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Effect of Ketuki Fiber on Morphology and Mechanical Properties of Thermoplastics Composites

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Abstract

Different amount of raw Ketuki powder (average diameter: 60 – 120 µm) was mixed with the thermoplastic polymers such as ethylene-1–octene copolymer (EOC) and isotactic polypropylene (iPP). The melt mixing was performed using an internal mixture and resulting composites were studied for the effect on morphology and mechanical behavior using electron microscopy, tensile testing and thermogravimetric analysis (TGA). The microscopic results showed that the polymer matrix is not compatible with filler resulting in worsening of mechanical properties especially in case of the iPP-based composites. For the EOC composites the rubbery nature of the matrix material remains still visible. The TGA analysis revealed slightly worsened thermal stability of composites, while tensile properties were found to be deteriorated as well.

Key words: Polymer composites, natural fibers, electron microscopy, mechanical properties

Introduction

The highly consuming materials of recent days are synthetic polymers. They have their own specific physical and chemical properties which can be altered or modified according to their applications. The conductivity, elasticity, hardness, brittleness, morphology, tensile property and solubility can be varied with the homogeneous distribution of foreign micro- and nanoparticles in polymer matrix. At around 1960s and 1970s a practice of distributing inorganic fillers (such as glass fibers, silica, calcium carbonate, boehmite, layer silicate, carbon nanotube (CNT), etc) in polymer matrix had started (Powell & Bell 2006). These particles either physically mix or create hydrogen bonds or van der Waals force with synthetic polymer and reinforce the properties of the latter.

Pavlidou and Papasyrides (2008) reviewed the layered silicate nanocomposites in which fillers were introduced by intercalation methods. They found the increase in storage moduli, barrier properties, thermal properties and flame retardance in the nanocomposites whereas decrease in elongation at break and toughness of the composites was observed (Pavlidou & Papasyrides 2006). Powell and Beall (2006) reported the increase in tensile modulus due to the addition of fluoromica in poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and polyamide 12 matrix (Powell & Beall 2006). Moczo & Pukanzsky

(2008) used micro and nano fillers like montmorillonite in elastomeric polymers to improve stiffness and wettability with the interfacial binder during compounding. The composite showed, however, the premature failure. Thostenson *et al.* (2005) reviewed the composites of thermosetting polymers (epoxy, polyimide and phenolic), thermoplastics such as polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyamide 12 (PA 12), polyetheretherketone (PEEK) etc. with different kinds of fillers such as multiwalled carbon nanotube (MWCNT), carbon nanofiber (CNF), single walled carbon nanotube (SWCNT), etc. and studied their properties. Anthoulis & Kontou (2008) studied the role of clay nanoparticles to reinforce the polymers. Schadler, Brinson & Sawyer (2007) studied the impact of large interfacial area of nanoscale spherical and tubular fillers (such as Al_2O_3, ZnO) in polymer matrix (such as polytetrafluroethylene; PTFE). Giannelis (1996) proposed the synthesis of nanocomposites by intercalation method which is superior to *in situ* polymerization and solution casting methods. The composites forming had high storage modulus. Fischer *et al.* (2003) dispersed platelets-like double layered hydroxide fillers in polymeric material using different procedure and incorporated silicate layers in organic and organic–inorganic hybrid coating by modified clay platelets on PMMA and polyolefinic matrix.

Nowadays, the polymer composites comprising inorganic fillers are becoming less attractive in some cases due to their relatively heavy weight, sometimes high cost, and problem with recycling and environmental issues (Panaitescu *et al.* 2011). To overcome these problems, current interest is on new composite materials with natural fibers as filler. The overview on applications of the commonly used commercial natural fibers (such as flax, hemp, jute, kenaf, ramie, abaca, cotton, sisal and wood fibers) for reinforcing polymer materials have been given by Pickering (2008), Mohanty *et al.* (2005), Bledzki *et al.* (2002) and Thomas & Pothan (2009). Natural fibers are light in weight, low cost, easily available (often worldwide and locally), environmentally friendly (Han *et al.* 2008, Panaitescu *et al.* 2011). Natural fibers will be available also in the future with steady prices. For instance, worldwide production of bast and leaf fibers was recorded to be 5.36 millions tons in 2006 (Nova-Institut 2006). Within the period from May 2003 to January 2006, for example, the prices for petroleum rose by 100% and for common plastics by 40% but virtually no increase for natural fibers (Nova-Institut 2006). In 2006, the price of short fibers (coco, hemp, flax, jute and sisal) was in the range of only 0.40 – 0.70 Euro/kg depending on the fiber type (Müssig & Carus 2007). Natural polymers are biodegradable lignocellulosics with very high strength than the glass fiber. Moreover, they are regenerative (Sun *et al.* 2004). New avenues of novel materials may be opened by blending natural polymers with synthetic polymers to reduce the dependence on petroleum byproducts and synthesize the low-cost based composites with light weight and improved properties profile. These biocomposites have many applications in the field of medicine, drug delivery, implant materials, composites for vehicles, housing, flooring, etc.

There are many research works devoted to the natural fibers reinforced composite materials. Okubo *et al.* (2005) used microfibrillated cellulose fiber in polylactic acid (PLA) to increase fracture toughness and bending strength so that they can be applicable in biodegradable housing of vehicles. Wang *et al.* (2008) also reported enhancement of mechanical properties by water bamboo husk (agricultural waste) in PLA matrix. Krishnaprasad *et al.* (2009) introduced high thermomechanical properties (such as transcrystallinity) in poly(3-hydroxybutyrate) (PHB) by addition of bamboo fibers. The comparative reinforcement of jowar, sisal and bamboo fibers were studied by Prasad *et al.* (2011), who concluded higher effect of jowar fiber for flexural properties of the composites. Tensile properties were comparable between jowar and bamboo fibers. Earlier, Holbery *et al.* (2006) had overviewed the low-cost based composites of polyhydroxyalkanoates (PHA), biodegradable polyesters and polyols matrix with natural fibers for the automotive manufacture.

In the line of those studies on natural fibers based composites materials, in this work, locally available fibers of *Agave americana* (Nepali name: Ketuki) were blended with thermoplastic polymers such as ethylene-1–octene copolymer (EOC) and isotactic polypropylene (iPP). The effect of the fibers in different concentrations was analyzed for morphology and mechanical properties of the composites.

Methodology

The polymer used in this work was ethylene-1–octene copolymer (EOC), a commercial product of Dow Chemical Company (trade name Affinity EG 8150). The melt flow index (MFI) was 0.5 g/10 min and melting point was 80 °C. The second polymer used as matrix was isotactic polypropylene (iPP) received from Shazand (Arak) Petrochemical Corporation (commercial name Moplen HP 648S) whose melt flow rate (MFR) is 35 g/10 min (230 °C/2.16 kg) and melting at 171 °C.

Extraction of Ketuki fiber (KF) from *Agave americana* was performed by underground composting for 15 days. It was washed properly under flowing water. The white shining long fiber obtained was dried, cut into pieces, approximately 2 cm long and powdered using grinding machine. The powder of the fiber was sieved through filters with different pore sizes. For preparing the composites, the flour with particle diameter 60 – 120 ìm were used. The fibers have been varied as KF in the following discussions.

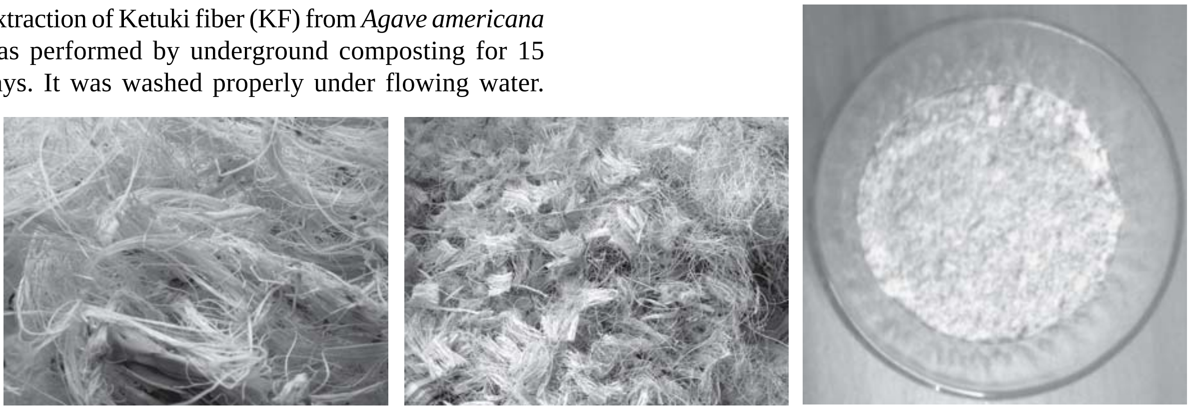

(a) (b) (c)

Fig. 1. Photographs of a) raw sisal fibers, b) chopped threads and c) seived powder

Composite preparation

The calculated amount of polymer and fiber were mixed using an internal melt mixing (Brabender Plasticorder) at 90 °C and torque of 50 rpm for EOC composites. The iPP composites were prepared at 180 °C and 50 rpm. The composites contained 5%, 10% and 20% weight of filler. The ingredients were mixed for 10 minutes inside the mixture for preparing any of the compounds. Then the composites were compression molded into 1 mm thick plaques using following conditions: (i) EOC based composites: 120 °C, 110 bar pressure for 4 minutes; (ii) iPP based composites: 180 °C, 110 bar pressure for 4 minutes.

Characterization methods

Electron Microscopy: The morphological characterization of the composite was performed using scanning electron microscope (SEM) JSM 6300 (JOEL). On the cryofactured surface a thin film of gold was sputter-coated to avoid surface charging. Images were collected in secondary electron (SE) mode.

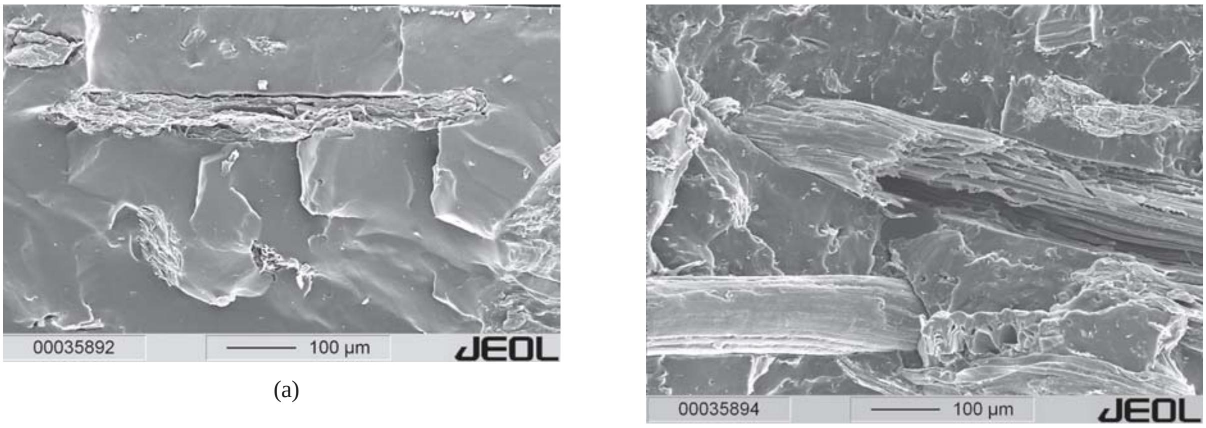
Tensile Testing: Dog-bone shaped tensile specimens (cut from compression molded plates) having total length of 75 mm and width of 4 mm of the parallel part (specimen type 5A) were subjected to strained according to ISO 527 using a Zwick Z020 universal tensile machine (Zwick/Roell Co., Germany) at crosshead speed of 50 mm/min and room temperature (23 °C). At least 5 experiments per sample were performed.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis of the samples were performed on the composites using TGA /SDTA 851 equipment (Mettler-Toledo) under the atmosphere of dry nitrogen from 30 °C to 900 °C.

Results and Discussion

Morphological characterization

The SEM micrographs of the EOC/KF composites with different compositions are presented in Fig. 2. At low filler concentration (Fig. 2a), strips of fibers located horizontally to the micrograph plane can be seen. The length of the strips lies in the range of 100 – 400 µm while the width is approximately 60 µm (Fig. 2a). Careful examination of the micrograph in Fig. 2a makes it evident that there is a gap between the filler and the polymer matrix. This observation implies the absence of filler–matrix bonding in the composite which may have negative effect on mechanical properties.



(a)

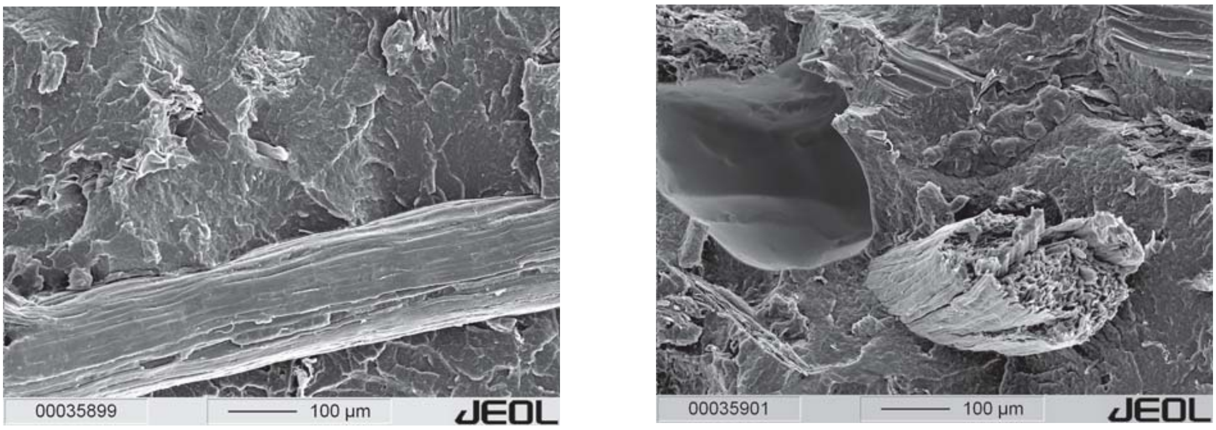
(b)

Fig. 2. SEM micrographs of EOC/KF composites comprising various amount of filler: a) 5 wt.-% KF and b) 20 wt.-% KF

Fig. 2b. depicts the higher concentration (i.e., 20 wt-%) of filler in EOC/KF composite. The micrograph of the cryo-fractured surface manifests inhomogeneous distribution of the filler. Some of the stripes of fiber tear off during cryofracturing. Fibers are located horizontally as well as in the micrograph plane. The length of the fiber is more than 600 µm and the width is approximately 100 µm. There are a number of micro-pores on the cryofactured plane (shown by dark likes on the micrographs). These features could have been produced due to the pull out of fibers from their position during the fracture process. Some of the fibers are projecting out from the examination plane. There is also a gap between the matrix and fiber which may contribute to the worsening of mechanical properties of the composites.

The SEM micrographs of composite of iPP/KF composites are shown in Fig. 3. The micrograph of lower concentration of filler in composite shows the non-uniform distribution of the filler. The fibers in the iPP matrix are very much incompatible as in the case of EOC/KF composite. Even the fibers are found to undergo slip during cryofracturing, (see Fig. 3a). There is much more gap between the matrix and filler in the iPP based composites than in the corresponding EOC/KF composites. The fiber lengths are more than 700 µm and the fiber width is in the range of 120 µm. There are many cracks that can be seen on the micrograph surface. This again leads to the deterioration of the mechanical properties of the composite.

The SEM image of 20% fiber in iPP/KF composite (Fig.



(a)

(b)

Fig. 3. SEM micrographs of iPP/KF composites comprising various amount of filler: a) 5 wt.-% KF and b) 20 wt.-% KF

3b) shows that examined fracture surface is rough. Moreover, the fiber surface is rough with many complex layers. There are many holes or depressions, some 300 µm in diameter, formed by pulled out fibers. The micrograph plan has many deep boars of fibers due to slip out during cryofracturing. The bored holes are in the range of 10 µm to 300 µm width. The matrix is too incompatible to fiber such that the mechanical strength can be lowered significantly compared with the EOC/KF composites.

Thus, in the absence of compatibilizers, both of the matrices (i.e., EOC and iPP) are incompatible to fibers. The hydrophobic nature of matrix and hydrophilic fibers do not form any bonds with each other in the composites. This result supports the deterioration of mechanical properties to be discussed later.

Mechanical properties characterization

The stress–strain plots of pure EOC and EOC/KF composites are shown in Fig. 4a. It is well-known, that the pure EOC behaves like a thermoplastic elastomer where its rubbery nature can be easily recognized by the typical S-shaped stress–strain diagram. The EOC does not show distinct yield point. As it can be seen in Table 1, the tensile modulus E_t and tensile strength σ_M are 10.5 MPa and 16.5 MPa, respectively, whereas the strain at break ε_B is about 800 %.

On addition of KF, the tensile property gets deteriorated which is manifested at the reduction in both tensile strength and strain at break. The deterioration of the properties increases as the weight percentage of filler increases. Thus, final elongation at break is observed at a strain of about 400 % and a stress of 4.5 MPa on addition of 20 wt.-% filler, which is one-third to half of the values of the neat EOC (see Fig. 4a & Table 1). However, in comparison, KF exhibits a clear reinforcing effect on EOC indicated by an increase in modulus up to two fold (i.e., 21.4 MPa for EOC with 20 wt.-% KF, see Table1). Interestingly, for all EOC composites the rubbery nature of the matrix material remains still visible and their stress–strain diagrams fall to the same line (except in the small-strain range). This behavior is due that there is no contact between filler and matrix whereby the particles including their surrounding gaps act as holes all the more the higher the tensile strain is. As a result, one the one hand, the reinforcing effect of the fibers is countervailed and, on the other hand, reduction in strain at break is induced.

Fig. 4b clarifies the dramatic decrease in tensile property in iPP/KF composite in comparison to EOC/KF

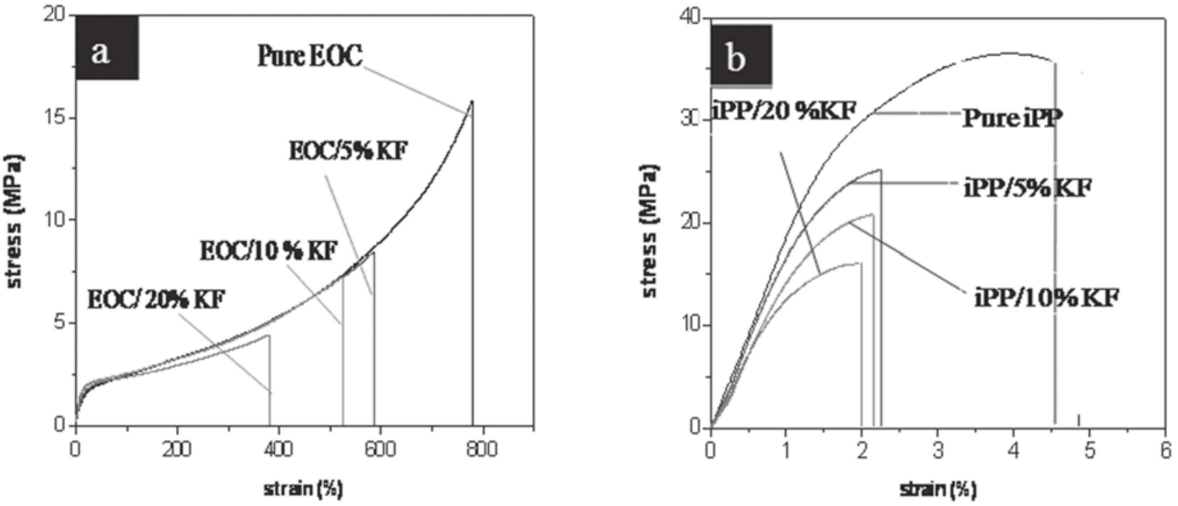


Fig. 4. Tensile stress–strain curves of the composites: a) EOC/KF composites and b) iPP/KF composites

Table 1. Mechanical parameters of the EOC materials

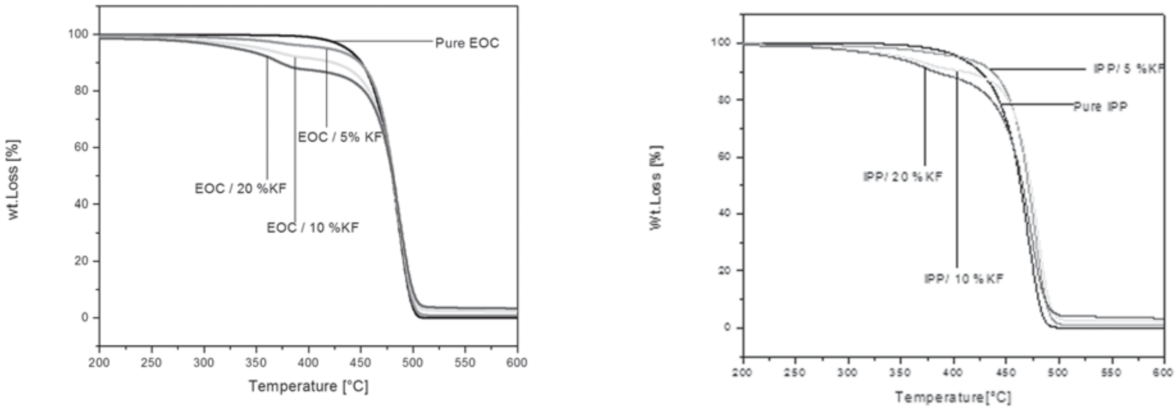
Filler fraction (wt.-%)	Tensile strength σ_M (MPa)	Elastic modulus E_t (MPa)	Strain at break ε_B (%)
0	16.5±2.1	10.5±0.4	782±29
5	8.7±0.9	13.9±0.5	591±34
10	7.3±1.5	18.3±1.2	520±80
20	4.5±0.4	21.4±1.8	381±22

composite due to the addition of filler. Generally, all iPP materials behave a brittle behavior. Pure iPP breaks on elongation when stress and strain are 36.1 MPa and 4.1%, respectively. The addition of only 5 wt-% of KF reduces the stress level to 25.2 MPa and that of the strain to 2.3%. By further addition more KF the tensile properties are further worsened. This worsening of property of the composites is well supported by the SEM micrographs, which demonstrated the incompatibility of matrix and filler (see Figs. 2 & 3). Based on fracture mechanics analysis, the critical length a_c of cracks $\{a_c \sim 1/\pi\cdot(K_{Ic}/\sigma_M)^2$, K_{Ic} – fracture toughness$\}$ inducing embrittlement {for iPP: $a_c \sim 0.9 – 1.1$ mm, with $K_{Ic} = 60 – 67$ MPa·mm$^{1/2}$ (Arencon & Velasco 2009) and $\sigma_M = 36.1$ MPa (this work)} is in the order of the maximum length of the fiber–matrix gap. Furthermore, in contrast to EOC composites no reinforcing effect in tensile modulus is visible; the modulus decreases by addition of KF as well.

As a consequence of the results of both the morphological and mechanical characterisation future work will concern in compatibilizing the composites by using maleic-anhydride modified iPP or EOC matrix polymers, as it has been done for iPP/wood composites in the study of Hristov *et al.* (2004), by the way of example.

Thermogravimetric analysis

The results of thermogravimetric analysis of the EOC/KF composites (i.e., the plot of mass loss versus temperature curves) are shown in Fig. 5a. The thermograms recorded at temperatures between 200 – 550 °C are analyzed.



(a) (b)

Fig. 5. TGA curve of the composites: a) EOC/KF composites and b) iPP/KF composites

As evident in Fig. 5a, pure EOC starts to degrade at 420 °C and degrades completely at 510 °C. EOC/KF composites show two peak temperatures for degradation. The first one corresponds to the degradation of the KF and the second corresponds to the EOC. EOC/5 % KF composite starts its first degradation at early temperature around 300 °C showing first transition at 370 °C, sharply degrades in second transition at 450 °C and decomposes completely at 510 °C with approximately 1% of residual mass. Similarly two phase degradation processes can be seen in EOC/10 % KF and composite burns up completely at 510 °C with 5% residual mass. EOC/20% KF composite also shows first degradation transition at 370 °C, second sharp degradation transition at 475 °C. Between two transition states, composite burns up to 15% of its weight and completely degrades at around 500 °C with 7 % residual mass. Similar behavior is exhibited by the composites of iPP with the KF (Fig. 5b).

The general trend of degradation behavior shows that, with addition of filler, the degradation temperature shift towards lower temperature value and with increase in filler content, residual mass also increases when the composite is heated up to over 500 °C.

Two different thermoplastics based composites materials were fabricated using Ketuki fibers (KF) produced from the common plant almost everywhere available in Nepal. The composites could be easily produced, however, showed deterioration in their mechanical properties, and thermal properties. The worsening of properties can be attributed to the formation of weak interface between the polymer matrix and filler. Thus, the future works should concentrate on the use of suitable compatibilizer to enhance the phase mixing at the interfacial region leading to stronger bonding between the components improving the mechanical properties.

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