

Modification of Polypropylene/Glass Fiber Composites with Nanosilica

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Summary: Poly(propylene) (PP) reinforced with short glass fiber was modified with precipitated nanosilica (pnS) by melt mixing. The weight of the glass fiber was varied by keeping the pnS at optimum level. The properties of the composites were studied using universal testing machine, dynamic mechanic analyser (DMA), differential Scanning calorimetry (DSC) and thermo gravimetric analyser (TGA). The amount of the glass fiber required for a particular modulus could be reduced by the addition of nanosilica.

Keywords: composites; DSC; modulus; poly(propylene); TGA

Introduction

Polypropylene (PP) is one of the fastest growing polymers today. The glass fiber reinforced PP is used in a variety of applications such as building construction, marine, automotive industries etc. The main advantages of glass fiber–reinforced PP over the other engineering plastics are low cost and low specific gravity.^[1] PP is also filled with particulate fillers for improving the hardness and modulus.^[2] High particle loadings result in products with much higher weight than that of the pure polymers. Hence a composite with improved properties at low particle concentration is always the optimum choice. Nano-structured materials often exhibit superior physical and mechanical properties compared to conventional materials. But the dispersion of the nanoparticles is the main difficulty in the development of nanocomposites.^[3] This is due to the hydrophobic nature of polypropylene, which limits its adhesion

to the ‘hydrophilic’ filler. This problem has been overcome by tailoring the affinity between the inorganic material and the organic polymer by in-situ polymerization, employment of silane coupling agents and other strategies.^[4–6] Such modifications have shown improvement in mechanical properties.

The effect of reinforcing polypropylene jointly by glass fiber and a nanofiller (nanosilica) is proposed to be investigated in this study.

Experimental Part

Materials

The polypropylene homo polymer (PP) used was REPOL H200MA provided by Reliance Industries Limited with a melt flow index of 20g/10 min (230 °C, using a dead weight of 2.16 kg). E-glass fiber (13 μm) was obtained from Sharon industries Ltd. India. Nanosilca was prepared from sodium silicate (commercial grade) solution with the precipitation method.^[7,8] The particle size was in the range of 30–40 nm.

Composite Preparation

Polypropylene granules, glass fiber and precipitated nanosilica particles were dried by keeping them in an oven at 100 °C for

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four hours. Glass fiber reinforced polypropylene composites were prepared by adding the glass fiber to the polypropylene melt in a Thermo Haake Rheocord 600 mixing chamber with a volumetric capacity of 69 cm³ and fitted with roller type rotors. Polypropylene was charged directly to the chamber and after it had melted and homogenized, glass fiber was added. Silica nanoparticles-glass fiber hybrid polypropylene composites were prepared by adding glass fiber into the nanosilica/polypropylene melt. The temperature was kept at 170 °C to ensure proper melting of the polypropylene. In the first series of experiments 10, 20, 30, 40 and 50 weight percentage of glass fiber reinforced polypropylene composites were prepared. In the second series 10, 20, 30 and 40 weight percentage of glass fiber were added together with 1 weight percentage of nanosilica powder to polypropylene melt to get nanosilica-glass fibre hybrid polypropylene composite. A mixing time of 9 minutes was used at a rotor speed of 50 rpm. In all cases the torque stabilized to a constant torque in this time.

The hot mix from the mixing chamber was immediately passed through a two-roll mill and the test specimens were prepared using a semi-automatic plunger type injection-moulding machine, with a barrel temperature of 190 °C.

Mechanical Testing

The tensile properties and flexural properties of the composites were studied using a Shimadzu universal testing machine (model-AG1) with a load cell of 50kN capacity. The tensile properties were determined at a crosshead speed of 50mm/min according to ASTM-D-638 standard. The flexural properties were determined at a crosshead speed of 5mm/min according to ASTM-D-790 standard. Six samples were tested for each case.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) experiments were performed in dual cantilever mode with a TA instruments Q800 DMA machine at a heating rate of 3 °C/min

from 35 °C to 160 °C at a frequency of 1 Hz. The sample dimension was 50 × 12 × 3 mm³.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC Q-100, TA Instruments) was employed to study the effect of precipitated nanosilica and glass fibre on the crystallization characteristics of nanocomposites. Indium was used for temperature calibration ($T_m = 156.6$ °C, $\Delta\hat{H}_m = 28.4$ J/g). All the samples were dried prior to the measurements and analyses were done in nitrogen atmosphere using standard aluminum pans. Calorimetric measurements were done while the samples (4–6 mg) were exposed to the following temperature scans: heating at a rate of 10 °C/min to 200 °C, holding for 5 min to erase thermal history effects, and then cooling to 50 °C at a rate of 10 °C/min during which the peak of crystallization exotherm was taken as the crystallization temperature, T_c . The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) were determined from the areas of the melting and crystallization peaks during heating and cooling respectively.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a Q50TGA, manufactured by TA instruments at a heating rate of 10 °C/min from 35 °C to 800 °C.

Results and Discussion

Mechanical Properties

Tensile tests were performed on dumbbell shaped samples prepared using semiautomatic plunger type laboratory injection moulding machine. The effect of glass fiber and glass fiber-nanosilica hybrid on the mechanical properties of polypropylene is given in Figures 1 and 2.

From the figures it may be observed that the mechanical properties of glass fiber/PP composite increase up to 40 wt.% fiber loading and then attain plateau height or slightly decrease. The glass fiber-pnS/PP

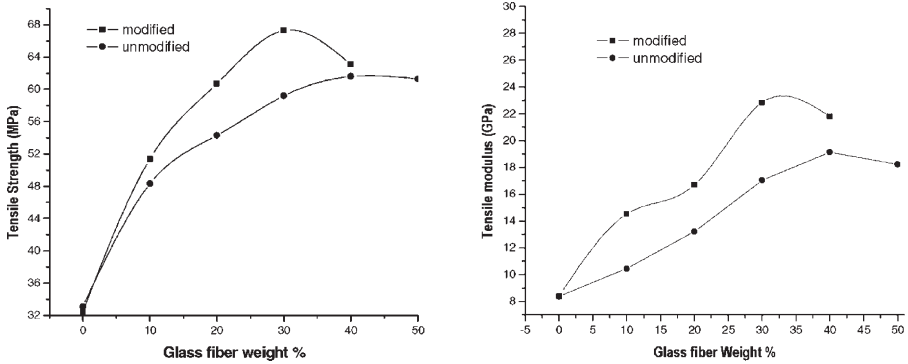


Figure 1. Variation of tensile strength and tensile modulus of PP/glass fiber composites and PP/glass fiber composites modified with pnS.

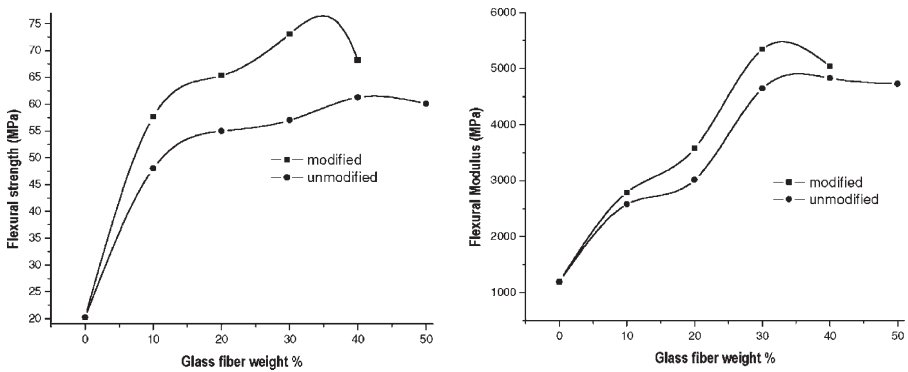


Figure 2. Variation of flexural strength and flexural modulus of PP/glass fiber composites and PP/glass fiber composites modified with pnS.

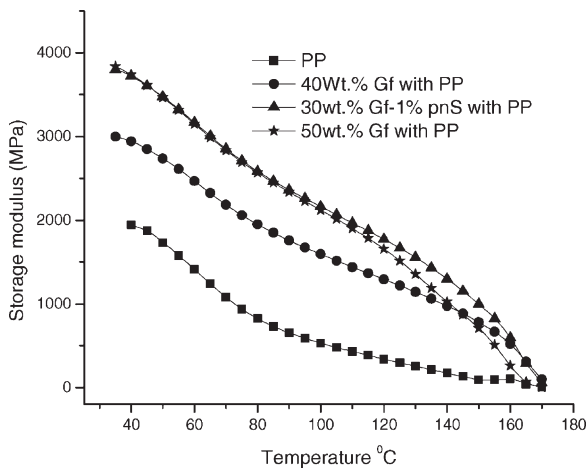


Figure 3. Variation of storage modulus of the PP composite.

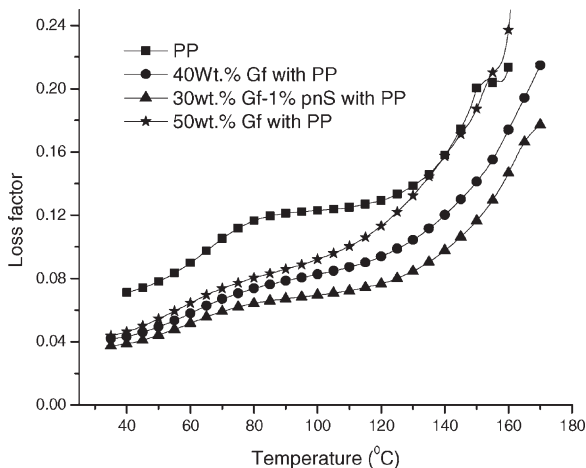


Figure 4.

Variation of loss factor ($\tan\delta$) of the PP composite.

hybrid composite shows superior property compared to glass fiber/PP reinforced composite. Tensile strength, tensile modulus, flexural strength and flexural modulus of glass fiber-pnS/PP hybrid composite are also found to increase up to 30 wt.% loading of glass fiber and then decrease. These results demonstrate that a small amount of nanosilica can substantially enhance the mechanical strength of the PP composites and that glass fiber and nanosilica show synergistic reinforcement.

Dynamic Mechanical Analysis

The results of dynamic mechanical analysis of the modified and unmodified PP/glass

fiber composites are shown in Figure 3. The storage modulus of PP is found to improve steadily with addition of short glass fiber. The modulus shown by the modified PP/glass fiber composite containing 30 wt.% glass fiber is almost at par with the unmodified composite containing 50 wt.% of glass fiber. This further show that the amount of glass fiber required for a particular reinforcement can be substantially reduced upon modification with nanosilica. The high temperature stability of the modified composite is found to be superior to the 50 wt.% glass fiber/PP composite. Another attractive feature of nanosilica modification is that the value of loss factor is at a low level

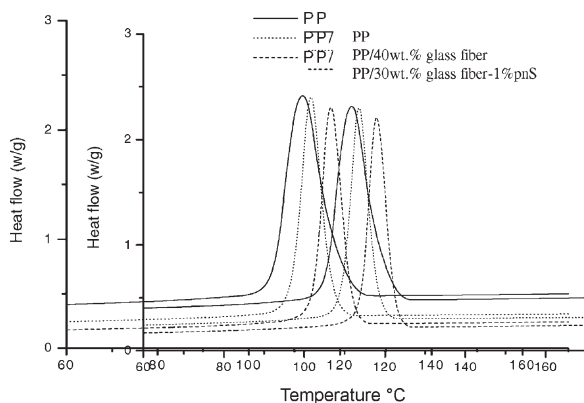


Figure 5.

DSC cooling curves of PP, glass fiber/PP and glass fiber-pnS/PP composite.

Table 1.

DSC-determined thermal characteristics of PP composites.

sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PP	110.7	102.2	165.9	86.21
PP/glass fiber	113.6	69.5	162.24	61.23
glass fiber-pnS/PP	116.5	69.1	166	59.75

showing that the elasticity of PP is improved by the addition of nanosilica.

Crystallization Characteristics

The effect of glass fiber and glass fiber-pnS on the crystallization of PP was analyzed with non-isothermal DSC experiments.

Figure 5 shows the DSC cooling scans of glass fiber-pnS/PP composite, glass fiber/PP composite and PP respectively. The peak crystallization temperatures (T_c) during the cooling scans, peak melting temperatures (T_m) during heating scans, as well as the associated enthalpies are summarized in Table 1. During cooling from the melt, the glass fiber-pnS/PP samples show crystallization exotherms at higher T_c than the pure polymer. The crystallization temperature of PP increased by 2.9 °C with glass fiber and 5.8 °C with glass fiber-pnS hybrid.

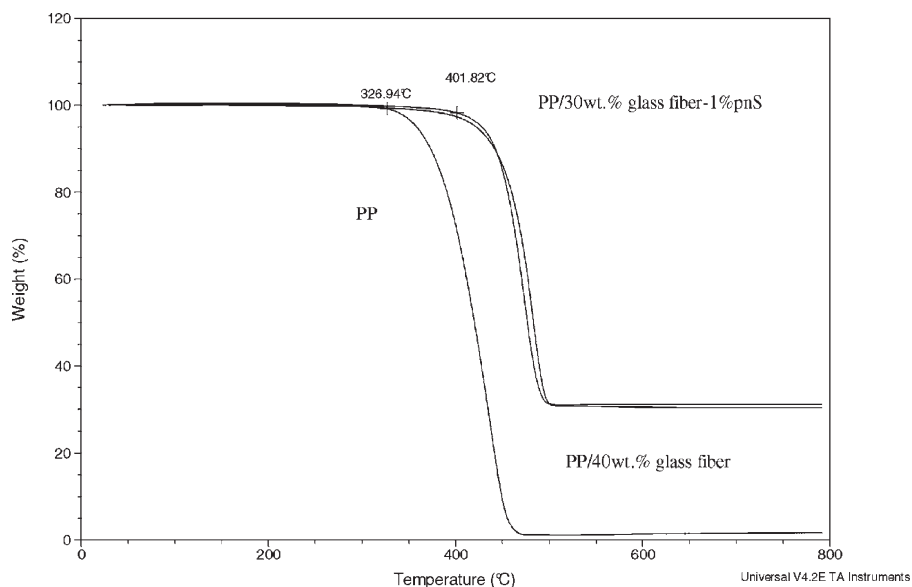
This shows that glass fiber-pnS hybrid can act as nucleating agent and induce crystallization at higher temperature than virgin PP.

Thermogravimetric analysis

The thermogravimetric analysis of the unmodified and modified PP composites is shown in Figure 6. From the figure we can observe that the degradation temperature of PP increases by the incorporation of glass fiber or glass fiber/pnS addition as expected.

Conclusions

The mechanical properties of glass fiber/PP composite can be improved by the incorporation of nanosilica. The maximum reinforcement for glass fiber-pnS/PP composite

**Figure 6.**

TGA curves of PP, Glass fiber/PP and glass fiber-pnS/PP.

is found to be at a fiber loading of 30 wt.%. The storage modulus of 30 wt.% glass fiber-1% pnS/PP composite is found to be same as that of 50 wt.% glass fiber/PP composite. The crystallization temperature of PP slightly enhances with the presence of glass fiber and nanosilica. Thermogravimetric studies show that the thermal stability of PP is also improved by the addition of glass fiber and nanosilica.

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