

Improving Foam Ability of Polypropylene by Crosslinking

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ABSTRACT: In this study, silane crosslinked polypropylene (PP) was prepared by grafting of silane onto the backbone of PP in a melt process using a twin-screw extruder and then crosslinking in warm water; an attempt was made to improve the melt strength of PP. In the present work, benzoyl peroxide was used as initiator, silane as a monomer, styrene as assisted crosslinking agent. PP foam board with well-distributed and fine blowing hole was prepared by compression molding technology, employing azodicarbamide as blowing agent, talcum powder as nucleation agent. The effects of silane and peroxide concentration on the silane crosslinked PP were investigated. The surface morphology of the foam was accomplished by scanning electron microscopy (SEM). The thermal behavior of the silane crosslinked PP was studied by differential scanning calorimetry (DSC) and the elastic response was investigated

by dynamic mechanical analysis (DMA). The melt strength of the silane crosslinked PP was characterized by tension strength at high temperature tests. The results showed that the melt strength of the crosslinked PP was significantly enhanced, whereas melt flow rate, sag resistance, and tension strength at high temperature tests facilitated the foam formation. DSC analysis showed that the crystallization temperature of the silane crosslinked PP was increased compared with pure PP, which leads to high melting temperature and increased crystallinity. The results revealed that high melt strength PP(HMSPP) could be prepared by a method of silane crosslinking. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 973–980, 2011

Key words: polyolefins; differential scanning calorimetry; viscosity; crosslinking; foam extrusion

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 Therefore, PP foam has been considered as a potential substitute for other thermoplastics foams in various industrial applications. However, as a linear polymer, it exhibits low melt strength (MS) and no strain hardening behavior in the melt state, which limits its use in applications such as foaming. The low melt strength of polypropylene (PP) tends to create cell walls during foaming process, which are not sufficiently strong to bear the extension force and rupture readily.²

PP would be more extensively utilized, if its melt strength is improved. Modifications of PP have been

conducted to improve the melt strength.^{3–7} It was found that high melt strength polypropylene (HMSPP) could be manufactured by several ways: by using metallocene catalyst or Ziegler-Natta catalyst^{8,9} by adding organic peroxide, crosslinking reagent, and acrylic monomer,¹⁰ and by using electron beam irradiation.¹¹

Crosslinking is an important way to improve the melt strength and the thermal and chemical resistance of polyolefins. There are three main crosslinking methods, i.e., radiation crosslinking, peroxide crosslinking, and silane crosslinking.^{12–16} Nojiri and coworkers¹⁷ 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. In the research of Fumio Yoshii et al.,⁷ HMSPP was achieved with irradiation by an electron beam generated from an accelerator in the presence of polyfunctional monomers (PFM). Dang and Dong¹⁹ also used the homo-polymer or copolymer of PP to form HMSPP by irradiation. However, the chain scission or degradation was often found during the irradiation.

The other method to improve the melt strength of PP is to introduce long chain branch (LCB) onto the PP backbone.^{7,20,21} The addition of long-chain branches to the PP backbone may be an alternative for improving its melt strength and foaming processability. The

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branched structure can stabilize the bubble growth and retard cell coalescence or rupture. It is well known that alkoxy-silane-grafted polyolefins are synthesized by hydrolysis of silyltrialkoxo groups and following condensation of the formed silanol groups.^{22,23}

Among the three crosslinking methods, silane crosslinking is cost-effective and easily operated.²⁴ The silane crosslinking technique offers technological advantages over radiation and peroxide crosslinking technique and improves many useful properties of crosslinked polymers (such as polyethylene and propylene-ethylene copolymer, etc.). This technique is commonly employed to produce wire and cables, plastic pipes, etc. Vinylsilanes are first grafted onto the backbones of polymers, and then the grafted polymers are hydrolyzed in the warm water to form silane crosslinked ones with siloxane linkages (Si—O—Si) to produce silane crosslinked polymers. In recent decades, the silane crosslinking of polyethylene has been the subject of considerable research.^{25,26} For example, a novel one-step technique is proposed to prepare the silane grafting and crosslinking PP in method in a twin-screw reactive extruder.²⁷

In this study, the co-rotating twin-screw extruder was used to prepare HMSPP in a melt process, and another objective was to investigate the effects of silane VTMS, benzoyl peroxide (BPO), on the gel content, melt viscosity, and on melt strength of the silane crosslinked PP and also the project aims to obtain an excellent foam material using this silane crosslinked PP as a foaming matrix, which has fine cell structure after extrusion process.

EXPERIMENTAL

Materials

A commercial grade PP resin, T30S (MFR 3.8 g/10 min), was supplied by Tianjin petrochemical Co. Ltd., China. PP resin grade K8303 was obtained from Yanshan petrochemical Co. Ltd., China. Daploy HMSPP WB130[®] was obtained from the Borealis Group. Vinyl trimethoxysilane (VTMS) was provided by Tianjin Chemical Reagent Factory of China. Benzoyl peroxide (BPO) was used as initiator and purchased from Tianlian Fine Chemical Company of Shanghai. VTMS was used as monomer, and styrene was used as assisted crosslinking agent, AC as foaming agent, talcum powder used as nucleation agent. All other chemicals including xylene and acetone were of reagent grade and used as received.

Crosslinking procedure

The silane grafting of PP was carried out in a TE-35 co-rotating twin-screw extruder with a ratio of length to diameter at 35 : 1. PP pellets were mixed

with the silane monomer, initiator, and other additives. Then the blends were fed into the extruder under the required conditions. The temperature profile of the extruder from fed zone to die varied at 130, 155, 175, 190, 195, and 190°C. The rotation speed of screws was maintained at 100 rpm. The material feeding rate was controlled in the range of 10 kg/h. The silane grafted PP was obtained in the form of strip, which was quenched in cooling water and separated into granules about 4 mm long. The grafted samples were immersed into 90°C water for 6 h, and then dried in an oven at 90°C for 4 h.

Determination of gel content

The gel measurements were carried out to analyze the crosslink degree of silane crosslinked PP. The reaction product from extruder was extracted by a soxhlet method. The sample (about 0.5 g) was cut into small pieces, then packaged in a copper cloth of 200 meshes, and extracted with refluxing xylene for 24 h, then washed with acetone, dried in a vacuum oven at 80°C for 24 h. The above process was repeated until the mass of gel became constant. Then gel content is expressed in the percentage of the weight remaining.

The gel percentage of the samples was calculated by using formula as follows:

$$\text{Gel percentage} = \text{gel weight}/\text{initial weight} \times 100\%$$

Melt flow rate

The melt flow rate (MFR) of the resins was examined by a μ PXRZ-400C melt indexer (Jilin University Testing Machine Factory) under the condition of 2.16 kg at 230°C, based on the international standard (GB/T 3682-2000).

Rheological analysis

Rheological characterizations were made with RH 2000 capillary rheometer, (BOHLIN Instrument) using a die with a 1 mm diameter and L/D = 40 at 190°C.

Morphology analysis

The cell morphology of the foamed PP was investigated by scanning electron microscopy (SEM, JEOL/EO and model JSM-6380, Japan) at an accelerating voltage of 10 kV. The samples were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before SEM examination.

Thermal analysis

Differential scanning calorimetry (DSC) analysis was performed under nitrogen flow at a scanning rate of

TABLE I
Analysis of Mechanical Performance of Pure PP
and the Silane Crosslinked PP

Samples	Tensile strength (MPa)	Flexural strength (MPa)	Notch impact strength (kJ m^{-2})
Pure PP	37.73	47.40	7.76
Silane crosslinked PP	41.14	58.87	13.83

10°C/min with a Setaram DSC-141 instrument calibrated with indium and tin standards.

Dynamic mechanical analysis

The dynamic mechanical analytical (DMA) spectra were recorded by (DMA, 242 C NETZSCH company, Germany). The storage and loss modulus were measured in the tension mode at a frequency of 1.0 Hz with the temperature ranging from 30°C up to 180°C at a heating rate of 5°C/min, in a nitrogen atmosphere. All the samples were dried at 80°C in a vacuum oven until no more weight reduction of the sample were observed.

Melt strength test

Tension strength at high temperature was used to represent melt strength as a new method according to the concept of melt strength in this experiment. To prepare samples for the mechanical characterization and melt strength test, the blends were both molded by injection molding (JDH50 P series model).

The strength of the samples made of these blends was measured by computer-operated materials testing machine (Shenzhen Sans Model CMT4503 China) using a dumbbell specimen according to ASTM D415-80 at $20 \pm 3^\circ\text{C}$ with a tension speed of 50 mm/min. The data presented are the average of five tests in each case.

Compared with the measurement tension strength of PP at high temperature, the melt strength of PP can also be characterized by measuring the sag-resistance of PP. The length of the melt sag is measured at the same time at different PP.

RESULTS AND DISCUSSION

Mechanical properties of the silane crosslinked PP

The mechanical properties of pure PP (T30S) and the silane crosslinked PP are presented in Table I. It is found from the data that the silane crosslinked PP had better mechanical properties than pure PP. The tensile strength, flexural strength, and notch impact strength increased considerably with increasing crosslinking. This increase is believed to be enhanc-

ing interaction among the molecule because of the formation of crosslinking network structure, and this allows the material to absorb more impact energy, and notch impact strength of the silane crosslinked PP performance improved significantly.

Effect of the BPO concentration on melt viscosity

The changes in structure could lead to an increase in the viscosity of the reaction system during the preparation of HMSPP. In the present study, changes in the modified polypropylene backbone were analyzed by measuring the melt viscosity, which provides valuable information about the processability of the polymer. A significant increase in melt viscosity was observed when PP was modified. The influence of benzoyl peroxide concentration on the melt viscosity at constant silane content is shown in Figure 1. It can be seen that the melt viscosity increased with increasing BPO content. This increase is due to the loss of molecule mobility, and it is similar to the gel content of the system increased with the increase of initiator content. This shows that the amount of initiator system affects the reaction process seriously. With the increase of initiator content, more free radicals generated in the system and led to more crosslinking, so that the melt viscosity increased with increasing initiator concentration.

Effect of the BPO concentration on MFR

The influence of BPO concentration on the MFR of the silane crosslinked PP is depicted in Figure 2. The outcomes showed that MFR of the silane crosslinked PP decreased with increasing BPO concentration. Initially the decreasing trend was so sharp, and then showed gradual trend when further increasing BPO content. This phenomena is probably due to the

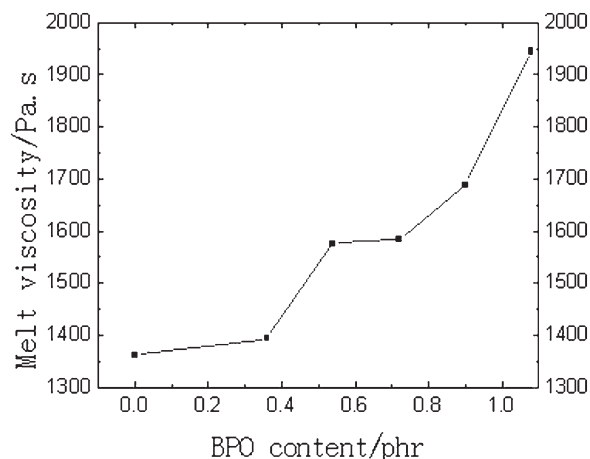


Figure 1 Effect of BPO concentration on the melt viscosity of silane crosslinked PP (VTMS = 2 phr, styrene = 2.3 phr).

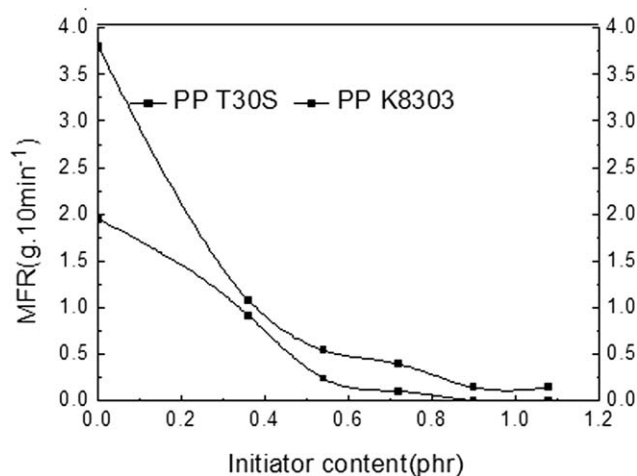


Figure 2 Effect of the BPO concentration on the MFR of the silane crosslinked PP (VTMS = 2 phr, styrene = 2.3 phr).

increasing number of free radicals produced by the peroxide decomposition which promotes the formation of reactive site on the polymer chain, which affects the degradation process and the crosslinking reaction significantly during the silane crosslinking of PP. It is observed from the experimental results that there is a slight difference in the MFR of PP T30S and PP K8303 in the initiator concentration ranging from 0.36 to 1.08 phr as examined here. Thus, the results showed that BPO has a certain compatibility to be used as initiator for different PP.

Effect of the BPO concentration on the gel content

The effect of the BPO concentration on the gel content of the silane crosslinked PP was also a source of investigation. The results are displayed in Figure 3, it is evident from the results that the gel content

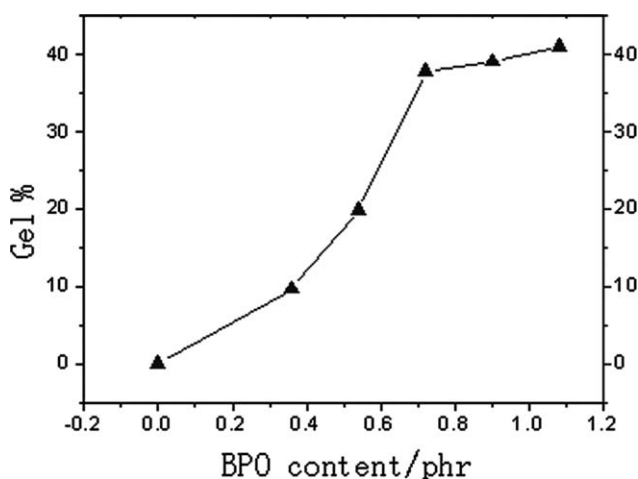


Figure 3 Effect of BPO concentration on the gel content of the silane crosslinked PP (VTMS = 2 phr, styrene = 2.3 phr).

increased sharply at first at then it gradually increased as the BPO concentration increased further at a fixed VTMS content of 2 phr. This increase is possibly due to the increasing number of free radicals produced by peroxide decomposition, which enhance the formation of reactive sites on the polymer chain. This higher concentration of free radicals is prone in promoting the crosslinking of PP, leading to high gel products. It is concluded that the more BPO is, the more silane crosslinked onto PP, thus the more gel produced.

Effect of BPO concentration on melt strength

It was expected that the instantaneous mechanical properties, namely melt strength, was found to depend exclusively on BPO concentration. The results are shown in Figure 4. As shown in Figure 4, the melt strength significantly increased up to 1.08 phr; then, it decreased continuously with increasing BPO concentration. This phenomenon can be explained on the bases of, when increasing the initiator concentration up to 1.08 phr the crosslinking degree grows, the melt strength increases, after that crosslinking degree becomes stable and the melt strength drops considerably. It can be seen from Figure 4 that the melt strength of polypropylene was increased to a greater extent, when BPO content was 1.08 phr.

Effect of the silane VTMS concentration

In this section, the effect of the silane VTMS concentration on the gel content of the silane crosslinked PP is outlined. The results are displayed in Figure 5, which indicate that the gel content increases gradually with the increasing VTMS concentration, at a

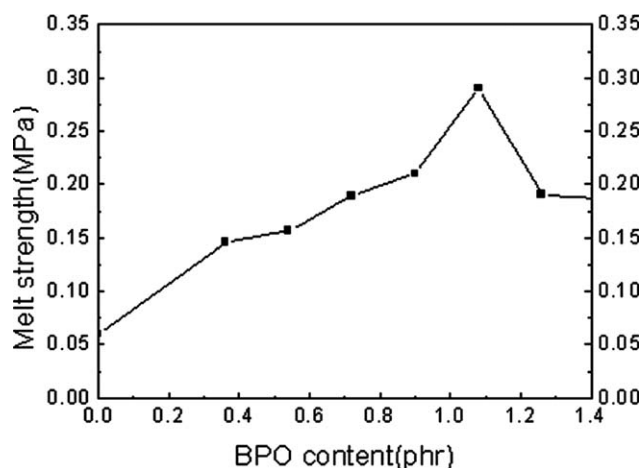


Figure 4 Effect of the BPO concentration on the melt strength of the silane crosslinked PP (2 phr VTMS, styrene = 2.3 phr).

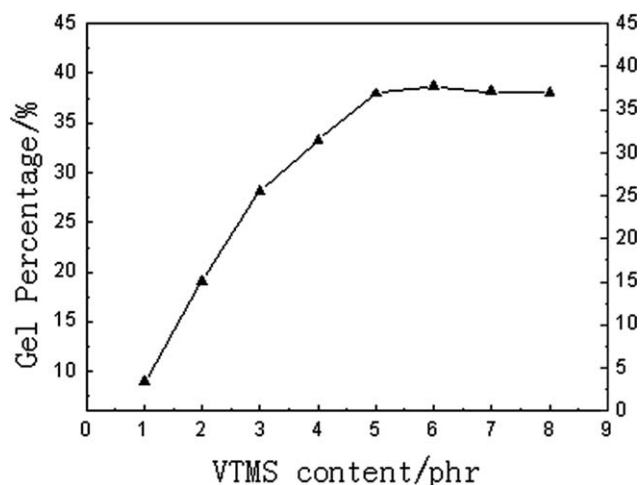


Figure 5 Influence of VTMS concentration on gel percentage of the silane crosslinked PP (BPO 0.72 phr, styrene = 2.3 phr).

fixed BPO content. An increase in the gel content is believed to be the more silane crosslinked onto PP. From the above experimental results it is concluded that the more silane is, the more silane crosslinked onto PP, thus the more gel produced. This result is in consistent with the literature.²⁸

The influence of silane content in the present work was confirmed by an investigation of the melt strength of the silane crosslinked PP. The results of melt strength of silane crosslinked PP at constant BPO content are displayed in Figure 6. From the figure it is revealed that melt strength increases as the amount of silane increases up to 4 phr, and then decreases with further increasing silane content. This increase in melt strength could be explained on the bases of, as the crosslinking degree grew, melt strength also increased. Yoshii and Makuuch⁷ in

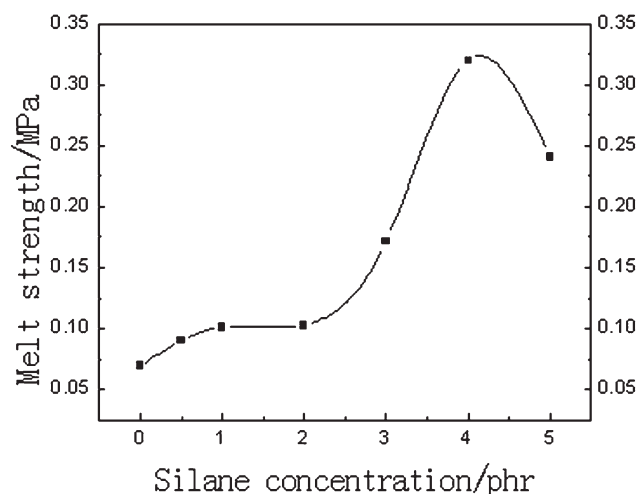


Figure 6 Effect of VTMS concentration on the melt strength of the silane crosslinked PP (BPO 0.72 phr, styrene = 2.3 phr).

TABLE II
Parameters of DSC Curves of Pure PP and the Silane Crosslinked PP

Sample	$T_{c,onset}$ (°C)	$T_{c,peak}$ (°C)	$T_{m,onset}$ (°C)	$T_{m,peak}$ (°C)
Pure PP	116.78	111.04	155.44	165.53
Silane crosslinked PP	130.85	152.56	164.97	

their patents study the effect of saline contact on melt strength and observed that the MFR is related to the melt strength of PP by inverse ratio rule in a certain range.

Thermal analysis of the silane crosslinked PP

Differential scanning calorimetry is a conventional method to study the crystallization process of polymers. DSC exotherms provides some useful information including the onset temperature, which is the temperature at the crossing point of the tangent of the baseline and the high-temperature side of the exotherm, the peak temperature of the exotherm, and crystallinity.²⁴ The results for pure PP and the silane crosslinked PP are listed in Table II, and the corresponding DSC curves are shown in Figure 7(a,b). It can be seen from Figure 7(b) the crystallization

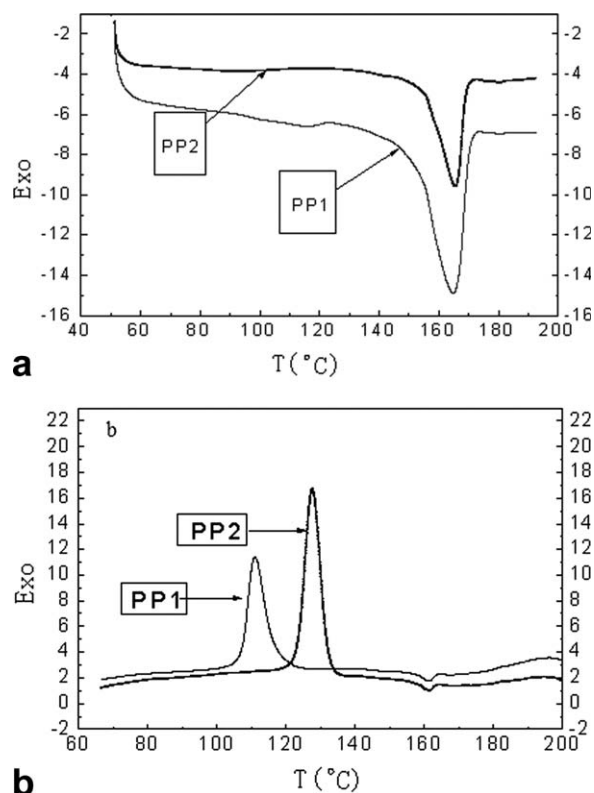


Figure 7 Curves of the melting and crystallization of pure PP and the silane crosslinked PP (PP1 is pure PP, PP2 is the silane crosslinked PP).

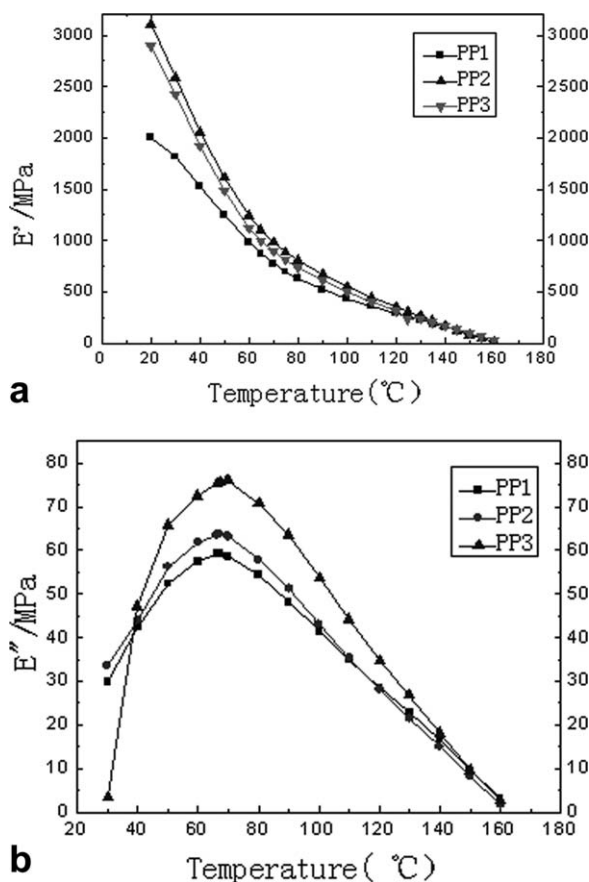


Figure 8 Dynamic mechanical properties of PP: (a) storage modulus–temperature curves; (b) loss modulus–temperature curves.

temperature (T_c) of the silane crosslinked PP shift to higher than that of pure PP, whereas the melt temperatures (T_m) were almost identical with Figure 7 (a). 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, PP and gas will expand instantaneously. 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 implied that the crosslinked 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 analysis of the storage modulus and loss modulus curves is very useful in ascertaining the performance of the sample under stress and temperature. Storage modulus is directly associated with elastic response. The plot of E' versus temperature is displayed in Figure 8(a). The E' curves for silane crosslinked PP decreased with increasing silane concentration. A gradual downward trend of storage modulus with increasing temperature is shown in Figure 8(a). But the fact is that HMSPP curve always

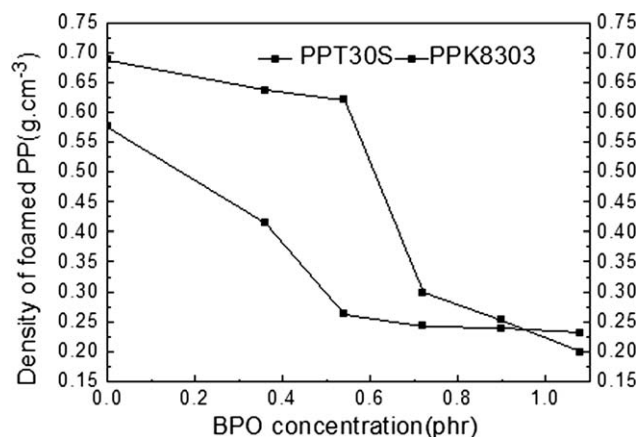


Figure 9 Effect of the initiator concentration on the density of foamed PP.

at the top shows the silane crosslinked PP has a higher mechanical strength at high temperature than that of pure PP.

The plot of E'' versus temperature is displayed in Figure 8(b). The E'' curves for silane crosslinked PP showed increased tendency with increasing silane concentration and then decreased. The increased in the damping behavior was due to the increased in the crystallinity of the system with increased in the silane content; additionally, melting temperature shifts to higher value up to maximum, then decreases with increasing crosslinking. This phenomenon can be explained by the fact that grafting and crosslinking degree increases. The melting temperatures of the samples are depicted in Table II. This clearly indicates that the T_m of silane crosslinked PP shifts to a higher temperature almost linearly with increase of grafting and crosslinking degree increases and then decreases.

Foam ability of the silane crosslinked PP

The effect of the initiator concentration on the density of foamed material with silane crosslinked PP is shown in Figure 9. At a given concentration of

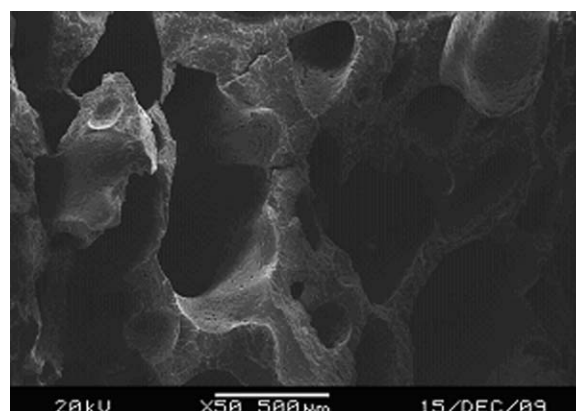


Figure 10 SEM images of the PP foam (3 phr AC).

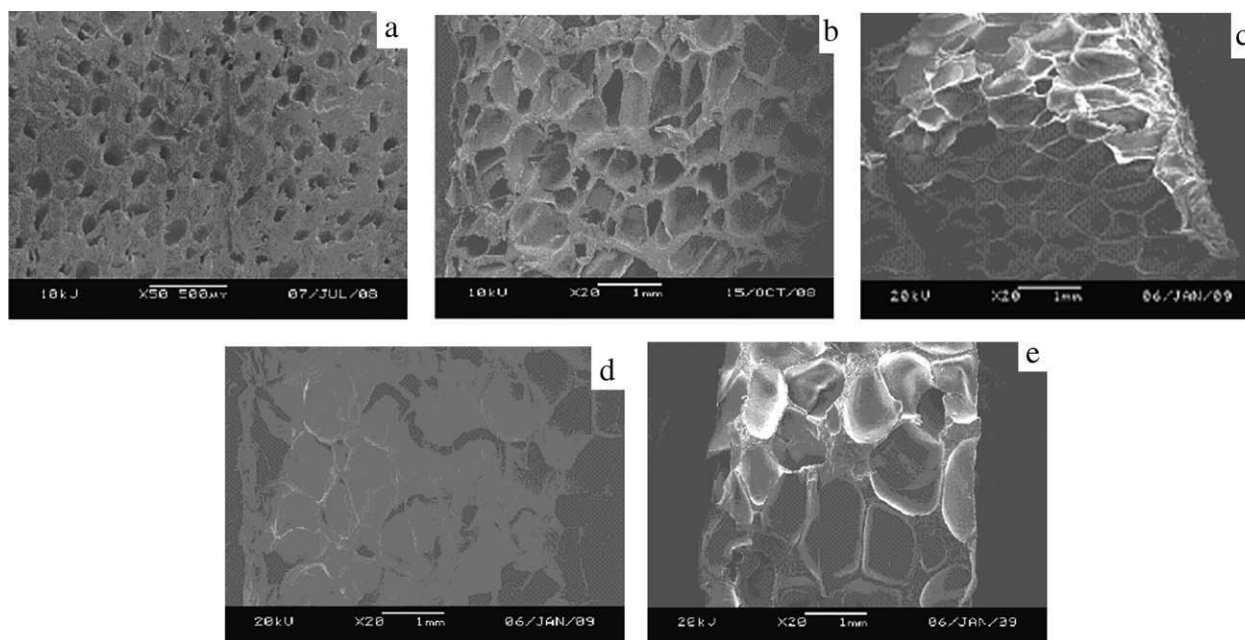


Figure 11 SEM images of the silane crosslinked PP foam: (a) 1 phr AC, (b) 2 phr AC, (c) 3 phr AC, (d) 4 phr AC, and (e) 5 phr AC.

VTMS, the density of PP foam decreased sharply at first, then decreased slowly with increase in the BPO concentration both PP T30S and PP K8303.

The SEM images of the PP foam and the silane crosslinked PP foam are shown in Figures 10 and 11(a–e). Clearly the foaming degree of the silane crosslinked PP increased compared with pure PP T30S. Because of the low melt strength, the cells in the pure PP inclined to coalesce, forming the foam with connected-cell structure. In Figure 11, the foam with fine cell structure was created by the cross-linked PP with high melt strength, which allowed the gas to be retained in well closed-cell structure foam in Figure 11(c,d).

CONCLUSIONS

Silane crosslinked PP was prepared using twin screw extruder. The effects of processing conditions, concentration of silane VTMS, and peroxide on the silane crosslinked reaction were evaluated. The mechanical and thermal properties of the saline cross-linked products were analyzed.

The results indicate that the BPO and silane VTMS concentration play an important role in the formulation and cooperate in the process of PP grafting and crosslinking and each are necessary. The quantity of the components significantly influence the MFR of the modified PP, especially, with the increment of the initiator, the MFR reduces sharply. The MFR of HMSPP highly affects the size, density, and morphology of the cells in the foam.

Compared with pure PP, the silane crosslinked products exhibit remarkably better mechanical and thermal properties. An improvement in the melt strength, modulus, and thermal transition were observed. The results showed that melt strength of the silane crosslinked PP was improved obviously than that of pure PP. Consequently, the temperature range of PP foaming was broadened after silane crosslinking.

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