

# Thermal and Mechanical Analysis of Covalently Linked Silica/Isotactic Polypropylene Nanocomposite

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## INTRODUCTION

Isotactic polypropylene (i-PP) is of great commercial importance and their thermal and mechanical properties can be enhanced by adding fillers, fibers and particles<sup>1</sup>. However, these properties are dependent on the compatibility of hydrophobic polypropylene and hydrophilic fillers. The compatibility can be increased by chemical modification of the polymer and the filler<sup>2</sup>. The polymer can be modified using alkoxy silane which can then serve as a crosslinker<sup>3,4</sup>. Recently, nanoparticles are being increasingly used as fillers due to their high surface area to volume ratio.

Crosslinking of PP using siloxane moieties have been reported. In this work, we want to report a new method of making nanocomposite where silica nanoparticles are covalently linked to i-PP using silane moieties. Isotactic polypropylene (i-PP) was modified by grafting vinyltrimethoxysilane (VTMS) using either benzoyl peroxide (BP) or dicumyl peroxide (DCP) as initiator. The silane end reacts with hydroxyl group on the surface of colloidal silica particles to form the covalent bond. The thermal and mechanical properties of thus formed nanocomposites (Si/i-PP/DCP and Si/i-PP/BP) were investigated.

## EXPERIMENTAL

**Materials.** All the chemicals were purchased from Aldrich Chemical Co. and used without further purification. The silica nanoparticles were Ludox-SM, 30 wt.% SiO<sub>2</sub>, particle size 7 nm, pH 10 and the M<sub>w</sub> of i-PP was 250,000.

**Instrumentation.** Silane grafted i-PP was analysed by IR. The TEM images were taken with JOEL 1200EXII operating at 80 kV. The samples were prepared by microtoming the nanocomposite embedded within the resin and the ultrathin sections were then mounted on to carbon coated copper grids (200 mesh). Differential Scanning Colorimetry (DSC) measurements were taken in TA instruments DSC Q100 at three different heating and cooling rates (5, 10, 20 °C/min). Thermal Gravimetric Analysis (TGA) was done using TA instruments SDT Q600 and scanning rate of 10 °C/min was implied for all measurements.

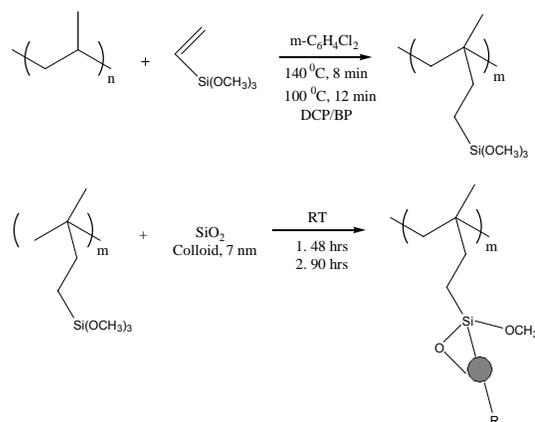
**Grafting Silane Moieties to i-PP.** i-PP was dissolved in degassed 1,3-dichlorobenzene at 140 °C under nitrogen atmosphere. Vinyltrimethoxysilane (VTMS) (4%) and initiator (0.4%) was added. The reaction mixture was heated at 140 °C for 8 min and then at 100 °C for 12 min, followed by immediate precipitation in excess acetone. The precipitate was separated, washed with acetone and dried under vacuum to obtain white fluffy solid in quantitative yield.

**Synthesis of nanocomposite.** Fine powder of silane grafted i-PP was shaken vigorously with Ludox colloidal silica for 48 hrs which was then washed with water and then with acetone and dried under vacuum.

## RESULTS AND DISCUSSION

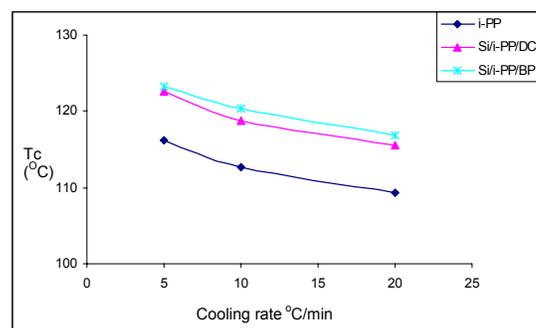
**Nanocomposite Synthesis and Characterization.** VTMS was grafted onto i-PP using either DCP or BP. Although DCP is a common initiator reported for grafting processes, polymer chain scission is known to occur whereas degradation of the chain is not observed while using BP<sup>4</sup>. i-PP with silane moieties were analysed by FTIR and the appearance of absorbance peaks at 808, 1102 and 1219 cm<sup>-1</sup> corresponding to Si-OCH<sub>3</sub> group confirmed the grafting of VTMS<sup>3</sup>.

The nanocomposite was prepared by forming siloxane linkage between the grafted VTMS and colloidal silica particles.



**Figure 1.** Synthetic steps for Si/i-PP/DCP and Si/i-PP/BP nanocomposites.

**Thermal Analysis of the Nanocomposite.** TGA analysis of the nanocomposites showed 5% loading of the inorganic filler for both Si/i-PP/DCP and Si/i-PP/BP. The melting temperature obtained from the DSC measurements was same (160 °C) for both neat i-PP and the nanocomposites. The cooling cycles of DSC showed an increase in the crystallization temperature (T<sub>c</sub>) at the studied cooling rates of 5, 10, 20 °C/min (Fig 2). The constant value of difference in T<sub>c</sub> between neat i-PP and nanocomposites (ΔT<sub>c</sub>) (Table 1) to the cooling rates indicated that the nanoparticles act as heterogeneous nucleating agents<sup>5</sup>.



**Figure 2.** DSC data showing the increase in T<sub>c</sub> for the nanocomposites at 5, 10 and 20 °C/min cooling rates.

**Table 1. T<sub>c</sub> and ΔT<sub>c</sub> Values for Neat i-PP and Nanocomposites at Different Cooling Rates**

Cooling rate (°C/min)	T <sub>c</sub> (°C)			ΔT <sub>c</sub> (°C) for Si/i-PP/DCP	ΔT <sub>c</sub> (°C) for Si/i-PP/BP
	Neat i-PP	Si/i-PP/DCP	Si/i-PP/BP		
5	116.2	122.6	123.3	6.4	7.1
10	112.6	118.8	120.4	6.2	7.8
20	109.3	115.5	116.8	6.2	7.5

**Mechanical Analysis of the Nanocomposite.** Analysis is going on.

## REFERENCES

- Manias, E.; Touny, A.; Wu, L.; Strawhecker, k.; Lu, B.; Chung, T. C. *Chem. Mater.* **2001**, *13*, 3516-3523.
- Leuteritz, A.; Pospiech, D.; Kretzschmar, B.; Willeke, M.; Jehnichen, D.; Jentzsch, U.; Grundke, K.; Janke, A. *Adv. Eng. Mater.* **2003**, *5*, 678-681.
- Sirisinha, K.; Kawko, K. *Macromol. Mater. Eng.* **2005**, *290*, 128-135.
- Haug, H.; Lu, H. H.; Liu, N. C. *J. Appl. Polym. Sci.* **2000**, *78*, 1233-1238.
- Wang, Z. M.; Chung, T. C.; Gilman, G. W.; Manias, E. *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 3173-3187.