

# **DEVELOPMENT OF HIGH PERFORMANCE POLYAMIDE BASED NANOCOMPOSITES FOR ENGINEERING APPLICATIONS**

Final Report of the Minor Research Project

(MRP(S)-1410/11-12/KLMG003/UGC-SWOO dated 17-01-2013)

Submitted to the

**UNIVERSITY GRANTS COMMISSION**

By

**Dr. Seno Jose**

Department of Chemistry

Government College Kottayam

Nattakom, Kottayam, Kerala

## 1. Introduction

*Nanocomposites* are materials that are reinforced with nano materials. In general there are three types of nanocomposites, viz. polymer matrix composites or polymer nanocomposites (PNCs), metal matrix composites and ceramic matrix composites. Polymer nanocomposites may be defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range. Over the past decade, PNCs have attracted great interests both in academia and industry, owing to their fascinating mechanical properties with only a small amount of the nanoadditives. This is fundamentally because of the large surface area to volume ratio of nanoadditives when compared to the micro- and macro-additives. Other superior properties of PNCs include barrier resistance, flame retardancy, scratch/wear resistance, as well as optical, magnetic and electrical properties. PNCs are prepared by incorporating nanoparticles in a single polymer or polymer blends.

Blending of these two polymers would lead to a new cost effective polymeric material with good mechanical properties. However, these blends are immiscible blends quite often possess inferior properties relative to their components due to the unfavourable interfacial interactions, which is manifested as coarse, unstable morphology that develops during melt processing and weak interface between the phases in the solid state. Compatibilization of these blends may alleviate these problems and lead to a polymeric materials with good mechanical properties. However, low stiffness of the resulting materials limits their use in high performance engineering applications.

It is now well established that incorporation of nanoparticles into polymer blends leads to advanced PNCs with excellent mechanical properties, including strength and stiffness. However, homogeneous distribution of nanoparticles in polymer matrix is a prodigious task because the particles have inherent tendency for agglomeration, which results in deterioration

of properties. Recently, it has been shown that addition of compatibilizer improved dispersion of the nano materials in the in polymer matrix.

Polyamides (PA) are engineering thermoplastics with wide range of applications. PA exhibits excellent mechanical (including impact) properties, but is expensive, while PP is one of the cheapest and lightest commodity thermoplastics with good strength. Both PA and PP have been widely used as matrices for the fabrication and development of nanocomposites. Su et al. [1] investigated the microstructure and mechanical properties of PP/organo-montmorillonite (OMMT) binary nanocomposites and PP/SEBS/OMMT ternary nanocomposites. Miquelard-Garnier et al. [2] observed an increase of 25-30 % in Young's modulus without significant reduction in elongation at break by the incorporation of nanoparticles in PP in the presence of PP-g-A. Gopakumar and Page [3,4] revealed that the addition of PP-g-MA in PP/graphite composites leads to an improvement in flexural properties and impact strength. Sui et al. [5] reported that increase in filler content increased the electrical and thermal conductivities of PP/CNF nanocomposites. Hine et al. [6] showed that the incorporation of even 5% volume addition of CNF into PP resulted in ca.60% enhancement in Young's modulus and 35% reduction in thermal expansion coefficient. Bao and Tjong [7] found that a small amount of CNF enhanced the tensile strength and impact toughness of PP. Chen et al. [8] observed that PP reinforced with CNF exhibited improved thermal stability and electrical conductivity. All these studies revealed that PP based nanocomposites exhibit good physico-mechanical properties. Very recently, Paramaswaranpillai et al [9-11] have shown that incorporation of nanoparticles has excellent reinforcing effects in terms of mechanical properties of PP based nanocomposites.

PA based nanocomposites have also been extensively studied by various researchers. For example, Chow et al [12] studied the Mechanical Properties and Morphology of Injection-Molded Polyamide 6/Polypropylene Nanocomposites. The observed a good balance between

strength and toughness at 4 wt % organoclay content. Kelnar et al [13] showed that the addition of a small amount of elastomer significantly enhanced toughness of PA based nanocomposites. Motovilin et al also observed a similar improvement in mechanical properties with the incorporation of nanoparticles in PA 6. Ou et al [14] have shown that the strength and stiffness of the PP/PA6 nanocomposites were significantly improved in the presence of PP-g-MAH.

The present research work is devoted to prepare and characterize of PNCs based on PA/PP blends. It is important to note that PA/PP blends are incompatible due to high interfacial tension and low interfacial adhesion between the component polymers due to their polarity difference. Therefore, compatibilization is essential. It is unequivocally established that PP grafted with maleic anhydride (PP-g-MA) can be used as the compatibilizer which can improve the compatibility of the blends through interfacial chemical reactions. Therefore, the present work focuses on the effect of incorporation of various nanoparticles in the mechanical properties of PA/PP blends in the presence and absence of compatibilizer. The mechanical and dynamic mechanical properties of nanocomposites have been studied as a function concentration of nanoparticles. Morphology of the blends and composites have been investigated using scanning electron microscope.

## **2. Experimental**

### **2.1. Materials**

Isotactic PP (Koylene 3060), having a melt flow index (MFI) of 3 dg/min (at 230°C/2.16 kg) and a density of 900 kg/m<sup>3</sup>, was kindly supplied by Indian Petro Chemicals Limited, Baroda, Gujarat, India. PA12 (Vestamid L1670), having a melt volume-flow rate (MVR) of 60 cm<sup>3</sup>/10min (at 250°C/2.16 kg) and a density of 1010 kg/m<sup>3</sup>, was kindly supplied by Degussa, High Performance Polymers, Marl, Germany. PP-g-MA (Polybond 3200), having MFI 110 dg/min and MA content 1.0 wt%, was obtained by the courtesy of Crompton Corporation, Middlebury, USA. Pyrograf III carbon nanofibre with diameter 150 nm and a length of 2.5 μm

was obtained from Deakin University (Australia). Exfoliated Graphene nanoplatelets (xGnP) – grade M was obtained from XG Science, Inc.

## ***2.2. Preparation of nanocomposites***

Both compatibilised and uncompatibilised blends were prepared by melt mixing in a Brabender Plasticorder. Appropriate amounts of PA12 and PP were mixed at 185<sup>0</sup>C and 60 rpm for 6 min to obtain blends of different compositions. The blends are represented as N<sub>70</sub>, N<sub>50</sub> and N<sub>30</sub>, where N stands for PA and subscripts represent the wt% of PA. Compatibilised blends were obtained in a two-step mixing process. In the first step, the ompatibilizer was premixed with PP for 2 min at 185<sup>0</sup>C and 60 rpm and, in the second step, PA was added to this mixture and mixing. Nanocomposites were prepared by three-step mixing process. In the first step, PA, PP were mixed for one minute, followed by the addition of compatibilizer. The mixing was continued for another one minute. In the final step, nanoparticles were added to the compatibilized blend and mixing was continued for another four minutes. The resulting composites were hot pressed into sheets and cut in to pieces and injection molded in a DSM explore, Micro 12cc injection molding machine at 190<sup>0</sup> C for preparing test specimens for tensile testing as per relevant ISO standards.

## ***2.3. Characterization***

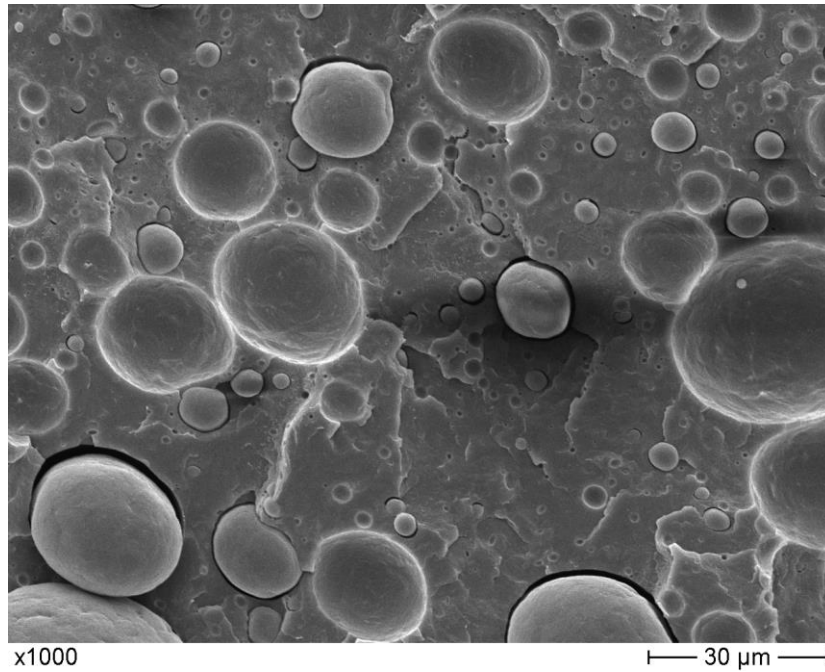
The specimens for morphology studies were cryogenically fractured in liquid nitrogen. The etched surface was sputter coated with gold for 150 s. A minimum of 5 photographs were taken for each sample using a scanning electron microscope. The tensile properties of the samples were measured using a universal testing machine (Tinius Olsen) model H 50 KT at a cross head speed of 50 mm/min according to ISO 527 on dumbbell shaped specimens. The sample dimensions were 75 x 5 x 2 mm<sup>3</sup>. The span length used was 55 mm. The dynamic mechanical properties of the blends were analysed using a dynamic mechanical thermal analyser.

### 3. Results and Discussion

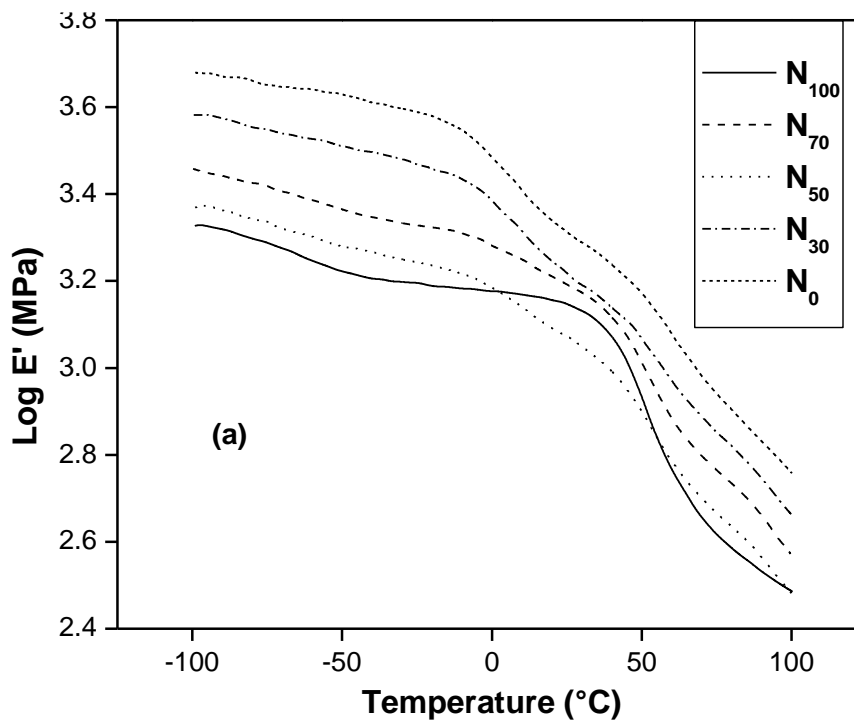
The uncompatibilized blends exhibited inferior mechanical properties (**Table 1**), due to non-uniform and coarse morphology as shown by the SEM micrographs (**Figure 1**). The storage modulus ( $E'$ ) curve shown in the **figure 2** can be roughly divided into three regions. (i) Glassy region (up to  $\sim 0^\circ\text{C}$ ) in which the chain segments are frozen as they can have only vibrational motions around fixed positions. But note that the  $E'$  curve of PA12 shows a small dip around  $-55^\circ\text{C}$ , due to the secondary relaxation. (ii) Glass transition region (leathery region) of PP (from  $0$ - $50^\circ\text{C}$ ), where there is a slight dip in  $E'$  curve. (iii) Glass transition region of PA12 ( $>50^\circ\text{C}$ ), in which a well defined drop in  $E'$  values is seen.

**Table 1:** Mechanical properties of uncompatibilized PA/PP blends

<b>Blend</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation at break (%)</b>
PA12	45 $\pm$ 1.2	1550 $\pm$ 20	75 $\pm$ 3
PA/PP (70/30)	24 $\pm$ 1.5	1530 $\pm$ 25	21 $\pm$ 2
PA/PP (50/50)	15 $\pm$ 0.8	1510 $\pm$ 30	23 $\pm$ 1.5
PA/PP (30/70)	21 $\pm$ 1.1	1560 $\pm$ 25	19 $\pm$ 1.5
PP	35 $\pm$ 1.3	1610 $\pm$ 15	20 $\pm$ 2



**Figure 1:** SEM micrographs of PA/PP blends



**Figure 2:** Storage modulus of PA12/PP uncompatibilized blends

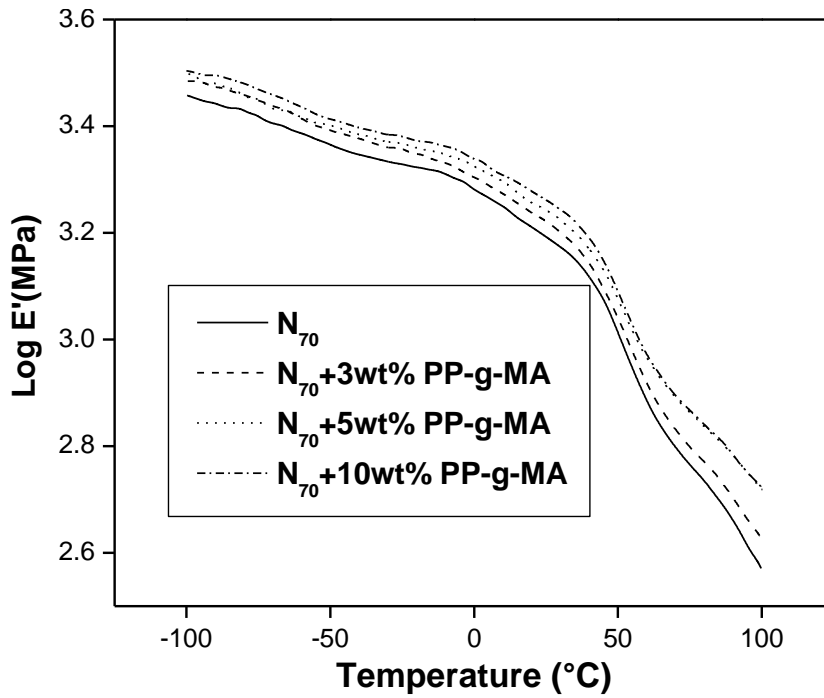
Compatibilization increased the tensile strength (**Table 2**) and storage modulus (**Figure 3**). This is due to the emulsifying action of the compatibilizer, which can be evaluated from the SEM micrographs showing the morphology of PA12/PP blends in the presence of compatibilizer (**Figure 4**). Note that the particle size registered a dramatic decrease with the addition of

compatibilizer. This clearly establishes the occurrence of interfacial chemical reactions between the amine group of polyamide and maleic anhydride group of the compatibilizer, which decrease the segmental mobility and increase the internal friction, nearer to the interface region, and enhanced the storage modulus of the blends.

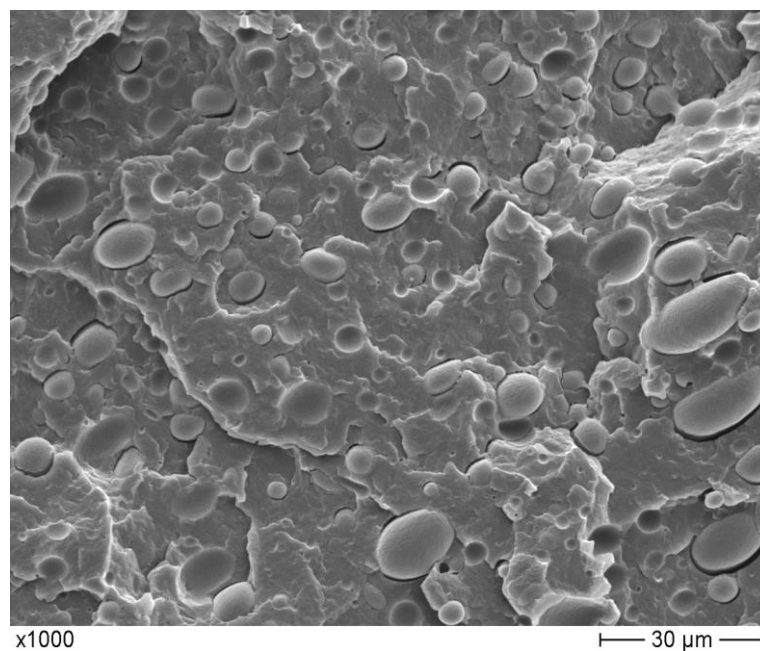
**Table 2:** Effect of compatibilization on the mechanical properties of PA/PP blends

<b>Blend</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation at break (%)</b>
PA/PP (70/30)	24±1.5	1530±25	21±2
PA/PP (70/30) + 1 wt% compatibilizer	27±1.7	1520±30	19±1.3
PA/PP (70/30) + 3 wt% compatibilizer	33±1.9	1500±20	17±1.5
PA/PP (70/30) + 5 wt% compatibilizer	37±2	1480±25	13±1.3
PA/PP (70/30) + 10 wt% compatibilizer	36±2	1470±25	12±1.4





**Figure 3:** Effect of compatibilization on the storage modulus of PA/PP blends



**Figure 4:** Effect of compatibilization on the morphology of PA/PP blends

Incorporation of nanofillers resulted in a remarkable increase in the strength and modulus of the compatibilized blends (**Table 4**). There is only a marginal decrease in the elongation at break. As the concentration of nanofiller increases strength and modulus increase. It is

important to note that beyond, 0.5 wt% of CNF, there is slight decrease in the strength and modulus. A similar decline in strength and modulus was observed beyond 0.3 wt % of xGnP.

**Table 3:** Mechanical properties of PA/PP/CNF nanocomposites

<b>Blend</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation at break (%)</b>
PA/PP (70/30) + 3 wt% compatibilizer)	33±1.9	1500±20	17±1.5
Compatibilized blend + 0.1 wt% CNF	35±2	1580±25	17±2
Compatibilized blend + 0.3 wt% CNF	37±1.7	1780±30	16±2
Compatibilized blend + 0.5 wt% CNF	38±1.7	1970±30	15±1.2
Compatibilized blend + 1 wt% CNF	36±2	1750±25	13±1.1

**Table 4:** Mechanical properties of PA/PP/xGnP nanocomposites

<b>Blend</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation at break (%)</b>
PA/PP (70/30) + 3 wt% compatibilizer)	33±1.9	1500±20	17±1.5
Compatibilized blend + 0.1 wt% xGnP	37.5±3	1630±22	16.2±2.1
Compatibilized blend + 0.3 wt% xGnP	39.2±2.3	1710±38	15.7±2.3
Compatibilized blend + 0.5 wt% xGnP	38.6±2.2	1920±36	15.2±1.7
Compatibilized blend + 1 wt% xGnP	37.7±2.5	1730±28	14±1.9

#### **4. Conclusions**

PA/PP blends were immiscible and incompatible and therefore exhibited inferior mechanical properties. Compatibilization improved the mechanical properties of the blends by stabilizing the phase morphology. It was observed that incorporation of nanoparticles remarkably improved the mechanical properties of the blends. Although both CNF and xGnP nanoparticles enhanced the mechanical properties, the latter was more effective in terms of tensile strength and modulus. In short, PA/PP/PP-g-MA/CNF and PA/PP/PP-g-MA/xGnP nanocomposites exhibited balanced mechanical properties suitable for making light weight, strong polymeric materials for engineering applications.

#### **5. References**

- 1) F. Su, H. Huang, Mechanical and rheological properties of PP/SEBS/OMMT ternary composites, *J. Appl. Polym. Sci.* 112 (2009) 3016.
- 2) G. Miquelard-Garnier, A. Guinault, D. Fromonteil, S. Delalande, C. Sollogoub, Dispersion of carbon nanotubes in polypropylene via multilayer coextrusion: influence on the mechanical properties, *Polymer* 54 (2013) 4290.
- 3) T.G. Gopakumar, D.J.Y.S. Page, Polypropylene/graphite nanocomposites by thermo-kinetic mixing, *Polym. Eng. Sci.* 44 (2004) 1162.
- 4) D.J.Y.S. Page, T.G. Gopakumar, Properties and crystallization of maleated polypropylene / graphite flake nanocomposites, *Polym. J.* 38 (2006) 920.
- 5) P. Hine, V. Broome, and I.M. Ward, *Polymer*, 46, 10936 (2005).
- 6) S.P. Bao and S.C. Tjong, *Polym. Compos.*, 30, 1749 (2009).
- 7) X. Chen, S. Wei, A. Yadav, R. Patil, J. Zhu, R. Ximenes, L. Sun, and Z. Guo, *Macromol. Mater. Eng.*, 296, 434 (2011).

- 8) Jyotishkumar Parameswaranpillai, George Joseph, K. P. Shinu, Seno Jose, Nisa V. Salim and Nishar Hameed, Development of hybrid composites for automotive applications: effect of addition of SEBS on the morphology, mechanical, viscoelastic, crystallization and thermal degradation properties of PP/PS-xGnP composites, *RSC Adv.*, 5, 25634-25641 (2015).
- 9) Jyotishkumar Parameswaranpillai, George Joseph, KP Shinu, PR Sreejesh, Seno Jose, Nisa V Salim, Nishar Hameed, The role of SEBS in tailoring the interface between the polymer matrix and exfoliated graphene nanoplatelets in hybrid composites *Materials Chemistry and Physics* 163, 182-189 (2015).
- 10) J Parameswaranpillai, G Joseph, KP Shinu, NV Salim, N Hameed, S Jose, High performance PP/SEBS/CNF composites: Evaluation of mechanical, thermal degradation, and crystallization properties, *Polym Compos.* doi: 10.1002/pc.23830 (2015).
- 11) W. S. Chow, Z. A. Mohd. Ishak, U. S. Ishiaku, J. Karger-Kocsis, A. A. Apostolov, The Effect of organoclay on the Mechanical Properties and Morphology of Injection-Molded Polyamide 6/Polypropylene Nanocomposites, *J. Appl. Polym. Sci.*, 91, 175–189 (2004).
- 12) I. Kelnar, J. Kotek, L. Kapraľkova, B. S. Munteanu, Polyamide Nanocomposites with Improved Toughness, *J. Appl. Polym. Sci.*, 96, 288–293 (2005).
- 13) Mladen Motovilín, Zlatan Denchev, Nadya Dencheva, On the Structure-Properties Relationship in Montmorillonite-Filled Polyamide 6 Nanocomposites, *J. Appl. Polym. Sci.*, 120, 3304–3315 (2011).
- 14) Baoli Oua, Duxin Li, Yuejun Liu, Compatibilizing effect of maleated polypropylene on the mechanical properties of injection molded polypropylene/polyamide 6/functionalized-TiO<sub>2</sub> nanocomposites, *Compos. Sci. Technol.*, 69 (2009) 421–426.