

# Thermal Stability of Polypropylene/Carbon Nanofiber Composite

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**ABSTRACT:** Thermal stability of polypropylene and carbon nanofiber composite system has been studied using Thermogravimetric Analysis, Limited Oxygen Index (LOI), Flammability, Calorimetry, and Oxidation Induction Time techniques. Definite improvement in thermo-oxidative stability of the composite system has been observed. Improvement in LOI and a distinct change in the burning characteristics suggest a reduction in potential fire hazards. The nano-

composite system will have enhanced anti-ageing characteristics and require more stringent conditions for the initiation of burning and the ultimate impact of burning will be less. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3574–3578, 2006

**Key words:** ageing; carbon nanofiber; nanocomposites; poly(propylene); thermal stability

## INTRODUCTION

Carbon nanotubes and nanofibres (CNF) are of great scientific interest since the properties of a material become increasingly size-dependant at low dimensions. A further advantage of such nanoscale reinforcement is an improved processability and recyclability of thermoplastic nanocomposites. CNF bridges the gap between the costly nanotubes and conventional fibers as fillers. Studies have been undertaken by different researchers on CNF-reinforced thermoplastic composites with improved in mechanical, thermal and electrical properties.<sup>1–13</sup>

Improvement in flammability properties of polymers has been obtained with nanoscale additives and these filled systems provided an alternative to conventional flame retardants. Effectiveness of layered silicates as flame retardants have been demonstrated in layered silicate/polymer nanocomposite.<sup>14–18</sup> The large aspect ratio of clay is said to be the reason for the effective flame retardancy. It has also been reported that carbon nanotubes are used as flame retardants because of their large aspect ratio.<sup>19</sup> The flame retardant effect of these nanoscale fillers was attributed to a barrier labyrinth effect where the diffusion of the degradation products from the bulk to the gas phase is slowed down.<sup>19,20</sup>

Very little information is available regarding the influence of CNF on the thermal properties of thermoplastic polymers. Lozano and Barrera<sup>8</sup> have reported increase in thermal stability of polypropylene (PP) in presence of CNF by Thermogravimetric Analysis (TGA) in nitrogen atmosphere. This enhancement was attributed to restriction of mobility of the polymer molecules by the CNF. This restriction reduced the tension induced by thermal excitation of the C—C bond leading to enhancement in thermal stability.

In the present study, the thermal stability of PP/CNF composite has been reported.

## EXPERIMENTAL

Isotactic polypropylene of 35 MFI, supplied by Reliance Industries Ltd., India and Pyrograf-III<sup>TM</sup> type carbon nanofiber, obtained from Applied Science Inc., USA, have been used. Films of PP and PP containing 1 and 10% CNF have been prepared in a compression-molding machine. PP homopolymer chips and PP chips premixed with CNF were compression molded at 170°C for 2 min under 2 MT pressure. The mold was then taken out and quenched in water at room temperature. TGA has been carried out in a PerkinElmer TGA 7 with a heating rate of 10°C/min under nitrogen and air atmosphere. Oxidation Induction Time (OIT) was measured in PerkinElmer TGA 7 by heating the sample to 200°C at the rate of 100°C/min and then holding at 200°C for 180 min in nitrogen atmosphere. LOI and flammability was measured using critical oxygen index equipment and flammability tester of S. A. Associates (India). In case of LOI and flamma-

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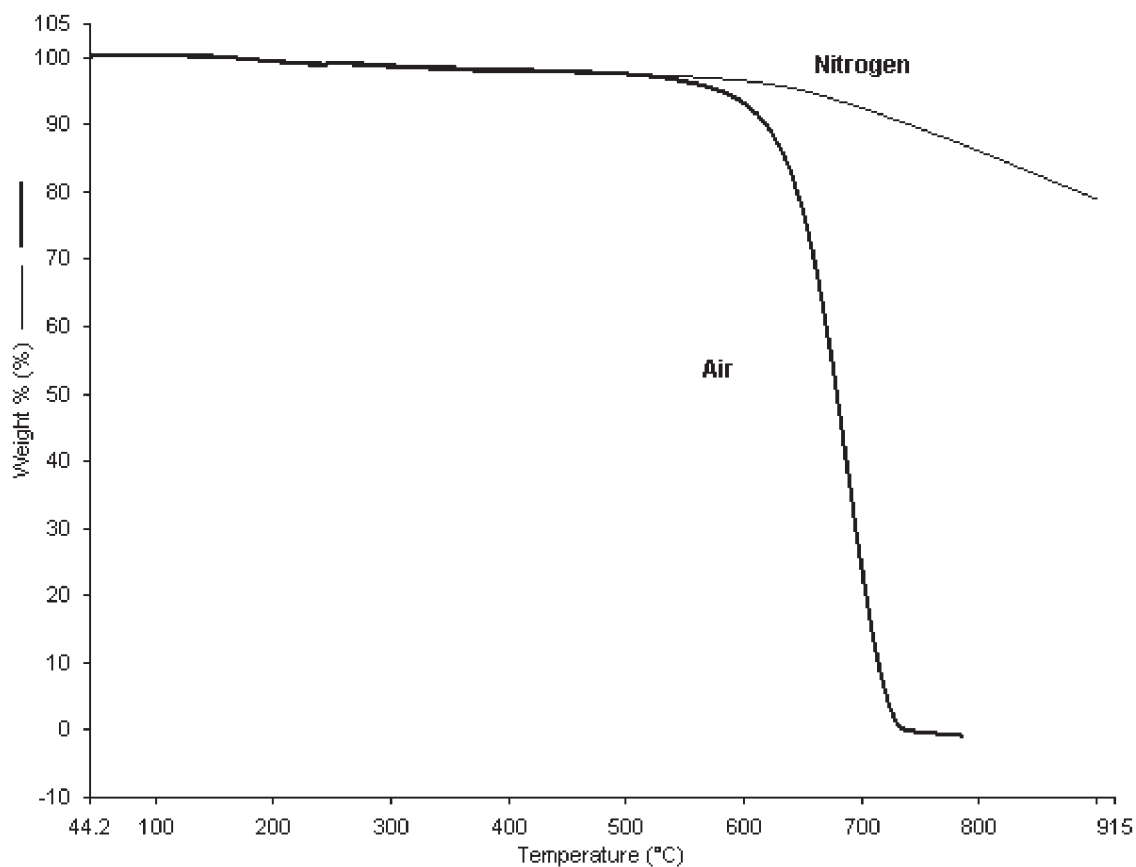


Figure 1 Weight loss (%) versus temperature curves of the CNF in nitrogen (N) and air (O).

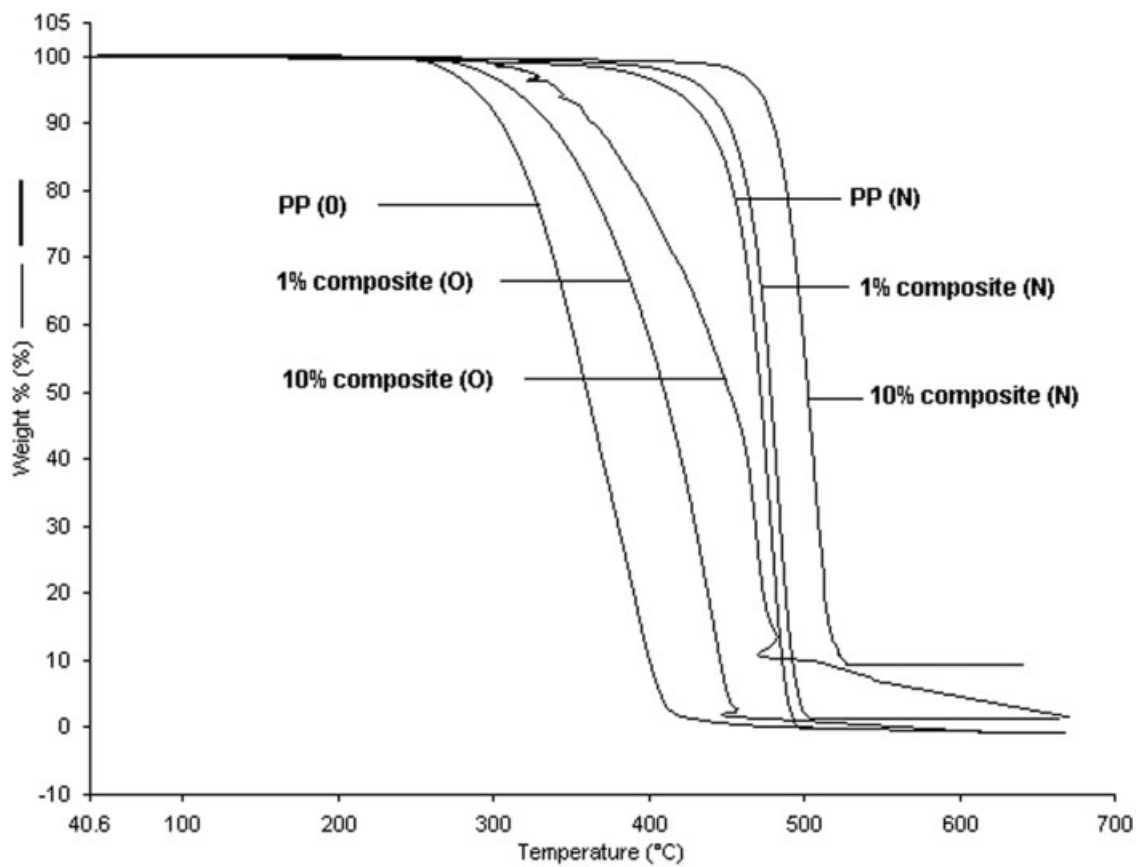


Figure 2 Weight loss (%) versus temperature curves of PP and nanocomposite in N and O.

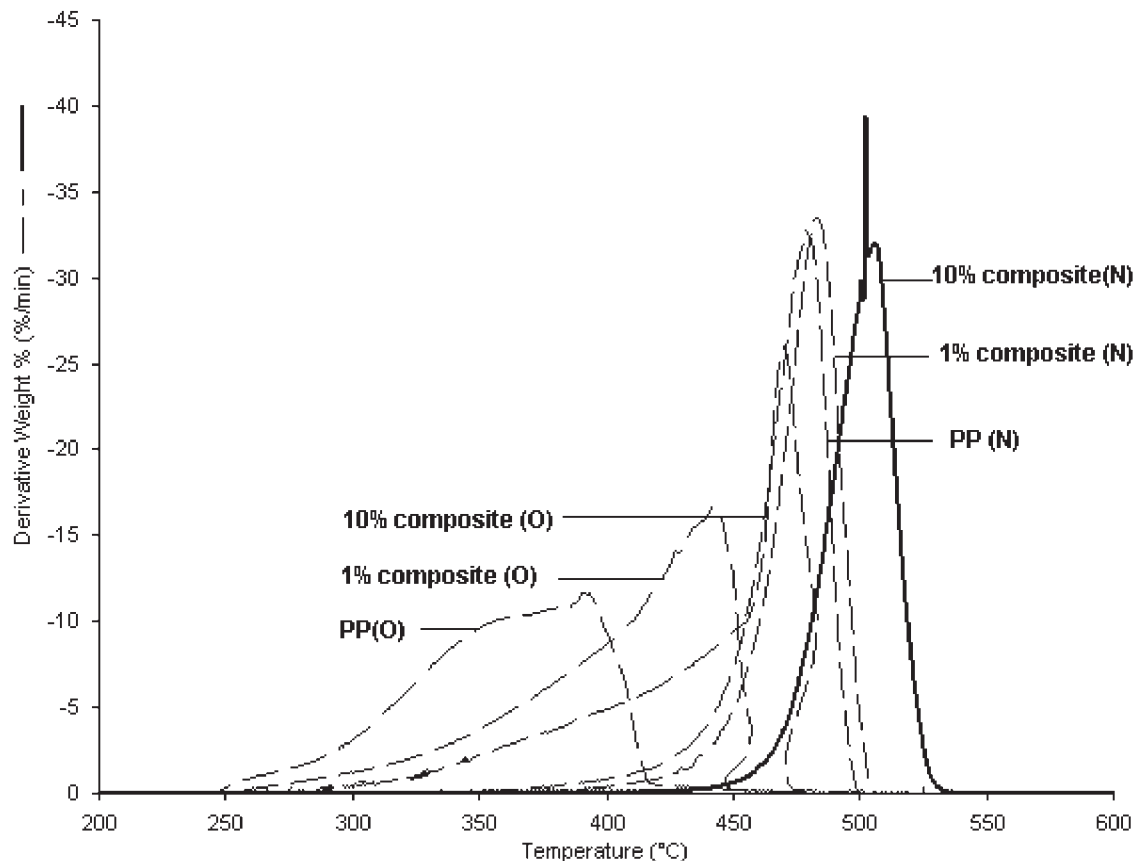


Figure 3 Derivative weight loss versus temperature curves of PP and nanocomposites in N and O.

bility, an average of three readings was taken. Heat Capacities of the samples were measured in a conventional Bomb Calorimeter.

## RESULTS AND DISCUSSION

### TGA results

The percent weight loss versus temperature curves of the CNF in nitrogen and air are given in Figure 1. In nitrogen, the weight loss was 0.5% up to 200°C, 3% up to 600°C, and 21.3% up to 900°C. Whereas, in air, the weight loss was 0.7% up to 200°C, 6.3% up to 600°C, and 100% at about 740°C. In both these cases the maximum weight loss occurred after ~600°C.

The percentage weight loss versus temperature curves and the derivative weight percent versus temperature curves, under nitrogen and air atmosphere, of PP and the nanocomposites are given in Figure 2 and Figure 3 respectively. These data show distinctly different mechanisms for thermal and thermo-oxidative degradation behaviors of nanocomposite.

In case of thermal degradation, the shift in the peak value, as shown in Figure 3, is in accordance with the rule of mixture as one of the components (CNF) is having higher thermal stability. Enhancement of degree of

crystallinity and restriction of molecular mobility around nanofibres will also play a role in this phenomenon.

In case of thermo-oxidative degradation, the shift in the peak value is much higher compared with the thermal degradation and can not be explained on the basis of rule of mixture or restriction of molecular mobility. In this case the explanation for the improved thermal stability is the char formation occurring under oxidative condition. The char acts as a physical barrier between the polymer and the superficial zone where the combustion of the polymer is going on.

A peculiar observation during TGA of nanocomposites in air is an endothermic reaction at the last phase of degradation leading to reduction in the temperature of the sample and is related to the mechanism of degradation.

### Oxidation induction time results

OIT, as shown in Figure 4, increased significantly with the addition of CNF. In case of PP, the induction time was about 29 min and the total weight loss after 180 min was about 29%. At 1% loading, the induction time increased to about 77 min and the total weight loss reduced to about 10% after 180 min. At 10% loading, there

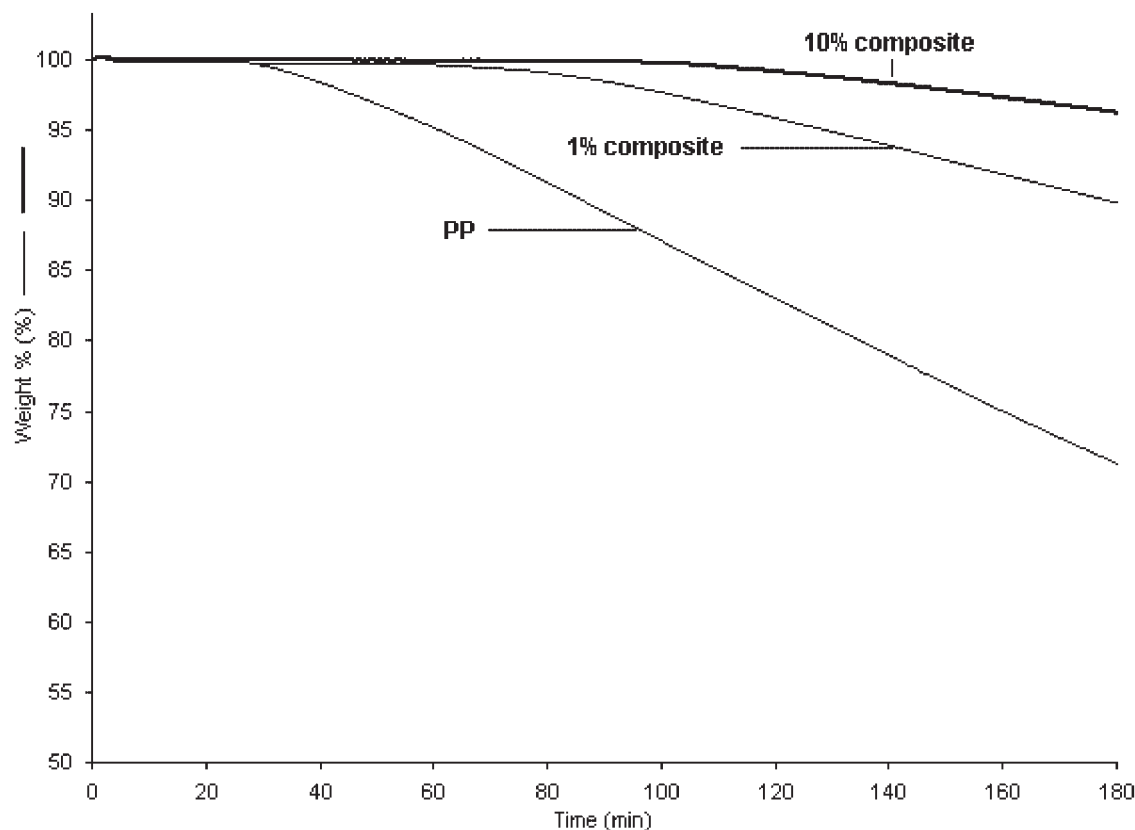


Figure 4 Oxidation induction time plots of PP and nanocomposites.

was further enhancement of induction time to about 115 min and a reduction in total weight loss to about 4% after 180min. It is known that the CNF will enhance the UV-resistance of the matrix material. A logical inference, based on these observations, will be a substantial enhancement of ageing time of the nanocomposites.

#### LOI, flammability, and calorimetric test results

LOI, flammability, and calorimetric test results are summarized in Table I. With the addition of CNF, the LOI values increased from 22 for PP to 24 for nanocomposite at 10% loading. The heat capacity values did not change much at 1% loading compared to PP but at 10% loading, there was a significant decrease. Surprisingly, no difference in the flammability values was observed with the addition of CNF. The highly

flammable matrix may be the reason for the same. But a distinct difference in the burning behavior was observed with the addition of CNF. The addition of CNF reduces the dripping tendency of the polymer while burning. At 10% loading, absolutely no dripping was observed. The whole film burnt and a black char in the shape of film was left intact, presumably of CNF. The char, which is formed during burning, will restrict the flow of the molten polymer and thereby restrict the dripping. More the char formation less will be the dripping and hence the 10% nanocomposite does not drip at all during burning. From the difference in weight loss before and after burning, it was noticed that 2.5% weight of the CNF has been lost during burning. This was confirmed by carrying out TGA of the remained char, which exhibited higher thermal stability than that of CNF. [Fig. 5].

The LOI of 24 indicates that, at least up to 10% loading, CNF are able to impart increased flame retardancy to PP, although fibers having LOI [ $\geq$ ] 27 are generally considered to be flame resistant.<sup>21</sup> But the combined effect of higher thermal stability, increased LOI, low heat capacity at 10% loading, and absence of melting and dripping during burning makes the nanocomposite less hazardous and advantageous from the point of view of specific applications.

TABLE I  
LOI, Flammability, and Heat Capacity Values

Material	LOI	Flammability (sec)	Heat capacity (kcal/gm)
PP	22	20	12
1% Nanocomposite	23	20	12
10% Nanocomposite	24	20	8.5

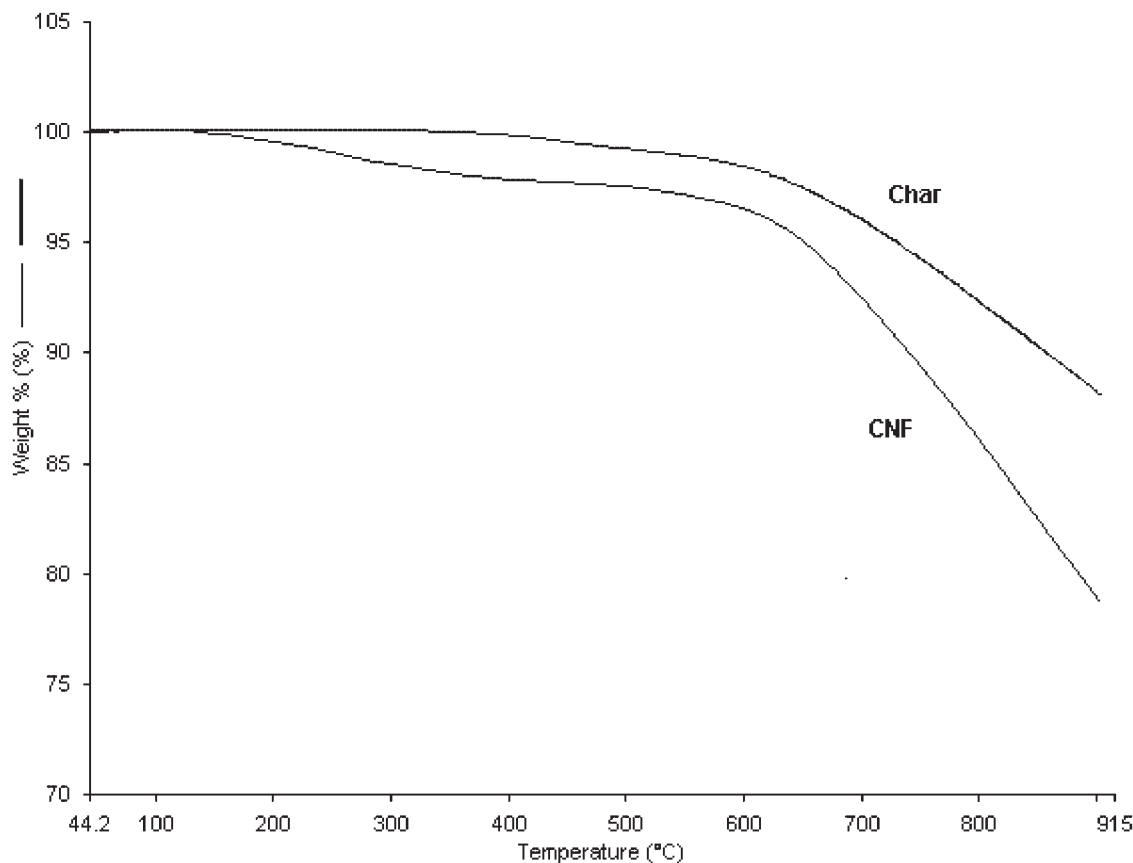


Figure 5 Weight loss (%) versus temperature plots of CNF and char of nanocomposite.

## CONCLUSIONS

Incorporation of CNF in PP enhances the thermal stability of the polymer both in nitrogen and air. There is a significant increase in OIT in case of nanocomposites, which would possibly enhance the ageing time of the composite material. The nanocomposite will require more stringent conditions for the initiation of burning and the ultimate impact of burning will be less. The mechanisms of the enhancement of thermal stability and thermo-oxidative stability of the composite system are distinctly different.

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