# Preparation and mechanical properties of pine needle/ polypropylene bio-composites

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## Abstract

The main objective of the present work is to develop a low-cost eco-friendly and biodegradable reinforced thermoplastic composites utilizing pine needle fibers as reinforcing materials. Pine needle/polypropylene composites were prepared with varying load of fillers, and varying dosage of compatibilizer (MA-g-PP) to improve the interface bonding between fiber and the matrix. Composites were prepared by using treated Pine Needle Filler (TPNF), Untreated Pine Needle Filler (UPNF) procured from the paper mill. Sample preparation was carried out in an injection molding machine. Tensile properties of the samples were measured on Shimadzu UTM. TGA and DTG were carried out simultaneously by using a Perkin Elmer Thermal Analyzer. Structural characterization was done using FTIR spectrophotometer. The flame retardancy of TPNF and UPNF reinforced polypropylene composites were characterized by the UL-94 test. The composite intact fracture surface morphology was analyzed on a field emission scanning electron microscope.

Keywords: *Composites, TGA, DTG, Field Emission Scanning Electron microscopy, FE-SEM, Flammability*

## 1. Introduction

Several billion tons of fillers and reinforcements are used annually in the plastics industry, and there is a huge potential market for recyclable, energy efficient and more eco-friendly composite materials. Natural fibers as reinforcing agents offer the potential to deliver greater added value, sustainability, renewability and lower costs. In addition to these advantages, easy of availability, biodegradability and light weight of natural fibers attracted our attention in the application-oriented research. At present, automotive industries throughout the world have particularly displayed greater interest in initiating the design and engineering of new products with eco-friendly advantages. The use of a thermoplastic matrix presents an opportunity to produce recyclable composites, but such composites require the use of durable natural fibers for reinforcement as opposed to brittle synthetic fibers. There is an increasing demand from automotive companies for materials with sound abatement capability as well as reduced weight for fuel efficiency. Natural fibers possess excellent sound absorbing efficiency, more shatter resistance, higher load bearing capacity and better energy management characteristics than traditional glass fiber reinforced composites. In automotive parts, such composite not only reduces the mass of the component but also lowers the energy needed for production by 80%. The variation in the properties of natural fibers is another important aspect that has to be considered.

A large genus of monoecious, evergreen, resiniferous trees, commonly known as Pines, distributed in the northern hemisphere, extending south across the equator in Indonesia. Pines occur widely in the temperate regions; in the warm temperate and subtropical countries, they are found chiefly in the hills. Five species occur wild in India in the Himalayas and the hills of Assam. Several exotic Pines have been introduced but

not to an extent that they can be of any economic importance to the country. *Pinus wallichiana* (*Kail also known as Bhutan pine, Blue pine, Himalayan pine and Himalayan white pine*), a soft pine, and *Pinus roxburghii (known as Chir pine and Indian long leaf pine)* a hard-pine, are the species occurs throughout the temperate Himalayan region [4]. Particularly, Uttarakhand (Himalayan region) has got about 4121 sq. km. (32.43%) or 412100 hectare Pine (Chir) forest along with other coniferous forests. The leaves of the tree are in clusters of three or more, and needle-like. There is a huge fall of pine needles (leaves) from the month of April to June.

Pinus wallichiana is a coniferous evergreen tree, native to the Himalaya, Karakoram and Hindu Kush mountains, from eastern Afghanistan east across northern Pakistan and India to Yunnan in southwest China. The leaves ("needles") of *Pinus wallichiana* are in fascicles (bundles) of five and are 12–18 cm long. They are noted for being flexible along their length, and often droop gracefully. The cones are long and slender, 16–32 cm, yellow-buff when mature, with thin scales; the seeds are 5–6 mm long with a 20–30 mm wing. Typical habitats are mountain screes and glacier forelands, but it will also form old-growth forests as the primary species or in mixed forests with deodar, birch, spruce, and fir. In some places, it reaches the tree line. *Pinus roxburghii* a native to the Himalayas, the range extends from northern Pakistan (North-West Frontier Province, Margalla Hills, Islamabad Capital Territory, Murree), across northern India (Jammu and Kashmir, Punjab, Himachal Pradesh, Uttarakhand, Sikkim) and Nepal to Bhutan. The leaves are needle-like, in fascicles of three, very slender, 20–35 cm (7.9–13.8 in) long, and distinctly yellowish green. [1]. Illustrations of needle like leaves and scientific classification of *Pinus wallichiana* and *Pinus roxburghii* are shown in figure 1. As per reported estimate [2], about three tons of pine needles are generated during peak season in one hectare, thus total 1236300 tons of pine needles may be generated from the pine forests every year. Demand for natural fibers in plastic composites is forecasted to grow at 15–20% annually with a growth rate of 15–20% in automotive applications, and 50% or more in selected building applications. Other emerging markets are industrial and consumer applications such as tiles, flower pots, furniture and marine piers [3]. Till today, there is no productive use of pine needles in India and it has become a persistent menace for foresters of the region. Although several usage of pine needles have been reported such as fiberboard, packing box, extracting essential oil, producing lingo-sulfonates and making pine wool etc. but still pine needles have not been fully utilized for any industrial purpose [4].

## 2 Experimental Procedures

### 2.1 Materials

Light brown coloured dry pine needles of length 150-200 mm and diameter 0.5 to 1.0 mm were procured from the forest area of Uttarakhand (Himalayan region). Polypropylene (H110 MA with MFI 11 g/10 min at 230°C/ 2.16 kg) obtained from M/s Indian Reliance Ltd, India. Maleic anhydride grafted polypropylene (MA-g-PP), OPTIM 405, as a compatibilizer, was

received from PLUSS Polymers Pvt. Ltd., India (http://www.manasindia.com/).

### 2.2 Synthesis of Pine /polypropylene composites

(a) Treatment of pine needle filler:

The dried pine needles of length about 150-200 mm were refined. The refining was done on (Model FDR, Make: Sprout-Bauer, Inc., Muncy, PA.) to make pine needles into 6 mm size of uniform length. Chopped pine needles were subjected to chemical pulping for chemical treatment. Alkaline pulping of the chopped pine needles was carried out in the laboratory digester. Alkaline-treated pulp was obtained by treating with 10% NaOH and 0.1% Anthra Quinone at 165°C for 2 hours with a bath ratio of 1:4. After cooking, the pulp was thoroughly washed, dried (Fig.2 (b)) and grounded the pulp to 40 mesh pass named as Treated Pine Needle Filler (TPNF). Whereas bundles of pine needles fed along with water into the hopper of the refiner to make them into 6 mm size of uniform length. Wet pine needles thus obtained were air dried (Fig.2 (a)) followed by grinding to 40 mesh pass named as Untreated Pine Needle Filler (UPNF).

b) Development of UPNF and TPNF/PP composites:

The composites were prepared with varying filler loading as shown in table 1.

**Table 1** Formulation of composite material with MA-g-PP in weight %

| Sample code | PP | MA-g-PP | Fiber content % |
|---|---|---|---|
| 100 % PP | 100 | 0 | 0 |
| 10% TPNF -M0 | 92 | 0 | 10 |
| 10% TPNF -M2 | 88 | 2 | 10 |
| 10% TPNF -M6 | 84 | 6 | 10 |
| 20% TPNF -M0 | 80 | 0 | 20 |
| 20% TPNF -M2 | 78 | 2 | 20 |
| 20% TPNF -M6 | 74 | 6 | 20 |
| 30% TPNF -M0 | 72 | 0 | 30 |
| 30% TPNF -M2 | 68 | 2 | 30 |
| 30% TPNF -M6 | 64 | 6 | 30 |
| 20% UPNF -M0 | 80 | 0 | 20 |
| 20% UPNF -M2 | 78 | 2 | 20 |
| 20% UPNF -M6 | 74 | 6 | 20 |

The higher fiber percentage (above 40%) causes deterioration of the tensile stresses and also reported that 6 wt. % of MA-g-PP addition gave rise to the increase in the mechanical properties of the composites [5]. Thus, 10-30% variation in filler loading was considered for TPNF composites. However for UPNF, 20% filler loading was chosen for comparison purpose. The effect of MA-g-PP compatibilizer on all the composites was studied by varying

| *Pinus wallichiana* (Kail also known as Bhutan pine, Blue pine, Himalayan pine and Himalayan white pine) | | |
|---|---|---|
|  | **SCIENTIFIC CLASSIFICATION** | |
| | Kingdom: | Plantae |
| | Division: | Pinophyta |
| | Class: | Pinopsida |
| | Order: | Pinales |
| | Family: | Pinaceae |
| | Genus: | Pinus |
| | Subgenus: | Strobus |
| | Species: | P. wallichiana |
| *Pinus roxburghii* (known as Chir pine and Indian long leaf pine) | | |
|  | **SCIENTIFIC CLASSIFICATION** | |
| | Kingdom: | Plantae |
| | Division: | Pinophyta |
| | Class: | Pinopsida |
| | Order: | Pinales |
| | Family: | Pinaceae |
| | Genus: | Pinus |
| | Subgenus: | Pinus subg. Pinus |
| | Species: | P. roxburghii |

**Figure 1:** Needles like leaves and scientific classification of Pinus wallichiana and Pinus roxburghii

concentration viz. 2 and 6 wt %. All the compositions were dry mixed and melt compounded using a co-rotating twin screw extruder, with 30 mm diameter and 33:1 L/D ratio (M/s Japan Steels works, Japan). The compounding temperatures up to 190ºC and the screw speed used were 100 rpm. The extruded strands were passed through a cold water trough at room temperature followed by pelletizing the extruded strands. The pellets of composites were oven dried at 105ºC for 24 h to remove moisture content before sample preparation.

*2.3 Characterization*

The tensile test specimens were prepared from composite pellets by using injection moulding machine (M/s ARBURG 500-210, Germany). The processing temperature for injection moulding was 185ºC. The injection pressure used was 70-80 MPa. Tensile properties of the samples were measured on Shimadzu UTM Equipment (Model: AUTOGRAPH AG IS 50KN). TGA and DTG were carried out simultaneously by using a Perkin Elmer (PYRIS Diamond TG/DTA) thermal analyzer. The pellets of different composites were subjected to a heating rate of 20ºC/min in the heating range of room temperature to 600ºC using $Al_2O_3$ as the reference material. Indium and gallium were used as standards for temperature calibration. Structural

characterization was done using a Tensor-27 FTIR spectrophotometer. The spectra were recorded from finely powdered fiber samples in KBr pellets. The flame retardancy of the TPNF and UPNF reinforced polypropylene composites were characterized by the UL-94 test. The samples submitted to tensile tests were cut and the composite intact fracture surface morphology was analyzed on a Quanta 200 FEG, 200V-30KV field emission scanning electron microscope.

## 3. Results and discussion

The values of the tensile properties of TPNF and UPNF reinforced PP composites were summarized in table 2. UPNF composites ranging from 0-6 wt% MA-g-PP showed a reduction in tensile strength over neat polypropylene due to high lignin content as shown in Figure 2.
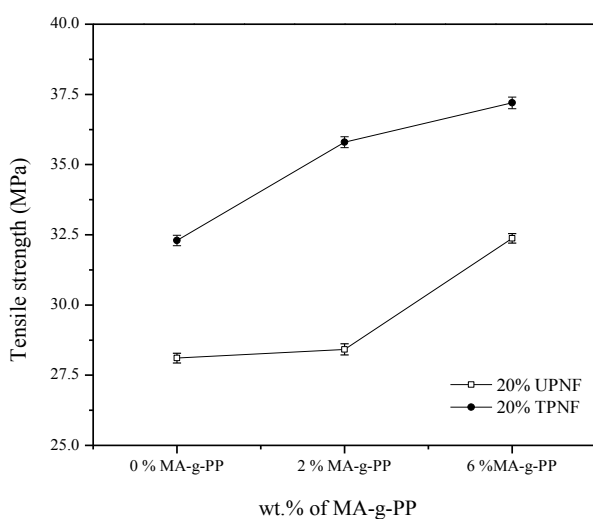


**Figure 2:** Tensile strength of 20 % TPNF and 20 % UPNF composites

This happened due to the poor adhesion between the components of the system which increased the chances of failure. The stress was transferred to the high lignin content fillers in a very poor manner and also the fillers were not very strong and chances of failure at lower stresses increased [6]. However, deterioration in tensile strength was observed in 20 wt% UPNF composites due to low cellulose fraction in the untreated filler.





Fig 3. Synthesized pine needle fibers (a) UPNF (b) TPNF

Effect of TPNF loading (10, 20 and 30 wt %) on tensile properties was studied using 2 and 6 wt% MA-g-PP. Figure 3 shows that the tensile strength of the composites increased linearly with TPNF content (10% to 30%) from 3% to 17.61% over the tensile strength of neat polypropylene.

TPNF/PP composites at 6 wt% MA-g-PP showed improvement over composites with 2wt% MA-g-PP. The composites with % MA-g-PP showed a decrease in tensile strength due to the lesser compatibility between TPNF and the matrix. The use of MA-g-PP improved interaction and adhesion between the fibers and matrix leading to the better matrix to filler stress transfer resulted in higher tensile strength.

**Table 2** Tensile properties of TPNF and UPNF composites with 0, 2 and 6% MA-g-PP

| Sample code | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|
| 100 % PP | 33.3 | 121 |
| 10% TPNF -M0 | 33.8 | 8.6 |
| 10% TPNF -M2 | 34.3 | 8.4 |
| 10% TPNF -M6 | 35.3 | 7.8 |
| 20% TPNF -M0 | 32.3 | 7.0 |
| 20% TPNF -M2 | 35.8 | 6.6 |
| 20% TPNF -M6 | 37.2 | 6.1 |
| 30% TPNF -M0 | 37.6 | 5.7 |
| 30% TPNF -M2 | 38.7 | 5.2 |
| 30% TPNF -M6 | 39.1 | 4.7 |
| 20% UPNF -M0 | 28.1 | 7.8 |
| 20% UPNF -M2 | 28.4 | 7.7 |
| 20% UPNF -M6 | 32.4 | 7.0 |

With increasing compatibilizing agent, the tensile strength of the composites improved and the composite began to exhibit brittle fractures due to the superior stress propagation. The improved interfacial bonding between the filler and the matrix polymer resulted in good stress propagation and improved the tensile strength, but fractures occurred at the filler, and these fractures were more brittle than those in the matrix polymer. The previous works have also reported the similar finding [7].

### Fourier Transform Infrared (FT-IR) Spectroscopy:

The various functional groups of the UPNF and TPNF composites are shown in detail in Figure 4.
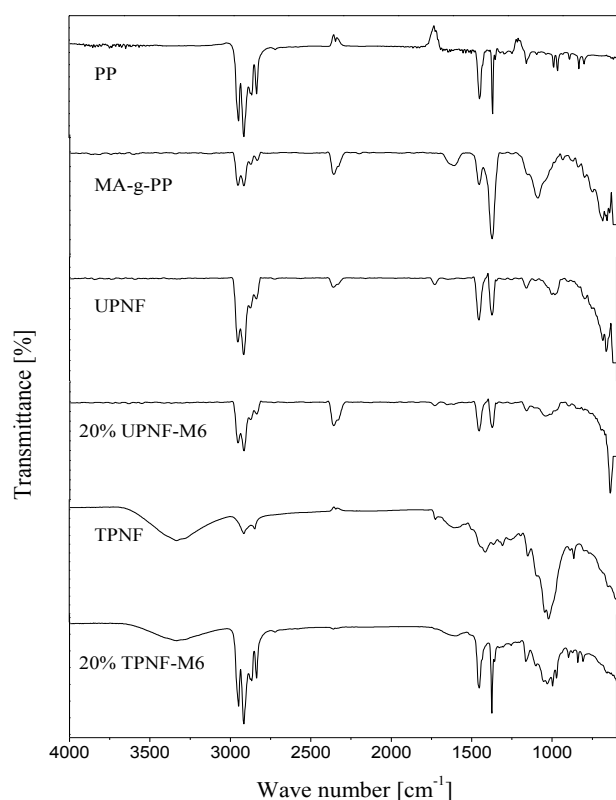


**Figure 4:** FTIR spectra of PP, MA-g-PP, UPNF, 20% UPNF-M0, TPNF and 20% TPNF-M0

The wave numbers of different functional groups in the composites were reported. [8]. FTIR spectrum of neat TPNF had a broad absorption band at 3340 cm$^{-1}$ corresponding to stretching of O-H bonds, which was also present in the same position in the FTIR of 20% TPNF-M6 composites. The absorption peaks between 2925 and 2860 cm$^{-1}$ were observed in all virgin polymers and composites, corresponding to the vibration of the C–H aliphatic and aromatic bonds. From the spectra of neat UPNF and 20% UPNF-M6, the short and sharp peak at 1426 cm$^{-1}$ was assigned to the characteristic absorption peak due to the asymmetric bending of CH. This revealed no interactions between matrix and UPNF fillers and thus,

composites became weaker. The reduction of CH stretching from 1323 to 1300 cm$^{-1}$ might be due to the hydrogen bonding between CH groups of TPNF and MA-g-PP. 1323 cm$^{-1}$ from the symmetry bending vibration of CH and 1166 cm$^{-1}$ from the bending of OH were assigned.

### Thermal analyses (TGA and DTA):

The thermal analysis of the raw materials and composite materials were carried out with TGA and DTG thermograms. TGA and DSC theorems of PP, MA-g-PP, UPNF, TPNF, 20% UPNT-M6 and 20% TPNF-M6 was shown in figure 5 and figure 6 respectively. From the thermogravimetric analysis, the degradations of PP, MA-g-PP, 20% UPNT-M6 and 20% TPNF-M6 composites started from 443, 454, 392 and 441$^{\circ}$C respectively in the temperature ranged from 35 to 600$^{\circ}$C. The thermal decomposition of UPNF occurred at 276$^{\circ}$C in a three step reactions with the first step decomposition due to evaporation of moisture, the second step to UPNF and third to oxidation of partial decomposition of UPNF. The decomposition of TPNF occurred at 290$^{\circ}$C and the three step decomposition reactions were similar to UPNF. From figure 5, it was seen that the mass residue content of MA-g-PP was higher than PP. Also, the mass residue content of UPNF was higher than TPNF. The decomposition temperature of 20% TPNF-M6 was 49$^{\circ}$C higher compared to 20% UPNT-M6. This revealed that by replacing UPNF with TPNF decomposition temperature of composites was increased.
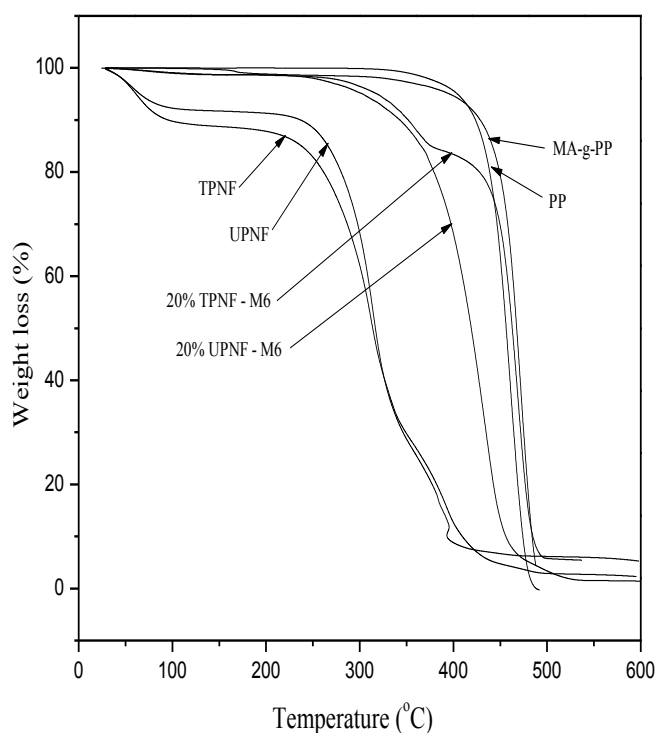


**Figure 5:** Thermo grams of TPNF, PP and MA-g-PP (a) TGA
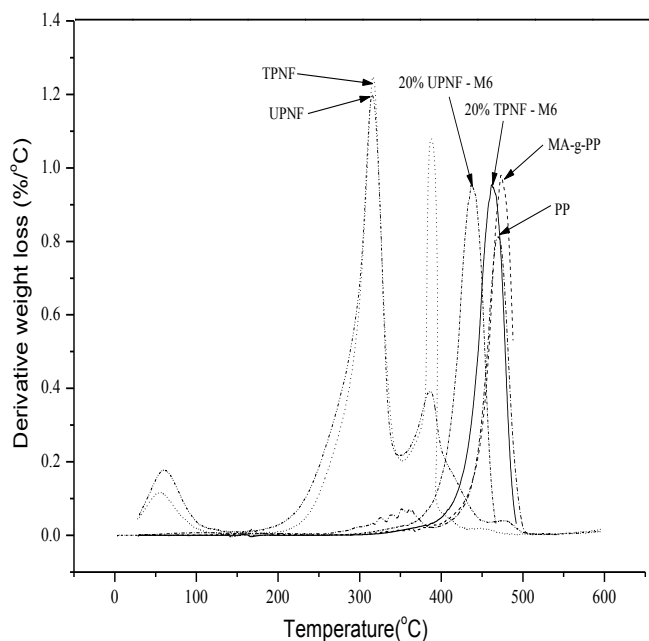
**Figure 6:** Thermo grams of TPNF, PP and MA-g-PP (b) DTG

The DTG degradation profiles of neat TPNF shown three peaks. The first peak indicated the loss of weight due to evaporation of moisture content. The degradation between 200 ºC and 400ºC was a two-step process indicated by second and third peak. The similar peaks were obtained in the case of neat UPNF, but the weight loss to corresponding peaks was less compared to neat TPNF. These results were consistent with previously published results. [9]. The first degradation event was observed in the second peak of TPNF between 236ºC and 350ºC, and could be attributed to the decomposition of hemicelluloses and the slower decomposition of lignin. The third peak shown the second degradation of TPNF between 350ºC and 400ºC which might be attributed to the degradation of cellulose. It is reported in the literature [10] that the hemicelluloses decompose before lignin and cellulose. The hemicelluloses degraded between 180 ºC and 350ºC. After adding MA-g-PP to UPNF and TPNF at 6 wt%, degradation temperature of the composites was increased [11]. As the filler loading increased, the thermal stability of the composites decreased and increased in the mass residue content was found.

### Micro Structure of TPNF/PP and UPNF/PP composites:

FESEM micrographs of TPNF/PP and UPNF/PP composites were shown in the figures 7 (c-d). Neat UPNF and TPNF without MA-g-PP compatibilizer were shown in figures 5 (a-b). More pulled-out traces of filler particles were seen in the micrographs of the 20 % TPNF-M6 composite with a compatibilizing agent, and this was due to the strong interfacial bonding between the filler and the matrix polymer as shown in figures 7 (c-b). It might be due to the fact that TPNF occupies substantial fraction in the

composites, the interfacial bonding between the filler and the matrix polymer is strong, thus, the fracture occurred not at the interface but at the filler itself. Figure 7 (a) and 7 (c) clearly shown the incompatibility of the UPN and PP. Few pulled-out traces of filler particles were seen in the case of 20% UPNF-M6 composite with a compatibilizing agent, and this was due to the poor interfacial bonding between the filler and the matrix polymer.

### Flame Retardancy Tests -Vertical UL-94:

The flame retardancy of all TPNF and UPNF reinforce based polypropylene composites were characterized by the UL-94 test. The rectangular shaped samples with dimensions of 127 ×12.7 ×3.2 mm were exposed vertically to a laboratory gas burner flame for 10 seconds as required by UL94V. The sample was ignited at the bottom and burnt upward. The time required for the flame to self-extinguish afterburner removal was measured and the occurrence of dripping onto a piece of cotton placed underneath the sample was recorded. If the sample does not burn for more than 10 seconds and the drips do not ignite the cotton, the material is classified as V-0. If none burns for more than 30 seconds and the drips do not ignite the cotton, the material is classified as V-1 but if the cotton is ignited, the material is classified as V-2. If any of the samples burns for more than 30 seconds or if the entire sample is consumed, the material is classified as non-rated (NR). Virgin polymers and the composites were shown high sensitivity to flame. Polypropylene is composed of aliphatic chains (MA-g-PP) and neat polypropylene has no flame retardancy [12]. TPNF and UPNF composites burnt for more than 30 seconds and the drips ignited the cotton, classified as V-2 according to UL-94 test. All composites of TPNF and UPNF exhibit the V-2 category of the UL-94 test as shown in table 3.

## 15. Conclusion

Pine needles were utilized successfully for making the polypropylene based low dense thermoplastic composites by using twin screw extruder. The tensile properties TPNF/PP composites increased with increase in TPNF content but elongation at break decreased. The tensile strength of UPNF/PP composites decreased with increase in UPNF content. Incorporation maleic anhydride grafted polypropylene enhanced the tensile properties of UPNF/PP and TPNF/PP composites. Thermal stability of composites UPNF/PP and TPNF/PP composites were decreased with increase in filler loading. Initial weight loss (5%) of neat UPNF and neat TPNF was observed at lower temperatures. Higher thermal stability was recorded in TPNF/PP composites compared with UPNF/PP composites. FTIR analysis showed the strong inter-atomic bonding between TPNF and MA-g-PP and weak bonding between UPNF and MA-
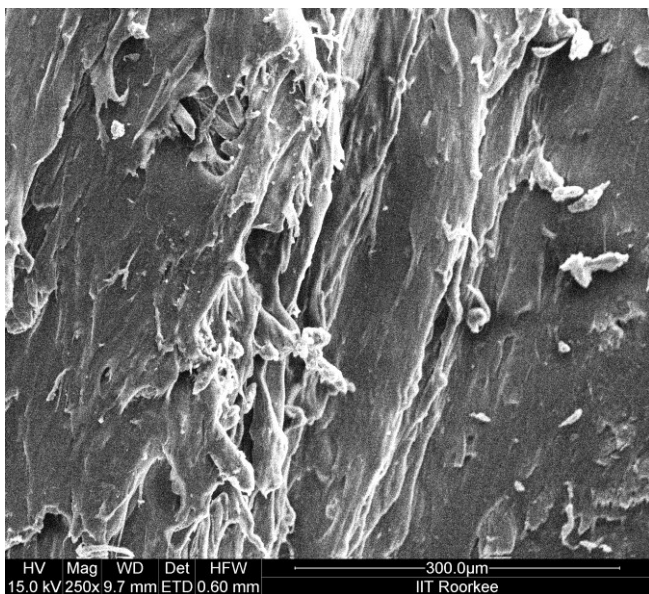
g-PP. By FE-SEM analysis, more pull-out of TPNF from the composites was observed, which in turn increased in MA-g-PP
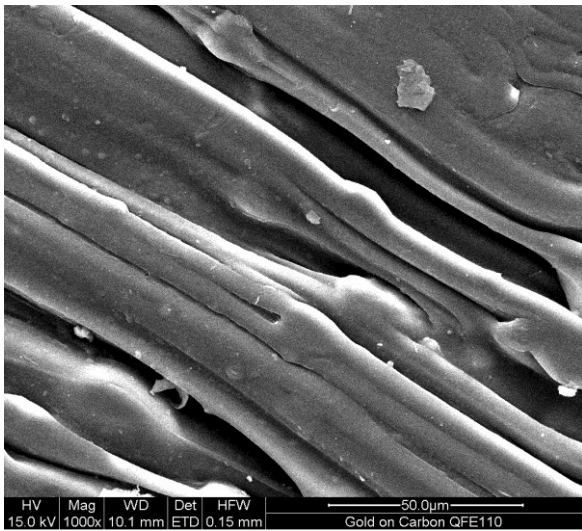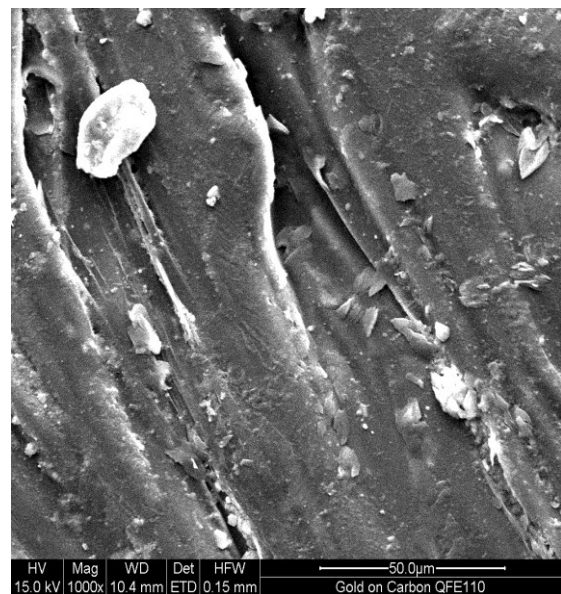


**(a) UPNF**
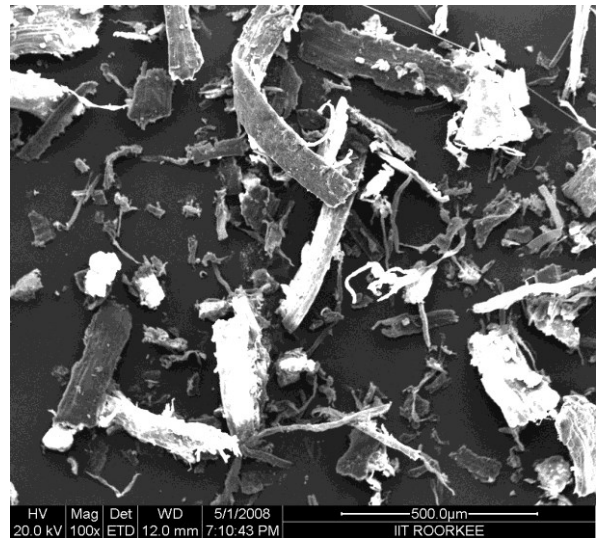


**(b) TPNF**



**(c) 20 % UPNF -M6**



**(d) 20 % TPNF-M6**

Figure 7: FE-SEM micrographs showing tensile fractured composites

content increased the interfacial bonding between the TPNF and the matrix. Few pull-outs of the UPNF fillers were observed in UPNF/PP composites due to weak interfacial bonding. Composites of TPNF and UPNF exhibited the V-2 category of UL-94 test. This indicated a good flame retardant property.

Table 3 Flammability of TPNF/PP, and UPNF/PP composites

| Sample | PP | MA-g-PP | TPNF | UPNF | UL-94 |
|--------|-----|---------|------|------|-------|
| PP | 100 | - | - | - | V-2 |

| | | | | | |
|---|---|---|---|---|---|
| MA-g-PP | 0 | 100 | - | - | V-2 |
| 10 % TPNF-M0 | 92 | 0 | 10 | - | V-2 |
| 10 % TPNF-M2 | 88 | 2 | 10 | - | V-2 |
| 10 % TPNF-M6 | 74 | 6 | 20 | - | V-2 |
| 20 % TPNF-M0 | 80 | 0 | 20 | - | V-2 |
| 20 % TPNF-M2 | 78 | 2 | 20 | - | V-2 |
| 20 % TPNF-M6 | 74 | 6 | 20 | - | V-2 |
| 30 % TPNF-M0 | 72 | 0 | 30 | - | V-2 |
| 30 % TPNF-M2 | 68 | 2 | 30 | - | V-2 |
| 30 % TPNF-M6 | 64 | 6 | 30 | - | V-2 |
| 20 % UPNF-M0 | 80 | 0 | - | 20 | V-2 |
| 20 % UPNF-M2 | 78 | 2 | - | 20 | V-2 |
| 20 % UPNF-M6 | 74 | 6 | - | 20 | V-2 |

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