

# Novel In Situ Nano Fibrous Reinforced All Polymer Polypropylene-Nylon Composite

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## ABSTRACT

All polymer composites contain blends of two or three polymers of which the minor phase is in fibrous form and acts as the reinforcement for the material. In the present studies polypropylene (PP) with nylon (Ny) were compounded extruded and then molded at temperature close to nylon. Crystallization kinetics and structure development was studied in the PP-Ny blends with composition. Nylon dispersed phase was found to nucleate PP giving rapid crystallization. There was extensive fibrous morphology and fiber diameter was dependent on composition. The tensile and impact strength were considerably improved by almost 1.5 to 2 times that of PP at certain concentrations of nylon. Thus, these blends behave as self reinforced composites due to the peculiar nanofibrous morphology getting developed during melt processing.

**Keywords:** polymer blends, nanofibrous, self reinforcing composite, polypropylene, nylon

## 1 INTRODUCTION

Blend technology of different polymers has been extensively used in recent years for a number of reasons: (a) create new materials with improved properties (b) create synergistic effects so that special properties of individual components are advantageously used (c) create miscibility / compatibility in mixed waste plastics for better recycling and so forth. The outstanding advantage of blending has been that of synergistic effects i.e. obtain properties which are not possible to achieve in individual polymer [1-4]. In the past, the miscibility, compatibility and increasing interfacial interactions or bonding between the polymers have been mainly investigated [5-7]. The effect of composition and processing conditions on melt morphology and subsequent structure development in immiscible blends have not been studied extensively. Recently we have reported the formation of microfibrillar morphology in polypropylene (PP) blends with other polyolefins which led to tremendous improvement in impact strength of the extruded films [8]. On the other side, polymer composites including nano-composites have been extensively studied

so as to obtain improved electrical and mechanical properties. The additives are externally added in such composites and the properties achieved depend on proper dispersion, appropriate filler and its optimum concentration. All polymer composites have great advantage of generation of the reinforcing phase in situ during processing[9]. These often contain speciality polymers such as liquid crystalline polymers, aromatic polyamides, etc.[10] which give reinforcement due to their fibrous morphology and strength. In the present studies, we have used these principles and attempted to make use of commonly available polymers such as PP and Nylon for generating morphological features and crystalline structure to enhance the properties.

## 2 EXPERIMENTAL

### 2.1 Materials

The PP and Nylon6 used in this study were commercial grade polymers and their characteristics properties as provided by the supplier are as follows. PP- Reliance Industries, Repol 6020EG, MFI 9.5, density 0.905, melting range 165-175 °C. Nylon – GSFC India, Gylon M28RC, density 1.14, melting 220-230 °C. The resin granules were thoroughly dried before use.

### 2.2 Melt processing and sample fabrication

Blending of both the materials was done by compounding in twin screw extruder (Brabender model) with the three zones kept at 190, 210 and 220 °C and 30 rpm. The proportion of Nylon 6 was varied from 10% to 50% in the blend with respect to PP. The melt flow (MFI) for each composition was determined using the standard temperature conditions (220 °C) and load (2.16 Kg) with 1.1 mm orifice. The extrudates obtained were also sectioned to observe the morphological features.

The granulated blends obtained as above were thoroughly dried and used for further injection molding of each composition into dumbbell and strip shaped specimens for tensile and impact strength measurements according to ASTM standards D536 and D256 respectively. The injection molding machine was set at

feed zone 190 °C, compression zone 220 °C and metering zone 220 °C. The mold was provided with water circulation channel. Three different flow rates of water (0, 340, 600cc/min ) were used for cooling of each sample and later ejected. This gives typically the cooling rates of 2, 5 and 10 degrees/second.

### 2.3 Structure development studies

Samples were prepared in laboratory under controlled temperature conditions in the hot stage of optical microscope under different conditions of cooling and annealing. The granules of the blends were melted between glass slides at temperature 220 °C followed by slow cooling to 35 °C. Some of the samples were annealed at the crystallization temperature of 110 °C then cooled to ambient conditions. The crystallization behavior for each composition was monitored on the hot stage of the polarizing microscope (Leitz having digital camera and image analysis software in the same manner as described elsewhere. The study of crystallization behavior and morphology was enabled by a polarizing microscope (Leitz Laborlux 12 Pol, Germany) coupled to an image analyzer system (VIDPRO 32, Leading Edge, Australia) in the same manner as reported elsewhere [11]

For studying the crystalline structure and morphology, samples were cut in the form of 1 mm thick sheet and area of 15mmx 12 mm for x-ray diffraction (XRD) using diffractometer Rigaku Geigeroflex, Cu K $\alpha$  with  $\beta$  Ni filter . Samples were also sectioned vertically from the above for scanning electron microscopy (SEM) using JOEL JSM 5900LV. These were sputter coated gold-palladium films in the usual way for increasing the contrast.

### 2.4 Measuring properties

The tensile as well as Izod impact strengths of molded samples were obtained using injection molding machine with different cooling rates. The tensile strength was measured for all samples prepared under different conditions with different cooling rates and varying by ASTM D 638 with Instron machine . Also Izod impact strength was measured using ASTM D 256 in the same manner as reported earlier for other systems. [12]

## 3 RESULTS & DISCUSSION

Figure 1 shows the isothermal crystallization of PP containing Ny for crystallization temperatures T<sub>c</sub> of 115 °C. It is evident from these graphs that the crystallization process becomes more rapid when nylon 6 is added to PP. This is true for both the high and low value of T<sub>c</sub> and the crystallization becomes more rapid in the latter case than the former. The effect of addition of nylon 6 on the rate of crystallization is shown in Figure 2 . This figure shows the crystallization half time (t<sub>1/2</sub> value) determined from the

curves of Fig.1. There is a rapid decrease of t<sub>1/2</sub> value with the addition of nylon6 and it attains a minimum for the composition of 10 to 15 % of nylon in PP. The t<sub>1/2</sub> value starts to increase for higher nylon concentrations above 20%. This suggests that the nylon moiety acts as nucleating agent for molten PP. This can be understood as follows. Since nylon 6 has much higher melting point than PP, during cooling of the melt ( melt temperature 250 °C), the nylon solidifies and phase separates to form a fine dispersed particles. These have nucleating ability for heterogeneous nucleation of PP crystals. It may be noted that when finer is the dispersed phase, better is the nucleating ability and lower is the t<sub>1/2</sub> value[13]. On the other hand, when nylon concentration increases above certain concentration, the domain size increases giving lower nucleation ability leading to increasing trend for the t<sub>1/2</sub> value.

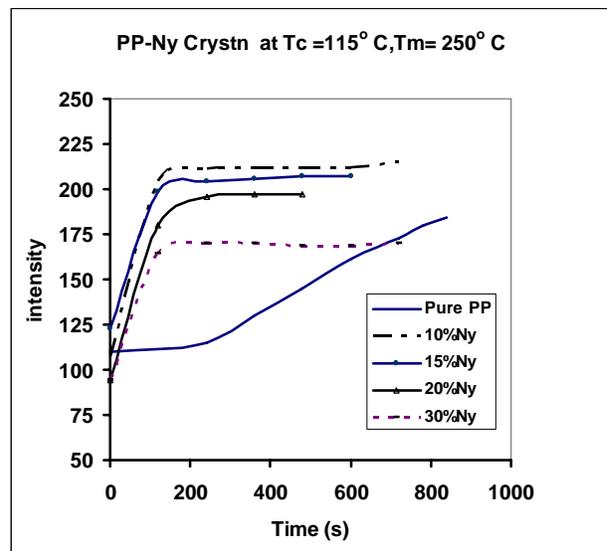


Figure 1 : Isothermal crystallization of PP-Ny at 115°C for different Ny contents.

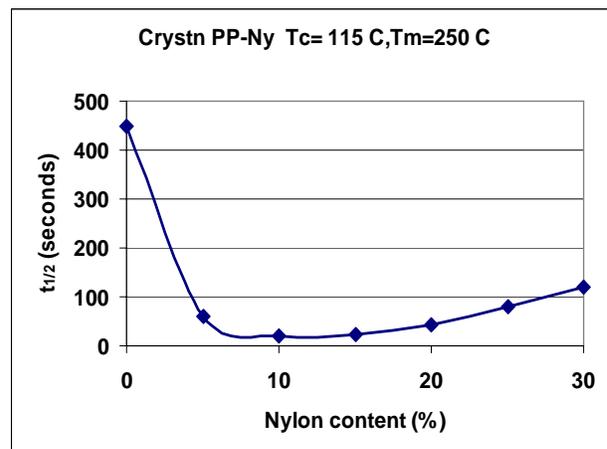


Figure 2 : Crystallization half time with composition

It is evident from the above Fig. 1 and 2 that Ny is very effective in nucleating the PP crystals. These samples were examined by XRD and scans are shown in Fig.3.

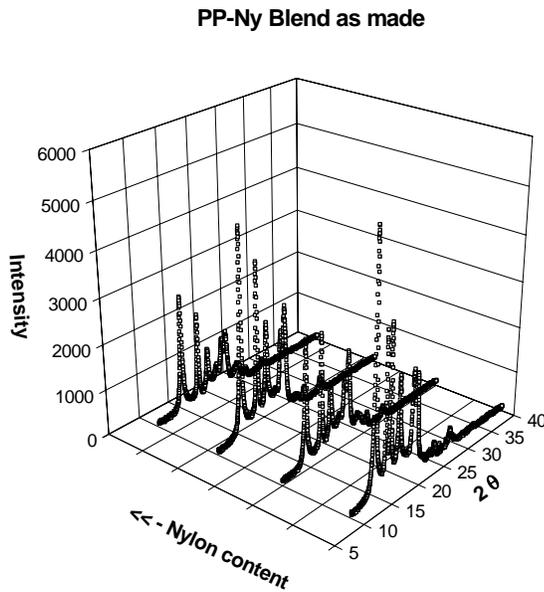


Figure 3: XRD scans of PP-Ny melt crystallized 115 C

All the scans indicate the  $\alpha$  form of PP with four prominent peaks in the region of 10 to 40 degrees. It is evident from the graphs that the intensities of the peaks depend very much on the composition especially the peak (I), (II) and (III) at  $2\theta$  of 14.1, 16.8 and 18.5 degrees respectively. These correspond to 110, 040 and 130 reflections from the  $\alpha$  phase of PP[14]. However the relative intensities of these peaks changed considerably in presence of Ny. In particular, the peak II at 16.8° is greatly affected by the presence of Ny. It is interesting to mention here that polyethylene terephthalate (PET) fibers also nucleate PP giving rise to transcrystalline morphology [15]. In that case also the intensity of peak (II) was found to increase considerably and peak (I) decrease drastically in presence of PET fibers. According to lattice mismatch theory, if the lattice parameter of the crystallizing phase matches well with that of the dispersed lattice, high probability of nucleation and even epitaxial growth exists. Typically, the condition for nucleation is favorable if [16]

$$\left[ \left| n(a,b \text{ or } c)_{\text{nucl}} - m(a,b \text{ or } c)_{\text{cryst}} \right| \right] / [(a,b,c)] \times 100 \text{ is } < 10\%$$

Here, the absolute value for difference is considered,  $n$  and  $m$  are non zero integers and  $a,b,c$  are lattice parameters for that crystal. The subscripts indicate the values for nucleating agent and crystallizing phase respectively. If one considers the above criterion in the present case, nylon 6 ( $\alpha$  phase being taken) has the  $a,b,c$  values of 0.958, 1.76, 0.776 nm respectively while the PP has 0.665

,2.098, 0.65 nm for its  $\alpha$  phase and 1.9, 1.9, 0.65 nm respectively for its  $\beta$  phase [14]. The above factor is estimated as

$$\left[ \left| 2(a)_{\text{Ny}} - 3(c)_{\alpha\text{PP}} \right| \right] / [(a,b,c)] \times 100 = 4\% \quad \text{---(1)}$$

$$\left[ \left| 2(a)_{\text{Ny}} - (b)_{\beta\text{PP}} \right| \right] / [(b)] \times 100 = 0.85\% \quad \text{---(2)}$$

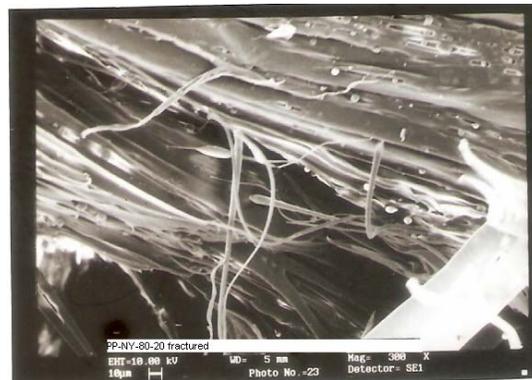
$$\left[ \left| 2(a)_{\text{Ny}} - 3(c)_{\beta\text{PP}} \right| \right] / [(b)] \times 100 = 4\% \quad \text{---(3)}$$

Thus Ny can be very good nucleating agent for both types of PP crystals.

The most interesting features of the present studies are noted in the morphology developed for the dispersed phase. Figure 4 shows the SEM micrographs of the PP-Ny blends fractured perpendicular to the specimen. Extensive fibrous morphology is quite evident in both the cases. Since Ny remains almost in the semisolid state during melt processing cycle of the blends, the shear deformation gives it an elongated shape which leads to fibrous morphology especially in the extruded strands.



(A)



(B)

Figure 4 : Sem of PP-Ny fractured surface A-50%, B-20% Nylon melt compounded and molded

It may be noted that the fiber diameter increases with the increase of nylon content which indicates that the fibers are indeed for the nylon phase. Further, the fibers appear to easily pulled out with clean surface for higher nylon content

than the lower case. In the latter (20% nylon), the fibers are quite tightly bound to the matrix suggesting good interaction between the two at this concentration. In fact for 10% nylon, it became difficult to obtain good contrast with independent fibers since these were fully embedded in the matrix.

The tensile and impact strengths of these PP-Ny injection molded blends were measured under standard conditions. The Figures 5 and 6 depict the variation of

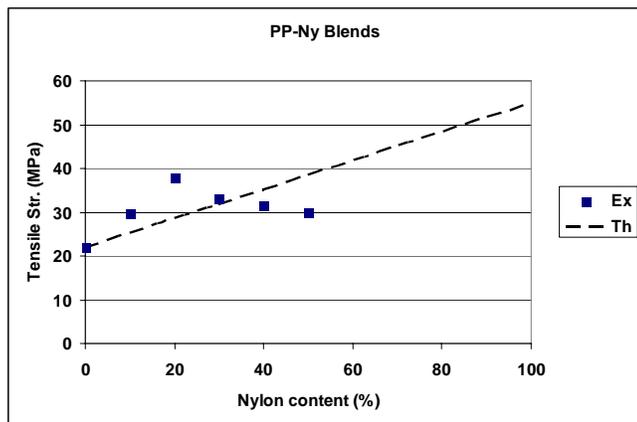


Figure 5: Tensile strength of PP-Ny blends with respect to Nylon content

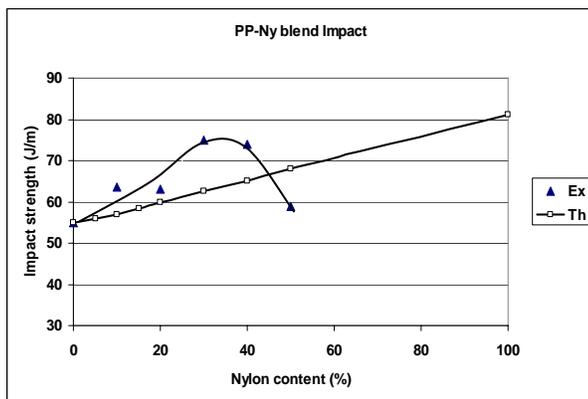


Figure 6 : Izod Impact strength of PP-Ny blends with Nylon content. (injection molded notched samples)

tensile and impact strength of injection molded PP-Ny samples with respect to Nylon content. These also show the values estimated from simple rule of mixtures wherein the two phases are assumed to be noninteractive uniformly dispersed and spherical in shape. It is clearly seen that the tensile and impact properties of the blends are much higher than the expected values. In fact both the tensile strength as well as impact strength are seen to be highest at Nylon content of 20-25%. This can be only due to the fibrous morphology and high crystallization of PP in presence of Nylon. Thus, one may say that these are all polymer composites containing fine fibers of one polymer dispersed in the

matrix of the major PP phase. Interestingly, the fiber matrix interaction is due to nucleation effects and not because of any compatibilizer. A few studies reported in the past have used the compatibilizers in PP-Ny blends. However, there was improvement observed in the impact property and not tensile strength. This could be due to reduction or nullified nucleation effects in presence of compatibilizers. It may be mentioned here that PP filled with fibers such as glass, carbon, etc. lead to improvement in either tensile or impact but not both. Further, there is considerable increase in weight in the case of filler loaded composites while such is not the case in the all polymer composites.

## 4 SUMMARY & CONCLUSION

The present studies clearly demonstrate that PP-Ny blends processed and crystallized in appropriate conditions contain extensive fibrous morphology. The Nylon moieties act as nucleating centers for PP crystals. These structure and morphology lead to the formation of all polymer composite having much improved mechanical properties than original PP matrix.

## 5 ACKNOWLEDGEMENT

The authors wish to thank Prof.V.D.Karad, Founder president of MAEER, Maharashtra Institute of Technology, Pune and Director, National Chemical for their support for completion of this project. They also wish to acknowledge the partial travel grant given by Prof.Karad, MAEER, Pune India.

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