

Characterization of High Melt Strength Polypropylene Synthesized via Silane Grafting Initiated by *In Situ* Heat Induction Reaction

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ABSTRACT: High melt strength polypropylene (HMSPP) was synthesized by *in situ* heat induction reaction, in which pure polypropylene (PP) powders without any additives were used as a basic resin and vinyl trimethoxysilane (VTMS) as a grafting and crosslinking agent. The grafting reaction of VTMS with PP was confirmed by FTIR. The structure and properties of HMSPP were characterized by means of various measurements. The content of grafted silane played a key role on the melt strength and melt flow

rate (MFR) of HMSPP. With increasing the content of grafted silane, the melt strength of HMSPP increased, and the MFR reduced. In addition, due to the existence of crosslinking structure, the thermal stability and tensile strength of HMSPP were improved compared with PP. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3727–3732, 2008

Key words: crosslinking; grafting; melt strength; polypropylene; silane

INTRODUCTION

Polypropylene (PP) is one of the leading and fast growing thermoplastic polymers worldwide due to its high tensile strength, stiffness and chemical resistance.¹ However, PP usually has relatively low melt strength which limits its use in applications, such as thermoforming, foaming, and blow molding.² To make PP have good mechanical properties and high melt strength, scientists have explored many methods to prepare high melt strength polypropylene (HMSPP), such as blending, radiation crosslinking and peroxide crosslinking.^{3–17} Unfortunately, these methods have some disadvantages. For example, blending damages the properties of PP, especially the high temperature properties. Radiation crosslinking is limited by the material's thickness, and the process needs an inert atmosphere, which results in high cost and complicated manufacturing technology. The peroxide crosslinking induces serious degradation of PP chains and even serious crosslinking. However, among the reported methods of preparing HMSPP, chemical modification of linear

PP chains is still the simplest and most appropriate for the applications relevant to this work.

Silane grafting and crosslinking of PP is a recently developed alternative approach to preparing HMSPP.^{18–21} When compared with radiation and peroxide crosslinked PP, the way of making crosslinkable PP through silane grafting followed by water crosslinking has various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials. The most commonly used silane is vinyl trimethoxysilane (VTMS). Nowadays, the vast majority of the investigations on silane grafting and water crosslinking techniques are concerned with polyethylene and ethylene copolymers.^{22–33} Not many studies concerning the grafting and crosslinking of PP have been reported.^{34–39} Recently, Guojun et al. studied the silane grafting and crosslinking of PP using benzoyl peroxide (BPO) as an initiator and styrene as a coagent.⁴⁰ As we know, when mixing PP with peroxide at high temperature, such as BPO, macromolecular chains of PP will undergo degradation leading to chain cleavage by β -scission. Furthermore, because of the high instability of tertiary macroradicals, the degradation process is extremely fast at high temperature. Therefore, the mechanical properties of PP decrease greatly.

It is important to understand the relationship between macromolecular structure and properties of HMSPP, such as melt strength, expansion behavior

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of melt and thermal stability. However, there are few reports about structure and properties of HMSPP prepared by silane grafting. In this work, the structure and properties of HMSPP which had been synthesized via silane grafting initiated by *in situ* heat induction reaction were characterized. Nascent PP powder *in situ* produced in the reactor without any additives was used as basic resin. During extrusion process in a twin-screw extruder at high temperature, PP macroradicals generated by heat induction abstracted the labile proton on the tertiary carbon sites. At the same time, the added silane as grafting agent reacted with tertiary macroradicals, and silane-grafted PP was formed. After the grafted PP was put into hot water such as 90°C for certain time, HMSPP was obtained. Comparing with the previous method containing peroxide as initiator for silane grafting, this method can avoid severe degradation and crosslinking of PP.

EXPERIMENTAL

Materials

PP used was fine powder with a MFR of 3.65 g/10 min (T30S from Daqing Petrochemical Company). Vinyltrimethoxysilane (VTMS) and dibutyltindilaurate catalyst were used as received by Harbin Research Institute of Chemical Industry and Shanghai Sanpu Chemical Industry, respectively.

Preparation of HMSPP

The PP powder was tumble-premixed with VTMS and dibutyltindilaurate. The silane grafting process was carried out in TSSL-25 corotating twin-screw extruder with a length/diameter ratio of 36/1 and a diameter of 25 mm. The screw configuration was designed to provide good dispersive and distributive mixing. The barrel temperatures from the feed zone to the die zone were set as follows: 190, 210, 225, 230, 230, 230, 230, 215, and 195°C. The screw rate and feed rate were kept constant at 65 and 21 rpm, respectively. After the reaction, the grafted products were shaped into 1-mm thick compression-molded sheets. After cooling, sheets were finally immersed into water at 90°C for 16 h. And then, a sheet was cut into tensile bars. The specimens were stored under dried conditions before testing.

Characterization

FTIR spectra were recorded with a FTIR spectrometer (GX-2000) in the range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1} . The reaction products from extruders were purified by first dissolving in xylene and then were precipitated in acetone to remove

unreacted VTMS. Films with 30- μm thick for FTIR spectroscopy measurements were prepared through melt compression in a hot press at 210°C.

The melting and crystallization behavior of the samples were studied with a Perkin–Elmer DSC1 differential scanning calorimeter under nitrogen atmosphere. The samples were first heated from 50 to 200°C at a scanning rate of 10°C/min and then maintained at 200°C for 5 min before cooling to 50°C at the same rate. After that, the samples were reheated from 50 to 200°C at a scanning rate of 10°C/min. The crystallinity of samples was calculated from the heat of fusion (a heat of fusion for 100% crystalline PP (H_0) was 207 J/g).⁴¹

Thermogravimetric analysis (TGA) was performed using Perkin–Elmer pyris 1 under nitrogen atmosphere at a heating rate of 10°C/min.

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature by a D/max-2500/pc X-ray diffractometer (Rigaku, Japan) using $\text{CuK}\alpha$ radiation operated at 35 kV and 50 mA. The data were collected from 6° to 50° at a scanning rate of 3° min^{-1} . Prior to testing, all specimens were treated uniformly.

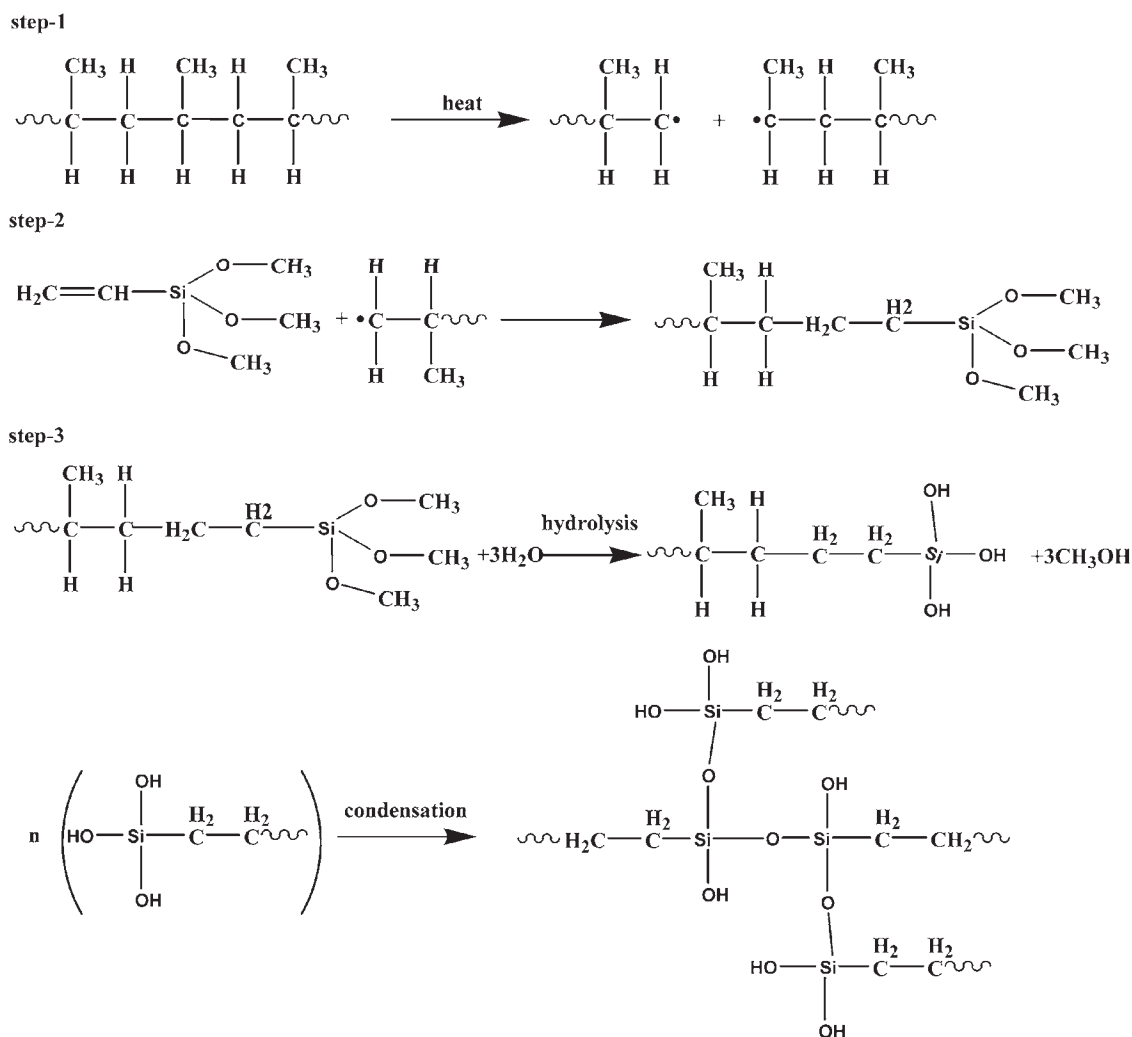
Melt flow rate (MFR) was determined using CEAST 6542 Modular Flow Index. The condition of experiment is at 230°C under a load of 2.16 kg.

The melt strength was measured by using Rheotens method with die $L/D = 20/2$ and melt temperature of 230°C. Here, a melt strand was extruded through a capillary die and pulled down with increasing velocity (at constant acceleration 27 mm/s^2) by using a pair of wheels, and the force was measured till the rupture of the melt strand occurred. The average force was defined as melt strength, and the drawdown velocity at break was a measure of melt extensibility.

The tensile strength was measured with a WD-20D Electronic Universal Testing Machine at the crosshead speed of 50 mm/min.

Measurement of gel content for the samples (thickness is 0.5 mm) was made according to the GB/T 9352-88. The sample was put into $(85 \pm 2)^\circ\text{C}$ water bath for 24 h, and then was took out and cut into the size pellets with $0.5 \times 0.5 \text{ mm}^2$. After that, 0.2–0.3 g pellets were wrapped with the quantitative filter papers. The sample was packaged in a copper net of 120 mesh and weighed by analytical balance.

The sample packaged in a copper net was put into the flask with boiling xylene for 16 h. After that, the sample was put in ventilates and volatiled to tasteless. The sample was dried for 2 h in the drying oven at 105–110°C, and then was taken out and put into the water extractor to cool 30 min and weighed by analytical balance. The gel content of crosslinked PP was calculated as the percentage of the weight remaining with respect to the initial weight of sample.



Scheme 1 Schematic diagram of reaction mechanism for preparation of HMSPP.

RESULTS AND DISCUSSION

Structural characterization of the HMSPP

The preparation process of HMSPP via silane grafting initiated by *in situ* heat induction reaction involves three main stages. In the first stage, PP chains break to form macromolecular radicals under shear field at high temperature. In the second stage, a silane-grafted PP is formed by the free-radical grafting reaction of vinyl alkoxy silanes onto the PP chains. In the third stage, the silane-grafted PP is crosslinked in hot water. The crosslinking reaction involves the hydrolysis of the alkoxy groups with water, followed by the condensation of the hydroxyl groups to form stable siloxane linkages. The grafting step was performed in a molten state of PP, whereas the crosslinking step was carried out after the PP was shaped. The whole reaction mechanism for process is shown in Scheme 1.

The composition of the products obtained in the second step was measured by means of FTIR after

the products were purified using a precipitation method. FTIR spectra of the pure PP and the purified HMSPP are showed in Figure 1. In the case of the HMSPP, a new absorption band at 799 cm^{-1} is observed, which can be assigned to the absorption

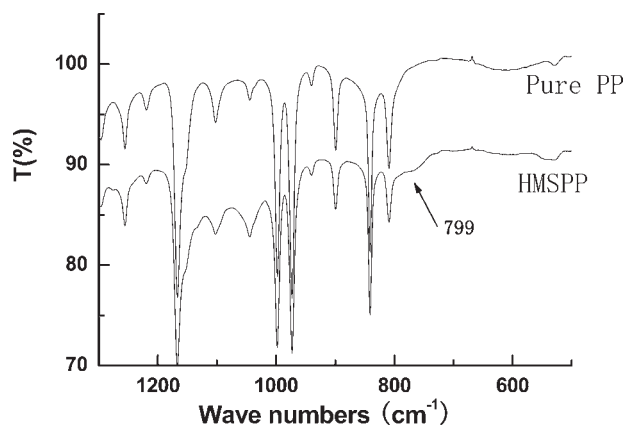


Figure 1 FTIR spectra of pure PP and HMSPP.

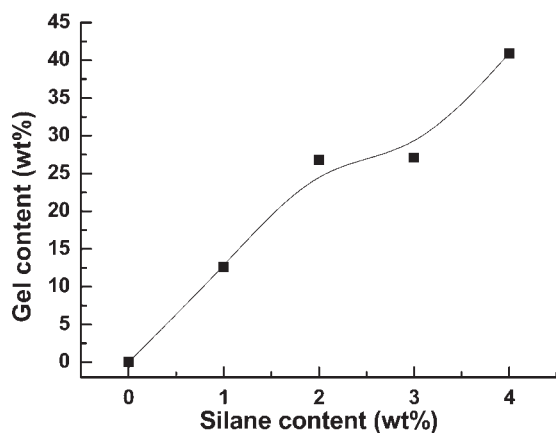


Figure 2 Effect of silane content on gel content of HMSPP.

of Si—C.⁴² This confirmed that the silane was grafted onto PP.

The gel content is generally used to evaluate the crosslinking degree of polymers. Figure 2 presents the effect of VTMS concentration on the gel content of the HMSPP. The gel content of the HMSPP increases gradually with the VTMS concentration. This means that the crosslinking structure was formed in the HMSPP. When the VTMS concentration was 4 wt %, the gel content of the HMSPP was 42 wt %.

PP is a crystalline polymer in three polymorphic forms, i.e., α (monoclinic), β (pseudo-hexagonal), and γ (triclinic), depending on the composition of PP and the crystallization conditions. Figure 3 shows the WAXD profiles of PP and HMSPP. The diffraction peaks of pure PP are located at 14.0° , 16.8° , 18.5° , 21.0° , and 21.8° in the range of 10 – 25° , which correspond to the α (110), α (040), α (130), α (111), and α (131) planes, respectively.^{43,44} It is clearly shown that there is a strong diffraction peak at $2\theta = 16.8^\circ$ for HMSPP, which is much higher than that of pure PP. Furthermore, the intensity of diffraction peak at $2\theta = 14.0^\circ$ for HMSPP is smaller than that of

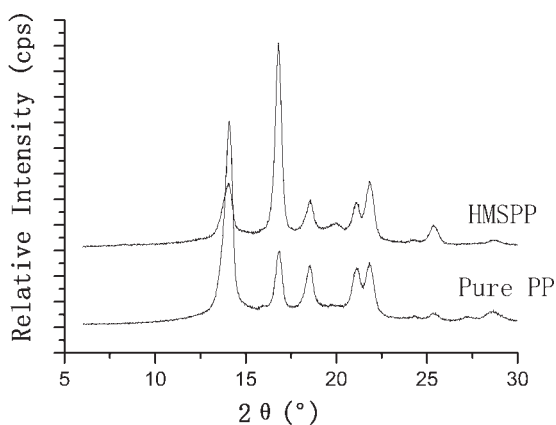


Figure 3 WAXD profiles of pure PP and HMSPP.

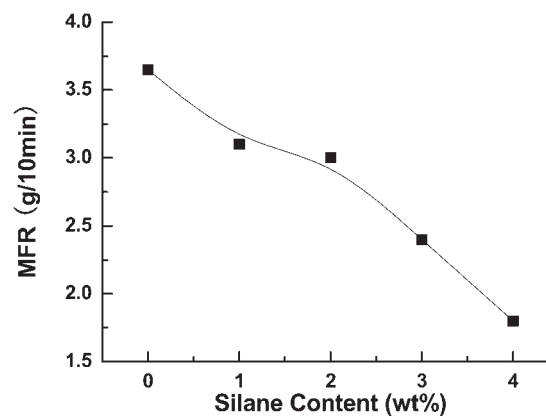


Figure 4 Effect of silane content on MFR of HMSPP.

pure PP at same peak. In addition, a small diffraction peak at $2\theta = 20.1^\circ$, which is from γ (117) reflection in the γ form,⁴⁵ becomes obvious in the HMSPP. It indicates that the crosslinking structure in the HMSPP leads to slight change of crystallization growth and crystalline form.

Melt properties of the HMSPP

Effect of silane concentration on MFR of HMSPP is showed in Figure 4. The MFR of HMSPP decreases with increasing concentration of the VTMS. The reduction of MFR values implies the decrease of the chain mobility because of the fact that some crosslinking occurs, which makes the molecular chains extended each other. The melt strength of HMSPP was measured by Rheometer-7D instruments. Here, the diameter of capillary die is 2 mm. Figure 5 presents the effect of silane concentration on expansion ratio and diameter of the HMSPP. The diameter and expansion ratio of the HMSPP increases gradually with the concentration of VTMS. The concentration of VTSM strongly influences melt strength of HMSPP (Fig. 6). It can be seen that the average melt strength of the HMSPP increases slightly with the

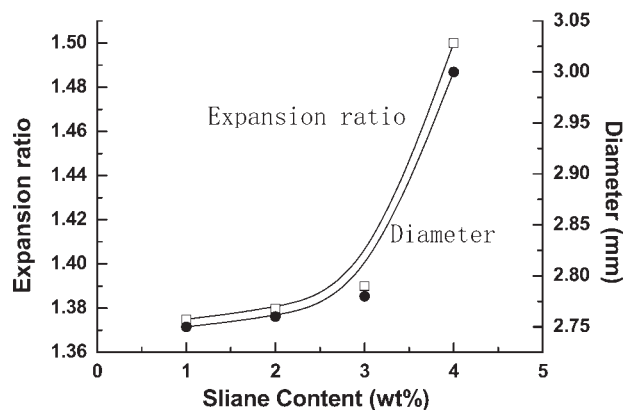


Figure 5 Effect of silane content on expansion and diameter.

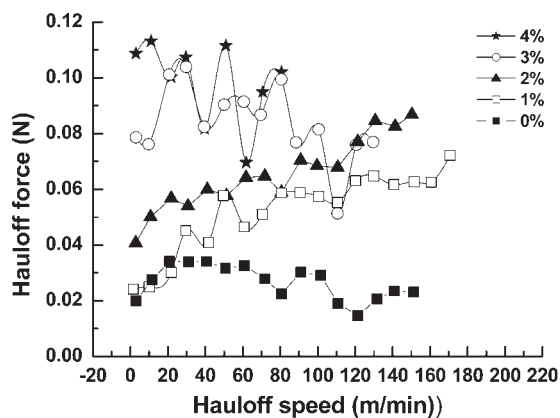


Figure 6 Effect of silane content on melt strength.

silane concentration. The melt strength of the HMSPP is 11 cN, when the silane concentration is 4 wt %. In contrast, the melt strength of pure PP is 2.6 cN. It further indicates that the structure of pure PP changes from linear structure to crosslinking structure after crosslinking reaction, which results in the increase of the melt strength of HMSPP.

Melting and crystallization behavior of HMSPP

Figures 7 and 8 present the heating and cooling thermograms of pure PP and HMSPP. From Figure 7, it can be seen that T_m (166°C) of the HMSPP is higher than that (164°C) of pure PP powder. In comparison with pure PP, the HMSPP shows evidently the higher onset temperature of crystallization and higher peak value of crystallization (T_c) (Fig. 8). This means that the crystallization of the HMSPP starts earlier than that of pure PP. The branching or crosslinking unit considerably increases the nucleation density of PP, which accelerates the crystallization. An important application of HMSPP is to make foam material. In the course of foaming, when the mixture of PP and gas is extruded out of the die, the

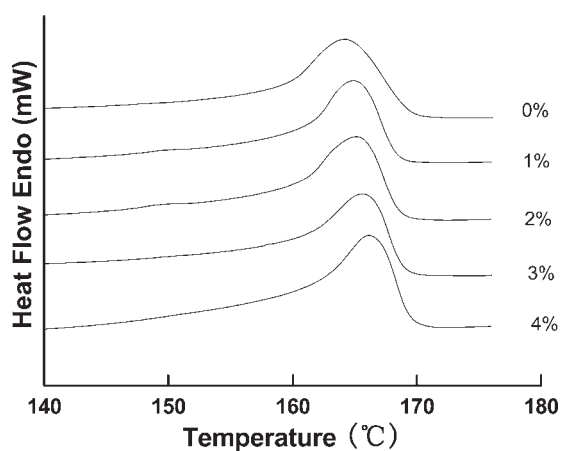


Figure 7 The melting curves of HMSPP.

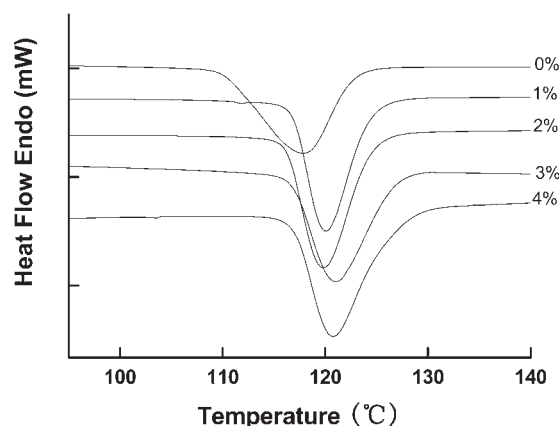


Figure 8 The crystallization curves of HMSPP.

pressure decreases sharply. Consequently PP and gas will expand instantaneously, especially the gas. At this time, if the crystallization temperature of PP is higher, the crystallization of PP will grow rapidly, which benefits the stability of foaming. The results also imply that the HMSPP could induce the rapid case-hardening of the foams. Therefore, the high crystalline temperature of the resin is propitious to the foam in the twin-screw extruder. In addition, the percentage of crystallinity of HMSPP is higher than that of pure PP.

Thermal stability of the HMSPP

TGA curves of the HMSPP are illustrated in Figure 9. The results show that the HMSPP has the higher decomposition temperature comparing with that of the pure PP. For example, when the silane concentration is 3%, the decomposition temperature (357.5°C) of 5% weight loss for HMSPP is much higher than that of pure PP (279.5°C). This indicates that the HMSPP became more heat resistant after crosslinking reaction and raised its upper temperature limit of application. The improved thermal

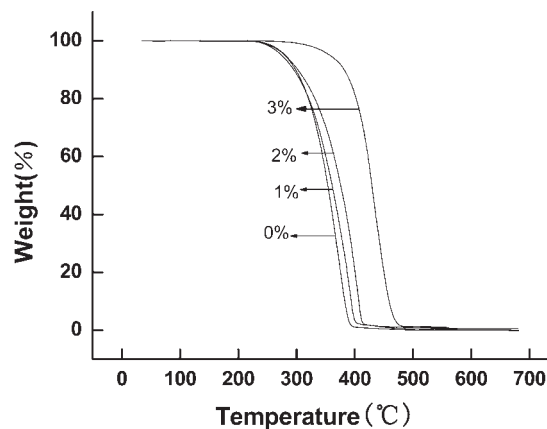


Figure 9 TGA curves of HMSPP.

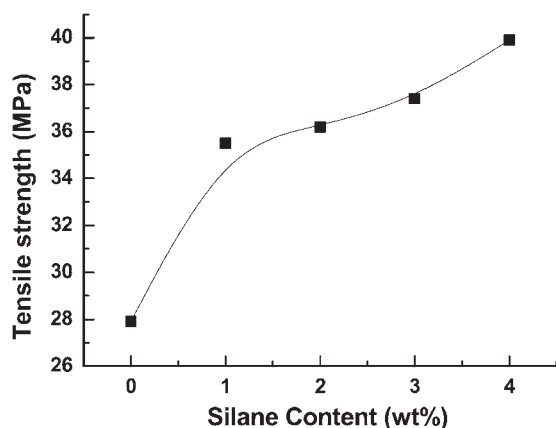


Figure 10 Effect of silane content on mechanical properties of HMSPP.

stability also ensures the applications of the grafted PP in many applications.

Mechanical properties of HMSPP

Effect of silane concentration on mechanical properties is shown in Figure 10. From Figure 10, we can see that, with the increase of silane concentration, the tensile strength of the HMSPP increases. It can, therefore, be concluded that the changes in the mechanical properties are due to the crosslinking reactions. After the crosslinking, many linear molecules of PP have been changed into three-dimensional network ones, leading to the increase in the tensile strength.

CONCLUSIONS

The HMSPP was synthesized via silane grafting initiated by *in situ* heat induction reaction, in which pure PP powders without any additives and VTMS were used as a basic resin and a grafting and crosslinking agent, respectively. The results indicated that the properties of HMSPP were greatly affected by the content of grafted silane. The melt strength of HMSPP was greatly improved due to crosslinking of the grafted silane onto PP. The HMSPP showed a better thermal stability and higher tensile strength than pure PP.

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