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TECHNICAL PAPER

Hybridization Effect of Micro Fillers on Mechanical, Thermal and Morphological Behavior of PA66/PP Blend Based Hybrid Thermoplastic Composites

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Abstract This article deals with the effect of hybrid fillers on mechanical, thermal and morphological behavior of hybrid fiber reinforced thermoplastic composite materials. Three material systems were selected: 80 wt% Polyamide66 and 20 wt% Polypropylene (PA66/PP) compatibilized blend as matrix (Blend), 10 wt% short glass fibers and 10 wt% short basalt fibers reinforced blend (BG) and micro fillers (PTFE, SiC and Alumina) filled hybrid composites (BGF). These composite materials were prepared by melt mix method with the help of twin screw extrusion technique. The mechanical properties were studied through tensile, flexural and impact behavior as per ASTM methods. Experimental results revealed that the effect of hybrid fibers enhanced greatly in terms of tensile and flexural behavior. But slight decrease in impact strength was observed. But the addition of micro fillers into hybrid fiber filled composites slightly decreased the strength of the composites. This might be due to the loss of ductility as a result of filler addition. The thermal stability of composites was studied through DSC technique to analyze the degree of crystallinity. But the effect of reinforcements decreased the degree of crystallinity due to loss in enthalpy. Further, the thermal stability of composites was studied through TGA. This study proved that the effect of reinforcement acted as resistance to weight loss of composites at different temperatures. The morphological study of the fractured surfaces of the composites through scanning electron microscope (SEM) images indicated that the fiber pull out and fiber fracture were the reasons for the failure of composite materials.

Keywords Hybrid fibers · Thermal · Morphology · PA66/PP blend · Micro fillers

1 Introduction

Thermoplastic composite materials are preferred over other materials due to their recycling capability, strength to weight ratio, aesthetic appearance, lubricity, light weight, specific modulus and specific strength. Their applications are gaining importance in the field of aerospace, automobile, medicine, sports and also in micro technology. It is very clear from the observation of different polymeric material's performance that performance of homopolymer is not so effective compared to modified homopolymer. Hence, homopolymer needs to be modified. There are three methods to modify polymer: copolymerization, reinforcing with fillers and/fibers and polymer blending. Polymer blending is one of the effective method of polymer modification due to low cost and variable improved properties. Also it is proved that performance of polymer blend is better than the component polymer [1]. Also the mechanical properties of homopolymer can be improved by reinforcing with fibers and/fillers. The modulus and stiffness of composite materials can be improved by the addition of fibers and fillers. Hybridization is a process of adding two or more fibers and or fillers into the base material for effective functioning of composites. The high strength and highly stiffened composites are the results of hybridization.

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The hybrid polymer materials are used in structural applications which require high thermal performance. Lot of research has been made on the effect of fibers and fillers on the mechanical and thermal performance of filled thermoplastic composites. The effect of mica filler and short glass fiber (SGF) on the mechanical and morphological properties of polyamide 6 (PA6) composites was studied by Unal and Mimaroglu [2]. It was observed that the addition of SGF into PA6 improved the tensile and flexural strength of composites whereas, the effect of mica filler on SGF reinforced PA6 composites showed insensitivity to increase in tensile and flexural strength of composites. This might be due to the loss of ductility and also formation of voids. The hybridization effect of SGF and SCF on the tensile properties of polypropylene composites was reported by Fu et al. [3]. It was observed from their study that the effect of hybridization was very sensitive to improvement of tensile behavior of composites. Also, they postulated that hybrid fibers followed the rule of hybrid mixture. Further, the failure strains of hybrid composites were found to be higher than the failure strain of individual fiber reinforced composites. The hardness, tensile strength and impact strength of PA6/SGF composites filled with various solid lubricants were studied by Li et al. [4]. The effect of PTFE, graphite, ultrahigh molecular weight polyethylene and their compounds on the mechanical behavior of SGF filled PA6 composites were studied and reported. The results showed that the graphite addition could increase the tensile strength of PA6/SGF composites, but the material became soft. Further, Graphite/UHWPE complex solid lubricants were effective in increasing the impact strength of the above mentioned composites. The hybrid effect of fibers on mechanical properties of jute/Rockwool hybrid fiber reinforced phenol formaldehyde (PF) composites was studied by ozturk [5]. The results showed that the tensile strength of composites increased up to 42% of reinforcement. Later it started decreasing due to brittle nature. The tensile, flexural and impact properties of jute/PF composites exhibited good trend than rock wool composites. Schneider and Karmaker [6] studied the effect of kenaf fibers and jute fibers on the mechanical properties of polypropylene composites. They reported that jute fibers provided better tensile strength than kenaf fibers. Effect of coconut shell particulates (CSP) on the mechanical properties of roselle fiber reinforced hybrid composites was reported by Navaneethakrishnan et al. [7]. The results revealed that the strength of composites was influenced when the CSP content was 5% in the composite. The flexural strength reached to maximum at the same percentage, later it got decreased due to filler addition. The effect of addition of SiO_2 on the mechanical properties of PBO-fiber filled HDPE composites were studied by Zhang et al. [8]. Surface treated Pbo-fiber exhibited good tensile, flexural and impact strength than non-treated ones. Effect of fiber treatment on the mechanical properties of date palm fiber reinforced PP/EPDM composites was reported [9]. It was shown that the effect of fiber surface modification enhanced the strength of composites than conventional fibers. But the negative trend was observed in terms of impact strength. Mechanical properties of composites reinforced with long glass fibers and mineral fillers were studied by Hartikainen et al. [10]. The results showed that the use of talc as hybrid filler in LGF reinforced polypropylene exhibited better mechanical properties than $CaCo_3$ filled composites. The effect of long glass fibers and particulate fillers on the mechanical behavior of Polypropylene was studied by Hartikainen et al. [11]. It was found that the filler addition had little effect on the crystallization behavior of PP. The addition of glass, carbon and basalt fibers improved the mechanical properties of polymers. The mechanical behavior of PA66/HDPE blends filled with PTFE and copper oxide and reinforced with glass fibers was reported by Palabiyik and Bahadur [12]. It was observed that the addition of SGF enhanced the tensile strength of composites, but the effect of PTFE addition on strength, hardness and ductility was fairly small. The tensile deformation mechanism of polyamide 66/SEBS-g-MA blend and its hybrid composites reinforced with SGF was studied by Jong et al. [13]. It was observed that the volume strain increased as an effect of SGF reinforcement. Morphological studies revealed that debonding of SGF from PA66 matrix created micro voids which were responsible for the cavitation strain in hybrid composites. The mechanical, morphological and thermal behavior of PTT/SCF composites was studied by Run et al. [14]. It is found that the impact strength and tensile strength of composites was improved. But the addition of SCF into composites improved the thermal stability of composites. Similar studies on PTT/ABS/SCF composites were reported by Run et al. [15]. It was reported that the addition of ABS at 5 wt% effectively improved the tensile, flexural and impact strength of composites. Further, reinforcing SCF into the blend enhanced the strength of composites and also the thermal stability of composites. The composite had larger crystallization rate. Negative effect on the same was noticed due to higher SCF reinforcement. The interfacial, mechanical and thermal properties of coir fiber reinforced Polylactic acid biodegradable composites was studied and reported [16]. The best tensile strength for composites was achieved by 20 wt% of reinforcement in the matrix. Further, thermal stability of composites was noticed at about 370 °C which was lower than neat resin. The fiber matrix interface was improved by alkali treatment of coir fiber. The effect of graphene on fire and mechanical performances of glass fiber reinforced Polyamide 6 composites containing aluminum hypophosphite was appreciable. The addition of Aluminium hypophosphate improved the thermal and fire retardant capacity of composites [17].

From the above literature survey, it is clear that for hybridization process only filler and fiber is used. The short glass fibers (SGF) are good in balanced mechanical properties and short basalt fibers (SBF) are good in thermal properties. Fillers such as PTFE, SiC and Alumina can be used in the composites for better wear resistance, hardness and thermal stability respectively. Keeping this in view, PA66 is a high performance polymer and polypropylene is a very good crystalline polymer with high stiffness. The blend PA66/PP is very rarely used as base material for any applications. The Maleic grafted anhydride (MAgH) is used as a compatiblizing agent for blending PA66 with PP. The main objective of this work is to study the combinative effect of SGF and SBF on mechanical, thermal and morphological behavior of PA66/PP based thermoplastic composites. Further, the effect of micro fillers on the aforesaid behavior of hybrid PA66/PP based hybrid fibrous thermoplastic composites has also been studied. Further, morphological behavior of composites has been studied by using SEM photographs of fractured surfaces.

2 Materials and Methodology

The details of materials used in the present study and their source are tabulated in Table 1. The material formulations of present study are also reported in Table 2.

3 Methodology of Fabrication

Polymer PA66 and PP along with fibers and fillers were dried at about 80 °C for 24 h in order to remove hydrolyzing and plasticization effect. Further, the PA66 and PP mixture along with MagH as compatibilizer was mixed in the mixer for uniform mixing. The polymer mixture was then subjected to melt mixing in the twin screw extruder (Make: CMEI, Model: 16CME, SPL, chamber size 70 cm^3). For uniform heating, the temperature maintained in five zones of the extruder barrel was zone1 (220 °C), zone 2 (235 °C), zone3 (240 °C), zone 4 (265 °C) and zone 5 (270 °C) respectively and the temperature at the die was set at 220 °C. The extruder screw speed was set at 100 rpm to yield a feed rate of 5 kg/h. These extrudates were palletized and quenched in cold water. The obtained pellets of blend were once again heated and then mixed with fillers and fibers. In the second step of extrusion, these hybrid micro filled extrudates which were in the form of cylindrical rods were quenched in cold water and then subjected to palleting using palletizing machine. The hybrid micro pallets were subjected to heating to remove moisture if any before injection molding. The zonal temperatures of the barrel of injection moulding machine were zone1 (265 °C) and zone2 (290 °C) and the temperature at the mould was 65 °C. The screw speed of 10–15 rpm with an injection pressure of 700–800 bars was maintained. The injection time and cooling time maintained were 10 and 35 s respectively. The ejection time of 2 s was needed to eject the parts. All the molded parts as per ASTM standards were tested visually and those found defective were rejected for testing.

4 Evaluation of Different Properties of PA66/PP Hybrid Micro Composites

4.1 Mechanical Measurements of PA66/PP Hybrid Micro Composites

The mechanical behavior of PA66/PP hybrid micro composites were presented in terms of tensile strength, flexural strength and impact strength at room temperature (Tables 3 and 4). The tensile behavior of composites was studied as per ASTM D638 at a cross head speed of 5 mm/min using universal testing machine. The specimen dimension for the test is shown in the Fig. 1a. The flexural behavior of composites was tested as per ASTM D790 with a strain rate of 1.33 mm/min using the same universal testing machine. The notched izod impact strength of composites was

Table 1 Details of the materials and their source used in the study

Material	Designation	Form	Size (μm)	Manufacturer	Density (g/cc)
Polyamide 66	PA66	Granules	–	DuPont Co. Ltd	1.14
Polypropylene	PP	Particles	12	DuPont Co.Ltd	.96
Short basalt fibers	SBF	Cylindrical	2–3 mm	Fine organics, Mumbai	2.4
Short glass fibers	SGF	Cylindrical	2–3 mm	Fine organics, Mumbai	2.5
Polytetrafluroethylene	PTFE	Powder	10–12	DuPont Co.Ltd	2.2
Silicon carbide	SiC	Irregular	5–10	Carborundum, India Ltd.	3.21
Alumina	Al_2O_3	Particles	5–10	Aldrich, Bangalore	3.95

Table 2 Material formulations in weight percentage of PA66/PP hybrid micro composites

Composition	Material ID	Weight percentage						
		PA66	PP	SBF	SGF	PTFE	SiC	Al_2O_3
Blend (PA66/PP)	Blend	80	20	–	–	–	–	–
Blend/SBF/SGF	BG	80	20	10	10	–	–	–
Blend/SBF/SGF/PTFE/SiC/Al_2O_3	BGF	80	20	10	10	5.0	2.5	2.5

Table 3 Tensile properties of PA66/PP hybrid micro composites

Properties	Units	ASTM method	Blend	Blend/SGF/SBF	Blend/SBF/SGF/fillers
Max. elongation	mm	ASTM D638	16.46	13.84	11.26
Peak load	N	ASTM D638	1617	2866	1941
Stiffness	N/mm	ASTM D638	98.24	207.08	172.38
Specific stiffness	N-mm^2/kg	ASTM D638	0.91E+08	1.73E+08	1.35E+08
Specific strength	N-mm/Kg	ASTM D638	3.68E+07	5.88E+07	3.73E+07

Table 4 Flexural properties of PA66/PP hybrid micro composites

Properties	Units	ASTM method	Blend	Blend/SGF/SBF	Blend/SBF/SCF/fillers
Flexural modulus	MPa	ASTM D790	2110.2	6968.83	5077.4
Peak load	N	ASTM D790	95.43	199.52	138.33
Max. deflection	mm	ASTM D790	8.43	6.07	5.66
Stiffness	N/mm	ASTM D790	11.32	32.86	24.33

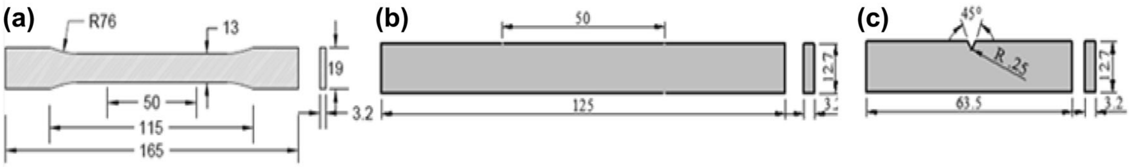

Fig. 1 Specimen standards: **a** ASTM D 638 **b** ASTM D790 and **c** ASTM D256

reported as per ASTM D256 using impact tester with a striking rate of 3.2 mm/s. All the dimensions of the specimen for the tests are presented in the Fig. 1a–c. Along with the mechanical properties, hardness and density of the composites were measured as per ASTM D792 and ASTM D2240. Minimum of three samples were tested and their average results were used for the data interpretation.

4.2 Crystallization and Melting Behavior

The crystallization behavior of PA66/PP hybrid micro composites was studied by using differential scanning calorimetric studies (DSC). The universal V4 .7 TA instrument was used for the study. The temperature range of 30–300 °C was recommended for the analysis. The polymer sample was heated to 300 °C at a heating rate of 10 °C/min under the influence of nitrogen atmosphere. The corresponding scans of the samples were recorded for the analysis. To remove previous thermal history, the sample was held at the same condition for about few minutes and then cooled back to 0 °C. The sample was treated for about 6 min and then its temperature was raised to 300 °C at the same heating rate. The onset, peak and crystallization temperature were recorded from the graph. From this record, the degree of crystallization was calculated with the help of heat of fusion of pristine polymer.

4.3 Thermal Stability Behavior

The thermal stability of PA66/PP hybrid micro composites were determined using Thermal gravimetric analysis (TGA). The temperature range used for the study was 30–800 °C under nitrogen atmosphere at a heating rate of 20 °C/min (Universal Instruments TGA Q50 V 20.13). The thermo grams from TGA showed the temperature at which the maximum weight loss of composites occurred. The derivative weight loss at different temperatures, degradation stage and their temperature were recorded and analyzed by using derivative TGA thermo grams.

4.4 Morphological Studies

The fractured surfaces of PA66/PP hybrid micro composites were studied by using scanning electron microscope (SEM) images. These fractured surfaces were subjected to gold sputtering for the effective conducting layer and scanned using SEM (Joel JSM—480 Microscope). The revealed mechanical properties were justified by using the SEM images.

5 Results and Discussions

5.1 Mechanical Behavior of PA66/PP Hybrid Micro Composites

The variation in tensile strength and elongation of PA66/PP hybrid micro composites are presented in the Fig. 2a. The tensile strength of the blend PA66/PP is 39.78 N/mm^2. But the effect of hybrid fiber reinforcement increased the strength to 70.5 N/mm^2 which is almost 77% increase. This shows the effective compatibility between the hybrid fibers and matrix. The grafted maleic anhydride (MAgH) as a compatibilizer helps in proper miscibility of PP with PA66. This may help to develop the good bonding between the associates of blend. The effect of fiber loading on the strength of micro composites is stronger than the filler addition. It is found from the figure that the tensile strength of the blend increases due to hybrid fiber reinforcement. The hybridization effect of short fibers on the blend enhances the tensile strength of BG composites by 77% [3]. This indicates the effective load carrying capacity of the composites. This is the evidence for the good compatibility between the matrix and the fiber. The mechanism of hybridization is very much significant in modifying the strength of composites. The ultimate strength of SBF and SGF reinforced composites get significantly improved. When hybrid fibers are used in the matrix, the effective mean SBF and SGF lengths decrease. Due to changes in the length of fibers, the strength can be calculated by using the rule of hybrid mixture [18]. From the rule of hybrid mixture (RoHM), it is found that the strength follows a positive deviation from RoHM, hence, positive hybrid effect. The value of interfacial shear stress is maximum at the ends of short fibers [19]. SBF has high stiffness and aspect ratio than SGF, the shear stress is maximum at the SBF ends as per stress transfer theory [20]. Therefore, the interfacial debonding first starts at SBF ends. Hence SBF acts as source of defects which in turn promotes micro cracks. As the stress increases, the cracks develop along the length of SBF and also across the surrounding matrix. The strong SGF acts as a crack arrester due to hybridization effect and supports SBF to improve the strength of composites. Therefore, the synergistic effect of hybridization improves the tensile strength of the studied composites.

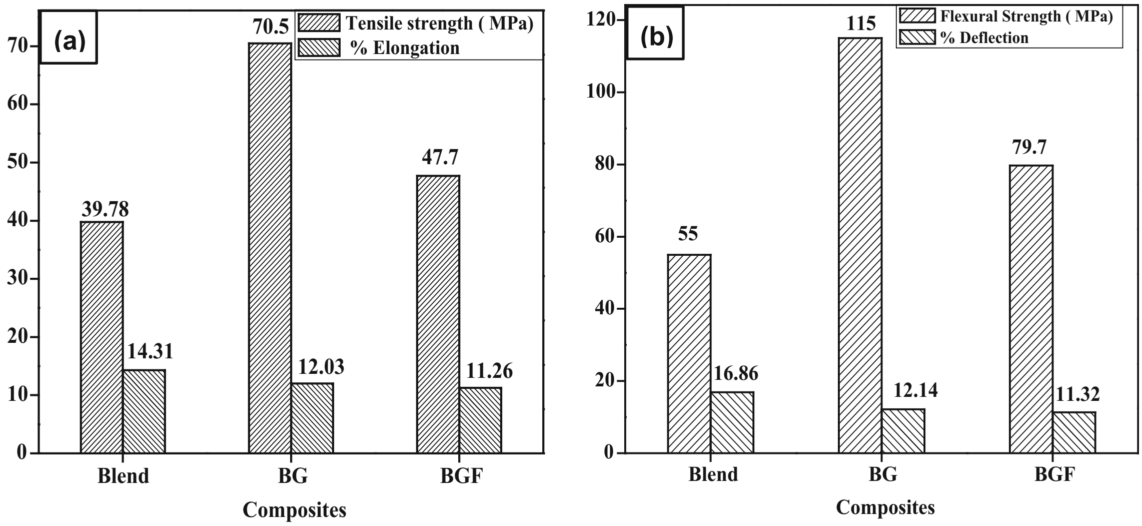

Fig. 2 Mechanical properties of PA66/PP hybrid micro composites: **a** tensile strength and % elongation and **b** flexural strength and % deflection

The tensile strength of micro composites (BGF) decreases below the value of BG composites but shoots above the value of blend as a result of filler inclusion. 20% increase in tensile strength and 32% decrease against the blend and BG composites are exhibited by BGF composites. The aspect ratio, length of fibers and modulus of fibers get enhanced effectively the strength of BG composites. The coated short fibers develop the interfacial bond between the fibers and matrix. But the BGF composites exhibit the tensile strength higher than the blend. This shows that the micro fillers has good compatibility with fibers and the matrix in the composites which facilitate the better load transfer to reinforcement phase and thus improve the strength of BGF composites higher than the blend [4]. It has been found that decrease in ductility is noticed due to the fiber reinforcement. This may be due to the effect of brittle nature of BG composites. Almost 16% decrease in ductility is shown by BG composites over blend. On the other hand, effect of micro fillers on hybrid fiber reinforced blend shows the ductility loss of 21% against neat blend and 7% against BG composites. This may be due to the immobilization of macromolecular chains due to multiphase reinforcement. This may increase the brittleness of composites [21]. The SBF and SGF when mixed with micro fillers, cracks may develop along the length of the fibers and also in the neighboring matrix. These cracks are filled by these micro fillers. This can enhance the strength of composites above the neat blend. In addition, the fillers act as stress barriers.

The flexural behavior of PA66/PP hybrid micro composites is shown in Fig. 2b. It is found that there is a significant improvement in flexural behavior due to the effect of hybrid fiber reinforcement. The hybrid fiber effect improves the flexural strength from 55 to 115 N/mm^2 which is a 114% increase. The inclusion of hybrid micro fillers into BG composites decreases the flexural strength. But the effect of hybrid fillers decreases the flexural strength of composites by 36%. This is mainly due to the effect of loss of ductility of composites. The hybridization effect of micro fillers creates voids in the composites, which results in loss of load carrying capacity. The stress can be easily transferred from the fibers to the matrix. The effect of micro fillers establishes the weak bond between the fibers and matrix in the composites. Even though, the synergistic effect of hybrid micro fillers and fibers develop good interfacial adhesion between the blend associates, the geometrical adoptability of fillers with fiber and matrix is not much compatible. This may decrease the flexural strength of the composites. Also, the flexural strength of composites depend on the shape of fillers, adhesion between associates of the composites and the surface area of the fillers in contact with other fillers.

The hybrid composites show the brittle fracture and follow the linear deformation at low stress and non-linearity later due to high stress (Fig. 3a). The hybridization of fibers causes the catastrophic crack propagation through the matrix pulling out fibers from matrix. Hence, the curve shifts from right to left (BG). But, the addition of micro fillers further increases the brittleness of composites. Hence, the loss of ductility shifts the curve of BGF composites to the right of BG composites and to the left of blend. Due to addition of fillers, the voids increases in the system. This may results in loss of load carrying capacity of BGF composites.

The deflection due to flexure is moderate. Practically there is no change in flexural deformation between BG and BGF composites (Fig. 3b). The decrease in flexural strength of BGF composites is due to the loss of effective area which is a result of the formation of voids and geometrical non adoptability of fillers and fibers. This is an indication of synergistic effect of multiphase reinforcement on PA66/PP blend composites. The loss of ductility due to the effect of micro fillers decreases the load carrying capacity of BGF composites. The same trend is noticed in flexural behavior also.

The impact strength and hardness of multiphase reinforced micro composites are shown in Fig. 4a. The effect of hybrid fiber reinforcement decreases the impact strength from 60 to 44 N/mm^2. Further, the addition of micro fillers into BG composites still weakens the impact strength. The BG composites under impact load can absorb more impact energy which results in the promotion of impact strength than BGF composites. This is due to hybrid fibers' effect. Whereas, the addition of micro fillers reduces the geometrical adoptability of fibers with the matrix. This may lead to overlapping of fibers and agglomeration of fillers which may create voids in the system. The non-resin zones which act as a void can contribute to the formation of stress concentration zones [22]. Another reason for the degradation of impact strength is the loss of ductility due to filler addition. This reduces the deformation ability of matrix and also ductility in covering area there by forming weak composite structure [21]. The energy absorption capacity of matrix has been made weak by the addition of micro fillers there by reducing the toughness of the material. Hence, impact strength decreases. PA66/PP blend itself is crystalline in nature. Further reinforcing fillers into composites increases the crystallinity of composites. This has a tendency to make the material brittle. Hence, this leads to increased hardness and loss of impact strength. The density of fiber filled composites is more than the blend. Further, addition of fillers into BG composites improve the density of BGF composites (Fig. 5b). This is due to the hard fibers' and fillers' effect. Hard fillers and fibers can enhance the density of composites. But, the theoretical density and the

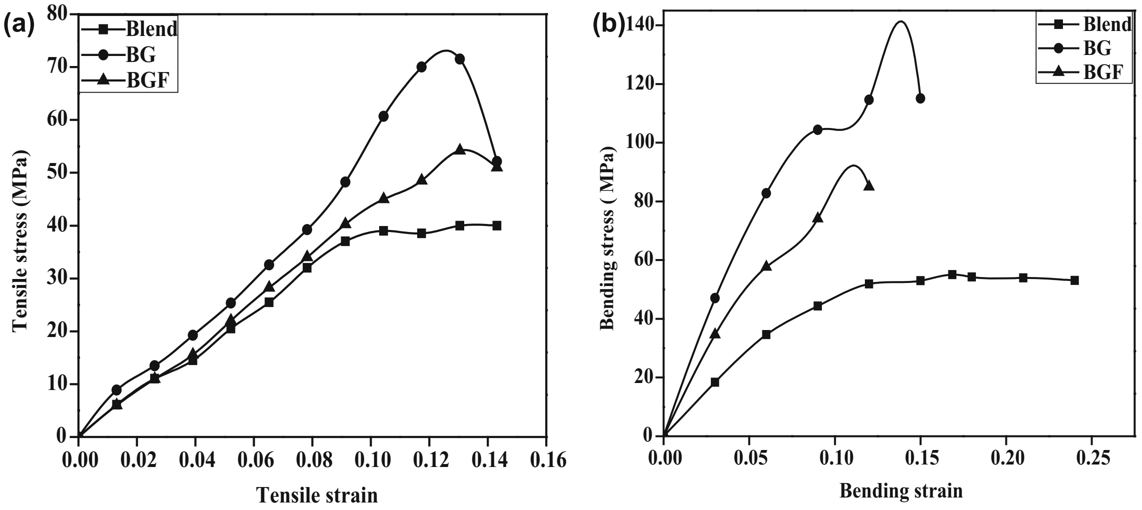

Fig. 3 Stress strain curve of PA66/PP hybrid micro composites: **a** tensile test and **b** flexural test

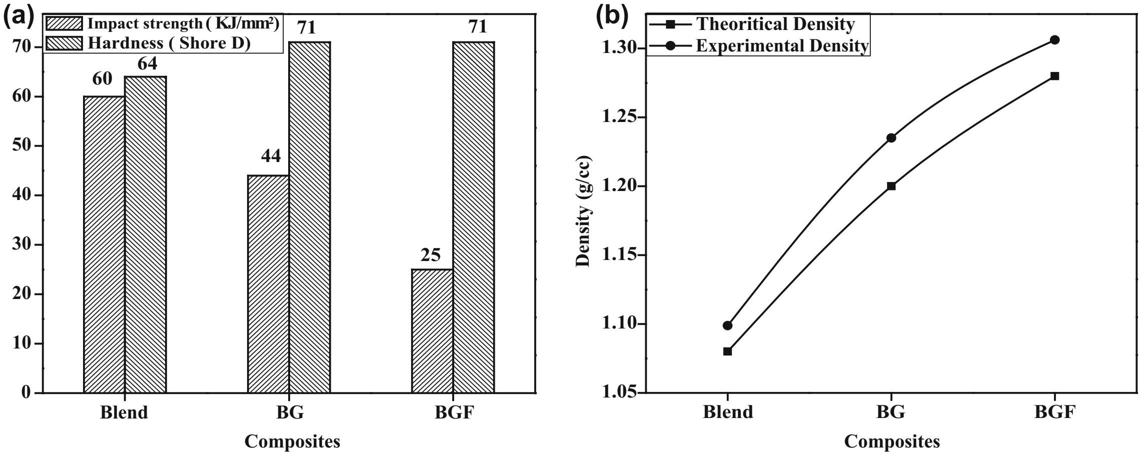

Fig. 4 Mechanical properties of PA66/PP hybrid micro composites: **a** impact strength and **b** density

experimental results show that the acceptable void fractions are exhibited by blend and their micro composites.

The hardness of PA66/PP hybrid micro composites is shown in the Fig. 4a. The hardness of composites is slightly increased as an effect of fiber reinforcement into the blend. The hard fibers and fillers enhance the hardness of the blend. As a result of filler addition, no change in the hardness of composites is noticed. Among the studied composites, BG composites exhibit good mechanical properties. But the effect of hybrid micro fillers decreases the strength of composites.

5.2 Crystallization and Melting Behavior (DSC)

The effect of heating on crystallization behavior of PA66/PP hybrid micro composites has been studied through differential scanning calorimetric studies (DSC) (Fig. 5a). The DSC thermo grams of studied composites are shown in Fig. 5a. The DSC studies helps to estimate the melting temperature (T_m), crystallization temperature (T_c), enthalpy of melting (ΔH_m) and degree of crystallanity. The details of DSC studies of micro composites are tabulated in the Table 5.

The degree of crystallinity has been calculated by using the following formula:

$$\text{Degree of crystallanity, } (X_c) = \frac{\Delta H_m}{\Delta H_m^*} \times 100.$$

where ΔH_m = enthalpy of composite, ΔH_m^* = enthalpy of pure crystalline base polymers.

The DSC studies of PA66/PP blend based composites are very much significant because of two step decomposition. The first step is due to the decomposition of Polypropylene. The degree of crystallinity remarkably

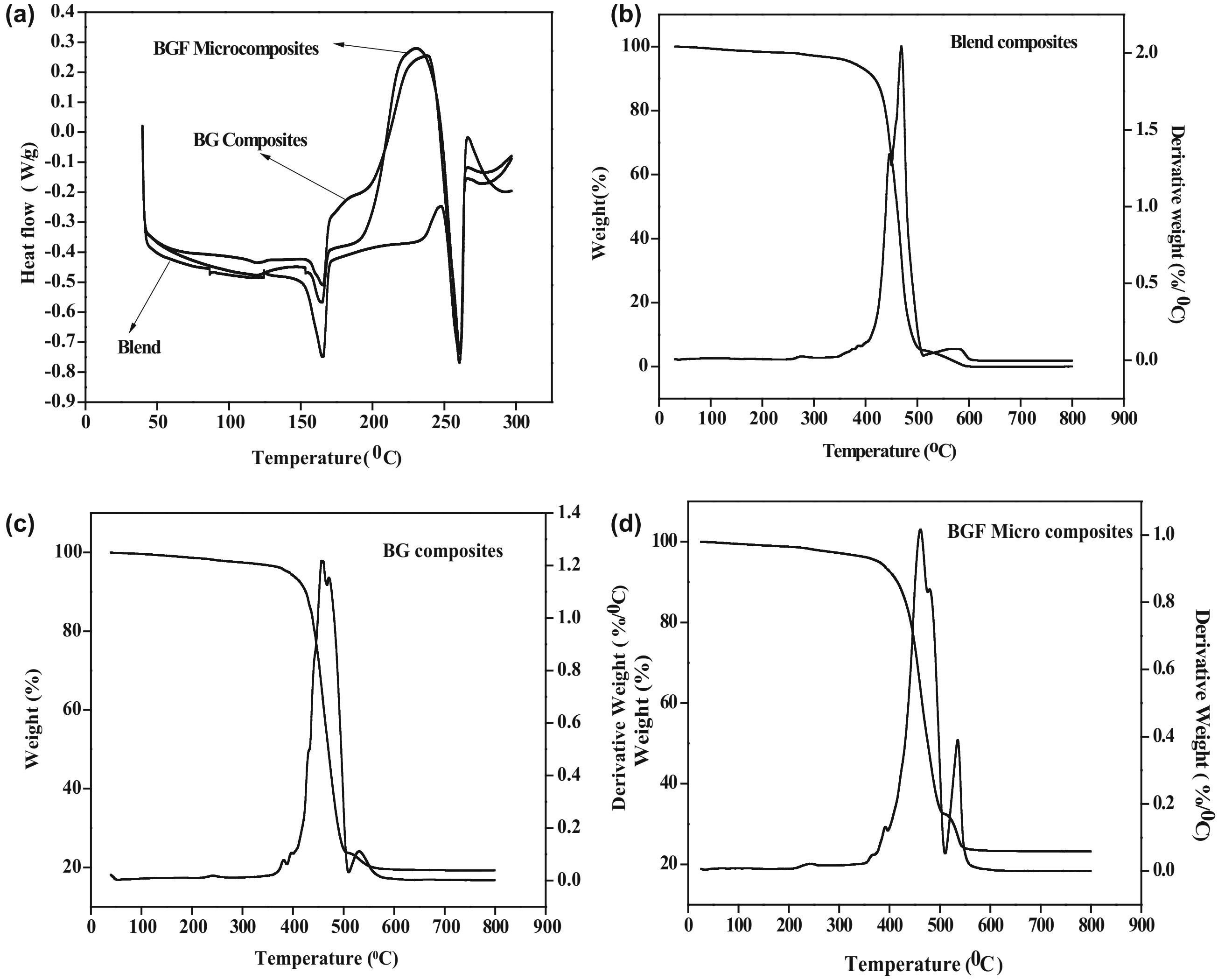

Fig. 5 Thermal properties of multiphase reinforced PA66/PP based micro composites: **a** DSC thermo grams and TGA and derivative thermo grams of **b** blend **c** BG and **d** BGF composites

Table 5 Thermal data obtained from TGA thermograms of multiphase reinforced PA66/PP hybrid micro composites

Composites	Temperatures (°C)			ΔH_m (J/g)	Crystallanity (%) (X_c)	Temperatures (°C)			ΔH_m (J/g)	(%) (X_c)
	T_o	T_m	T_c			T_o	T_m	T_c		
Blend (PA66/PP)	145	153	178	18.09	8.73	247	250	266	35.64	18.18
BG	153	155	174	8.29	4	237	246	268	47.8	24.38
BGF	151	153	172	7.736	3.73	232	248	266	37.08	18.91
The heat of fusion value for 100% crystalline PP is 207 J/g						The heat of fusion value for 100% crystalline PA66 is 196 J/g				

decreases due to addition of short fibers into the blend when PP is considered for the study. The hybrid effect of short fibers decreases the crystallinity of the composites by almost 50%. Further, decrease in the degree of crystallinity is noticed due to effect of micro fillers. The study reveals that there is a significant change in the microstructure of blend due to the effect of multiphase reinforcement [14, 23]. The enthalpy of melting, ΔH_m is proportional to the degree of crystallinity. The ΔH_m of pure blend is 8.73 J/g at the melting temperature. But the fiber reinforcement decreases the ΔH_m. Further, the effect of micro fillers on BG composites still decreases the value of ΔH_m. This is obviously expected due to decrease in X_c of the multiphase reinforced composites. The change in crystalline temperature is noticed during the study. Similar observations have been made when Polyamide 66 is considered for the analysis. Basically, PP, the crystalline polymer after decomposition adds up to the crystal nature of composites. Due to the addition of short fibers, there is a slight increase in crystalline temperature. The enthalpy of fusion also increases. But the effect of hybrid fillers declines the crystalline temperature and decreases the heat of fusion which results in decrease in degree of crystallinity. It is evident from the study that the micro structure of composites significantly changes due to the effect of multiphase reinforcements.

5.3 Thermo Gravimetric Analysis (TGA)

TGA of multiphase reinforced PA66/PP micro composites are studied and their thermal data was recorded in the Tables 6 and 7. TGA thermo grams and their derivative curves of the studied composites are shown in Fig. 5b–d. The TGA curves show two step degradation for all the composites tested. For the whole sample of composite tested, the thermal decomposition is completed at a temperature range of 658–799 °C. The weight loss of the composites is restricted beyond 799 °C in the operating range up to 800 °C. The weight loss due to the moisture content is spanned in the temperature range from 50 to 300 °C. The gradual weight loss of composites due to the loss of matrix contents of composites is observed in the temperature range from 352 to 520 °C [15, 23]. The weight loss occurring in the thermal range of 510–653 °C is the second stage decomposition. The weight loss in this zone is due to the thermal degradation of PA66.

The decomposition of blend starts at 329 °C and reaches almost 100% at 799 °C. The different temperatures at which the weight loss of composites (0, 10, 20, 50% and maximum) occurs are recorded and are tabulated in Table 6. The temperatures (T_0, T_p and T_c) corresponding to the respective degradation stage are noted and tabulated in Table 7. The tabulation shows that the addition of short fibers resist the weight loss of composites at higher temperatures. Also, the micro particulate effect further acts as a barrier for the weight loss of composites at higher thermal zones [14, 23]. This study suggests that the composites are thermally stable in nature.

6 Morphology of PA66/PP Hybrid Micro Composites

The SEM images of fractured surfaces of mechanical tests of BG composites are shown in Fig. 6a–c. The tensile fracture surface images of hybrid fiber filled composites are shown in Fig. 6a. It is found from the figure that the major cause for the failure of composites is due to fiber pull out. It is clear that the fiber and matrix interface is good and hence have good tensile strength. The fiber pull out impressions are clearly seen in the figure. It is observed that the fiber delamination also occurs. The flexural failure of fiber filled composites is shown in the SEM images of Fig. 6b. It is evident that the fiber fracture is the main failure mechanism associated with flexure. Also, it is witnessed that the matrix deformation is much higher than others. Also, fiber delamination is seen in the figure. This may lead to the formation of resin free zone which acts as voids. A network of chain structure of fillers and fibers are also seen. This may help the composites to possess good flexural strength. The SEM images of impact fracture of hybrid fiber filled composites are shown in Fig. 6c. The degree of crystallization is more for the fiber filled composites. Due to the effect of hybrid fibers, agglomeration of fibers is seen. But the degree of compatibility between the fibers and the matrix seems to be good. The SEM picture displays the brittle nature of composites. Due to the brittle nature, impact strength decreases due to the loss of ductility.

Similar observation is made for the composites filled with micro fillers. The SEM micrographs of fracture surfaces of BGF composites are presented in the Fig. 7a–c. The tensile fracture surface image is presented in Fig. 7a. It is observed from the figure that the fiber pullout impressions are more when compared to BG composites. But the synergistic effect of fillers is seen through the interfacial interaction between fillers and the matrix. Still the material remains brittle as an effect of filler addition. The flexural failure of the surface is presented in Fig. 7b. This shows severe matrix deformation. But the layer wise structure is

Table 6 Thermal data obtained from TGA thermo grams of multiphase reinforced PA66/PP composites

Composites	Temperatures at different weight loss (± 2 °C)				
	0%	10%	20%	50%	Maximum
Blend	338	418	438	461	613
BG	346	425	442	470	583.87
BGF	330	416	442	476	627

Table 7 Thermal data obtained from derivative TGA curves of multiphase reinforced PA66/PP composites

Composites	Degradation stage and their thermal behaviors					
	Stage-I			Stage-II		
	T_o	T_p	T_c	T_o	T_p	T_c
Blend	338	469	514	514	574	612
BG	345	457	510	510	531	583
BGF	330	461	510	510	536	627

T_o onset temperature, T_p peak temperature, T_c crystalline temperature

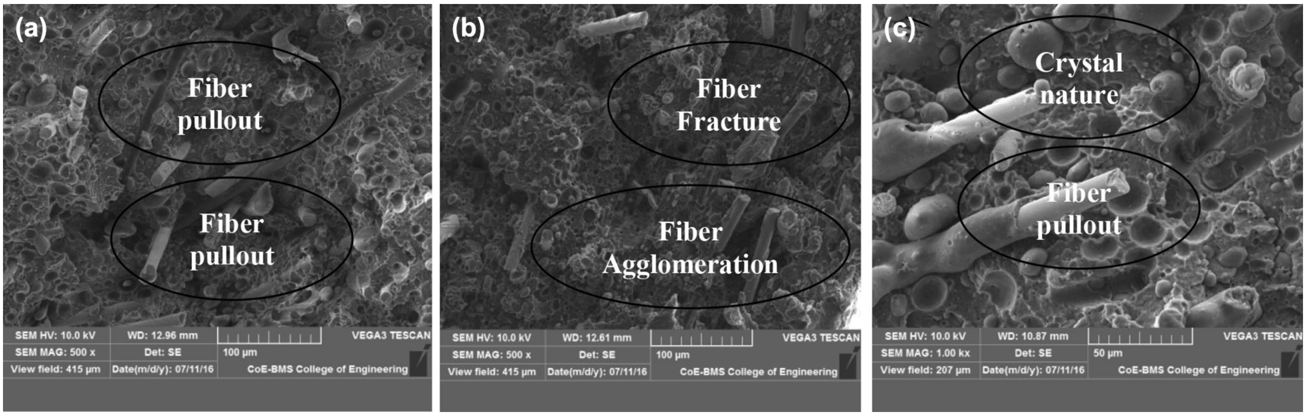

Fig. 6 SEM photographs of fractured surface of 10 wt% SGF and 10 wt% SCF filled 80/20 wt% PA66/PP blend: **a** tensile fracture, **b** flexural fracture and **c** impact fracture

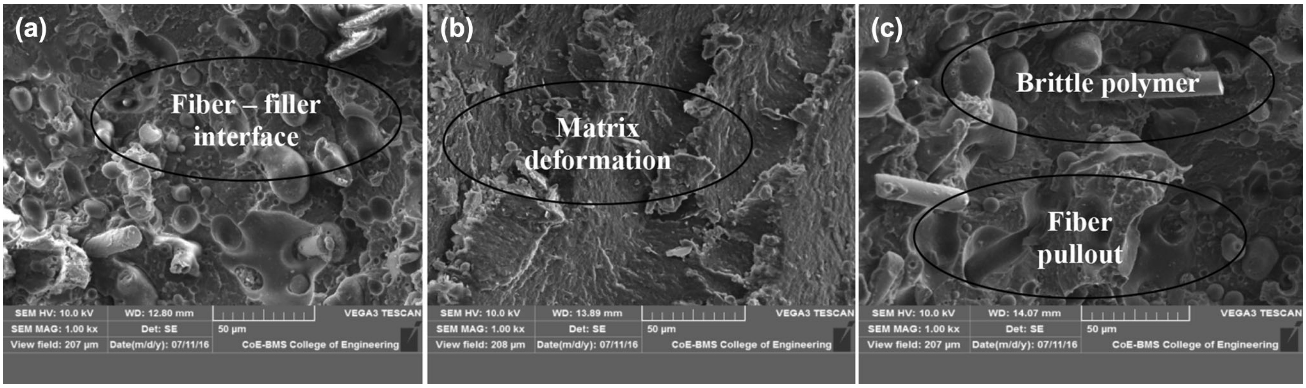

Fig. 7 SEM photographs of fractured surface of 10 wt% SGF and 10 wt% SCF filled 80/20 wt% PA66/PP blend with fillers: **a** tensile fracture, **b** flexural fracture and **c** impact fracture

noticed as a result of deformation. This is mainly due to the effect of filler addition. These fillers increase the adhesion between the fibers and matrix and hence good flexural strength. But the void occurrence in these zones is less. The impact failure through SEM image of BGF composites is presented in Fig. 7c. The loss of ductility is clearly shown in the Fig. 7c.This can be witnessed by the presence of more number of voids and also deep cracks in composites. The brittle nature of material results in the loss of ductility. Severe matrix deformation along with micro fillers is seen in the figure. This SEM picture witnesses the presence of good bonding between the fillers and matrix. But the high degree of crystalline nature of composites results in loss of impact strength of composites.

7 Conclusions

1. The mechanical behavior of hybrid fiber reinforced composites (BG) exhibited excellent mechanical properties.
2. The loss of ductility was noticed due to the effect of fiber reinforcement.
3. The effect of micro fillers on mechanical properties was most appreciable.
4. The hybrid effect of micro particulates deteriorated the mechanical behavior of fiber reinforced composites. But the strength of BGF composites was higher than blend.
5. The incorporation of hybrid fibers into the blend improved the thermal stability of composites (BG).
6. Hybrid effect of micro filler enhanced the thermal resistance of advanced composites (BGF).
7. The degree of crystallanity decreased as a result of multiphase reinforcement during first decomposition and later it got increased due to an effect of fiber reinforcements.
8. The heat of fusion was obviously proportional to the degree of crystallanity.
9. Morphological studies showed that the failure of composites was due to fiber fracture, fiber pullout and severe plastic deformation of matrix.

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