Figure 10, the shear viscosities for both resins decrease as the temperature increases. However, the grafted PP exhibited much higher viscosity. This implied that the grafted PP had high melt strength, thus enabling the resin to retain more gas in the melt body and to expand the range of foaming temperature. In fact, the melt strength should be strong enough to keep the walls of separating resins and gas stable. Otherwise, the melt fracture would occur easily, and the gas would escape from cells. So, high melt strength PP will retain more gas. On the other hand, the viscosity of the grafted PP is higher than that of original PP, and less sensitive to temperature, as shown in Figure 11. The relation between the viscosity and temperature can be described by the Arrhenius type equation as follows:

$$ln\,\eta_a = \ln A + \Delta E/RT$$

where η_a is the apparent viscosity, A is a constant, ΔE is the activation energy of viscosity fluid (kJ/mol), R is the gas constant, and T is the absolute temperature (K). The activation energies for the original PP and
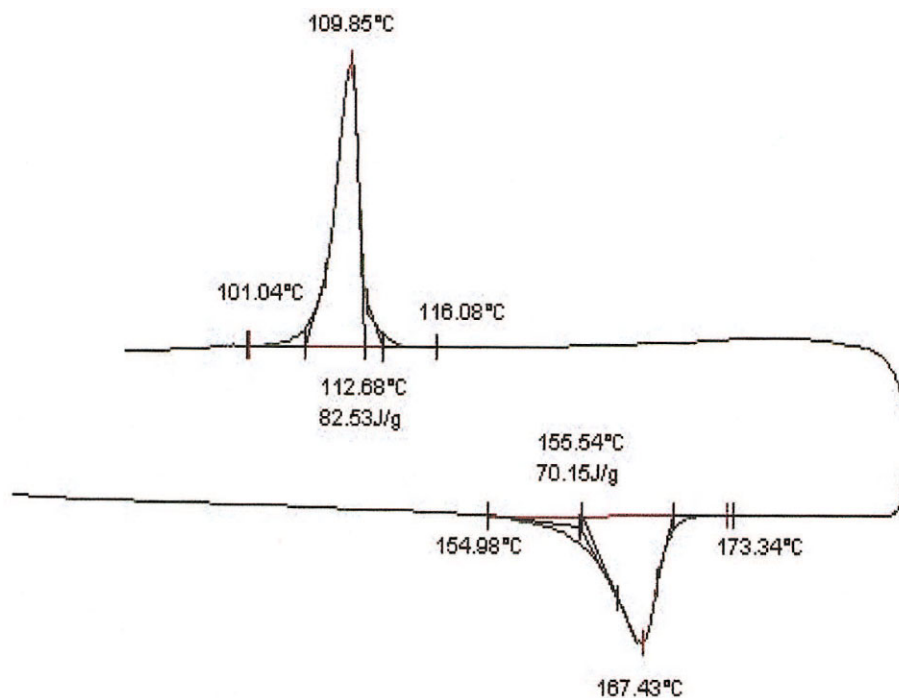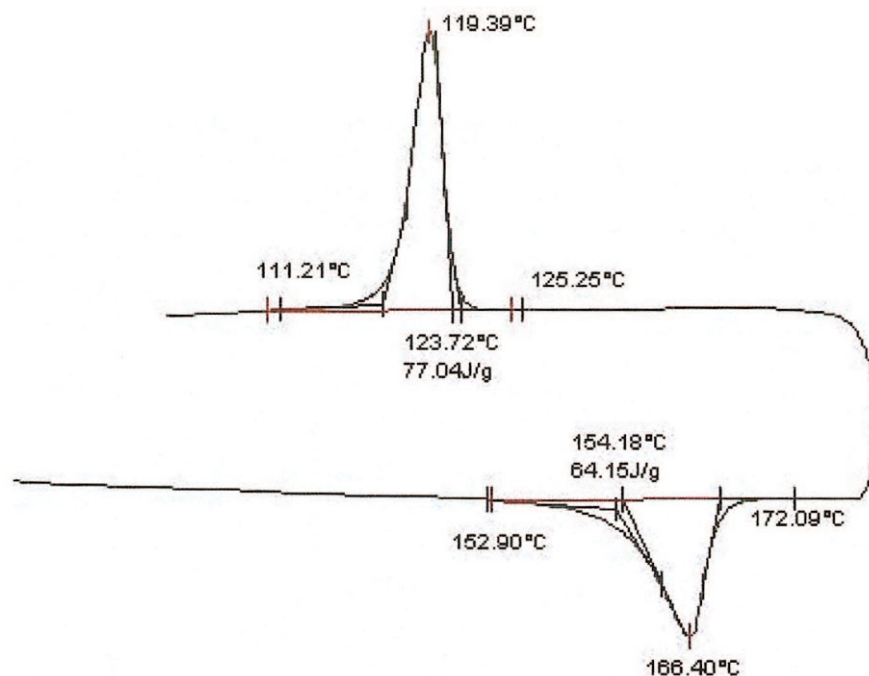

Figure 8 DSC curve of the original PP. [Color figure can be viewed in the online issue, which is available at www.inter-science.wiley.com.]
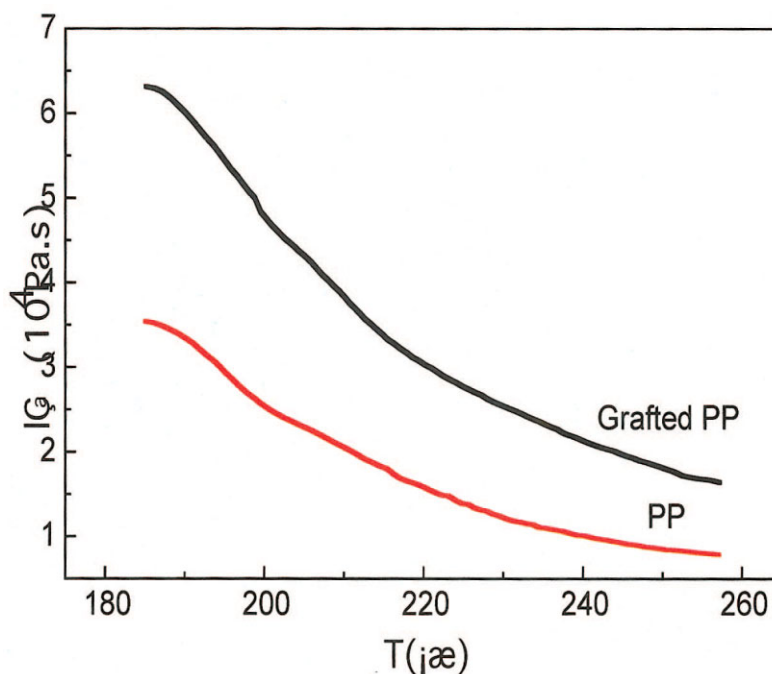
Figure 9 DSC curve of the grafted PP. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

grafted PP, estimated from the slope of the lines in Figure 11, were 4.36 and 3.82 kJ/mol, respectively. The lower activation energy suggested that the viscosity of the grafted PP was less sensitive to the temperature than that of the original PP, which also implied the

temperature dependence of the melt strength for two resins was different.

The relation between the strain and temperature is presented in Figure 12. As can be seen, the strain of the original PP is approximately 4 times as high as that of

Figure 10 η_a–T Curve of the original PP and grafted PP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
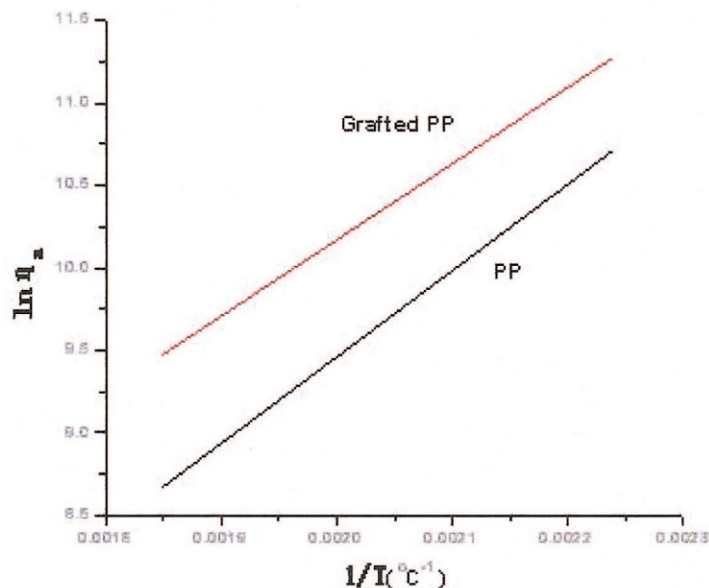
Figure 11 $\ln\eta_a$–$1/T$ curve of the original PP and grafted PP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the grafted PP at the same shear stress and temperature, which further indicates that the grafting renders PP high melt strength.
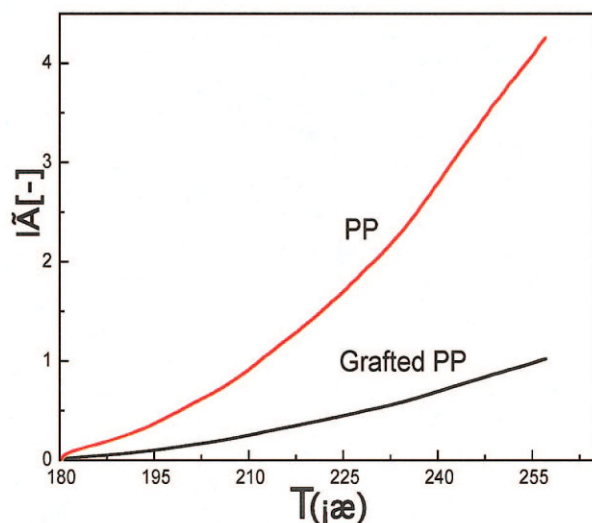
The mechanical properties of original PP and grafted PP

The mechanical properties of the original PP and grafted PP are summarized in Table III. The yield elongation and the breaking elongation of the grafted PP were similar to those of the original PP, whereas

the tensile strength, bending modulus and impact strength dropped to a certain degree. Although they still maintained at the acceptable level, perhaps the negative influence of grafting on the mechanical properties needs further investigation.

The foamability of grafted PP

Figure 13 shows the SEM images of the foam. Clearly the foaming degree of the grafted PP increased and the size of the cell decreased, compared with the original PP. The foam with fine cell structure was created by the grafted PP with high melt strength, which allowed the gas to be retained in well closed-cell structure foam. Because of the low melt strength, the cells in the original PP inclined to coalesce, forming the foam with connected-cell structure. In addition, from the SEM micrographs it could be observed that as the talc content increased, the fine cell structure in the foam was further improved. The effect of the talc on the cell density, while other additives contents were kept constant, is shown in Figure 14. It was found that


Figure 12 γ–T Curve of the original PP and grafted PP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
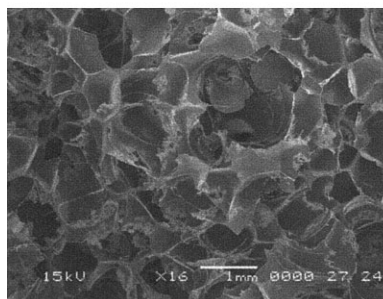
TABLE III
Mechanical Properties of Original PP and Grafted PP

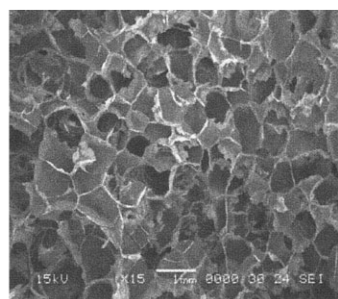| Mechanical Properties	Original PP	Grafted PP
Yield elongation (%)	25.2	26.1
Breaking elongation (%)	428	440
Tensile strength (MPa)	40.4	34.9
Bending modulus (MPa)	1864	1723
Impact strength (kJ/m^2)	22.8	17.25
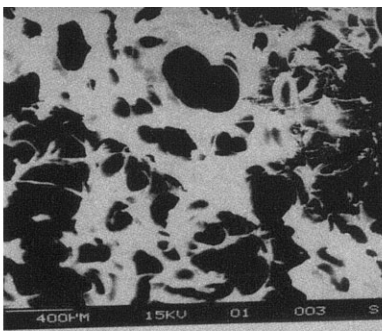
(a) PP: talc content=5%

(b) Grafted PP: talc content=5%

(c) Grafted PP: talc content=9%

Figure 13 SEM images of the cross sections of PP and grafted PP extrudate.

the cell density increased greatly as the talc content increased. The results suggest that the talc is very effective for nucleation of the foam and there is an optimal talc content to receive a desired cell density for foam materials with fine cell structure.

CONCLUSIONS

After the grafting modification with ULP and styrene in a twin-screw extruder in the presence of diisopropylbenzene hydroperoxide, the melt
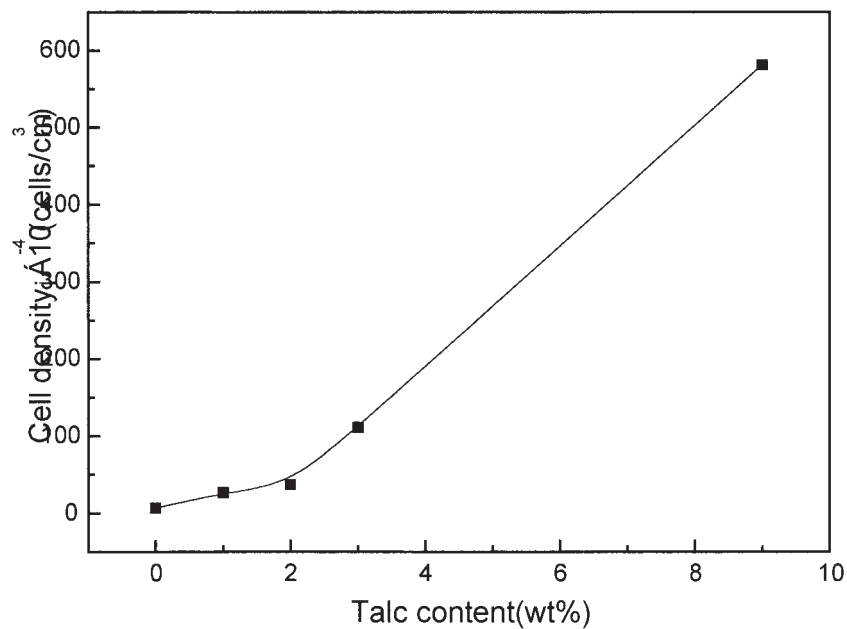

Figure 14 Effect of the talc content on the cell density.

strength of the grafted PP was improved effectively, and the melt viscosity of the modified PP was not so sensitive to temperature change. Consequently, the temperature range of PP foaming was broadened when the modified PP was used. Compared with the original PP, the mechanical properties of grafted PP were deteriorated slightly, however, the overall performance of the resins maintained at an acceptable level. The grafted-modified PP enabled the preparation of foams with fine cell structure; whereas the negative impact of the grafting on the mechanical properties of PP needs to be investigated further.

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