Role of graphene nanoplatelets and carbon fiber on mechanical properties of PA66/thermoplastic copolyester elastomer composites

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Abstract

In this work, the effect of graphene nanoplatelets (GNPs) on the physico-mechanical properties of short carbon fiber (SCF) reinforced polyamide 66/thermoplastic copolyester elastomer composites was investigated. The composites were fabricated with extrusion followed by injection molding method. The host matrix, fiber plus host matrix and graphene nanoplatelets loaded hybrid composites were examined for density, hardness, tensile, flexural and impact properties according to the governing ASTM standard. Fiber reinforcement decreased void content to < 1 % but GNPs were able to keep void content under limits. Hardness and impact strength augmented with 2 wt. % graphene nanoplatelets loading, owing to superficial dispersion developing the relationship between the hardness and impact strength. Graphene nanoplatelets loading benefitted the tensile property. However, the same has a deteriorating effect on flexural strength. Flexural modulus increases until 2 wt. %. Improvement in mechanical properties upon GNPs loading is very feeble when compared to the enhancement with SCFs loading to the host. Upon comparing the properties, it was observed that 2 wt. % of graphene nanoplatelets performed admirably and was recognized as an optimum filler loading. Morphology of fractured surfaces was studied by analyzing the scanning electron microscope images to understand the various features and mechanisms.

1. Introduction

The requirement for composite material development is proliferating day by day in the field of marine, automotive, construction, aerospace, defense, bio-medical applications and so on due to its exorbitant strength to weight ratio, thermal and visco-elastic behavior [1–3]. The corporate average fuel economy regulations restrict vehicles to use more fuel. So reduced component weight makes the vehicle lighter leading to fuel economy [4]. Fiber-reinforced polymeric composites are very popular in the afore-mentioned technical fields. Among the polymers sets, the thermoplastics have a wide advantage when compared with the thermosets such as reusability, simple and short processing time and environmental effects.

Polyamide66 (PA66) is an aliphatic polymer that is derived out of amide monomer (–CONH–). PA66 is recommended for applications at an operating temperature ranging from 120 °C to 150 °C without losing their property, this is because of their crystallinity [5]. In recent years, there is a lot of research that is being carried out on PA66. PA66 has got an obligable mechanical properties which makes it feasible to use it in applications like carpets, cloth coating, fishnets, sportswear, tyres, and belts to advanced aerospace components [6, 7]. Hence, in the current investigation, PA66 was chosen as a primary matrix material. Alongside, all these preliminary investigations, a few kinds of literature were found on examining the degradation and effect of moisture on PA66 [8–10]. Recent progress in the polymer sector is to blend two or more polymer of similar chains to attain the benefits of both the polymers [11–14]. Kelnar et al modified the PA6 with ethane-propene elastomer and
reinforced with graphene oxide (GO) and revealed that the material system demonstrated increased strength, stiffness and toughness [15]. There are only a few researchers who worked on thermoplastic copolyester elastomer (TCE) composites [16–20]. TCE has found its applications in flexible couplings, gears, coverings for wire and optical fiber cables [21]. Hemanth et al. studied the properties of TCE and polyoxymethylene filled polytetrafluoroethylene (PTFE) [22]. TCE is a novel material which is a cross-linked polymer having a stable property within its operating temperature range [22]. There is a potential need for exploring the potential of TCE. Hence, this study investigates TCE as secondary matrix material along with the PA66 which was opted to improve the ductility and also owing to a very feeble amount of literature.

The polymers of different nature will not blend properly in their molten phase which makes them unproductive upon cooling. Hence, stable compatibilization is essential. Maleic anhydride is the most widely used compatibilizer used to get good miscibility between polymer/polymer blends and polymer/polymer/reinforcement blends. There are many well discussed literature on use of the polymer grafted maleic anhydrides [23–27]. Palabiyik and Bahadur observed the swelling of polymers during fabrication when compatibilizer was not used [28].

The mechanical strength of the host/alloying polymer alone is not sufficient to use it for end applications. So fibers and fillers have to be incorporated to improve its properties. To improve the mechanical properties, fiber reinforcements such as glass, carbon, aramid, basalt were incorporated with the polymer matrix/alloy were found in various literature [29–33]. The short fiber reinforcements are the bridge to mechanical properties between the conventional fabric composites and neat matrices [34]. Short carbon fibers (SCFs) has got high mechanical stiffness, thermal and electrical properties. Zhao et al. have done a comparative study between the SFGs and SCFs on mechanical and tribological properties and concluded that SCFs are better in both aspects [35]. Fu et al. have proved that tensile property enhances with an increase in the volume fraction of SCFs [36]. Saleem et al. have discussed the electrical and thermal conductivity of SCFs filled polymers and concluded the enhancement in both the properties [37]. Zhang et al. have discussed the benefits of the SCFs with tribological properties with SiO₂ and graphite fillers in a polyimide matrix [38]. Rezaei et al. have evaluated the properties of SCFs reinforced polypropylene (PP) composites for car bonnet applications [39]. There is a potential need to explore the behavior of SCFs with the two-phase matrix. In the present investigation, SCFs were chosen as primary reinforcement with PA66/TCE alloy to study their role on mechanical properties.

To further improve the mechanical properties, nanoparticles were reinforced in matrix or fiber/matrix material combination. Generally, nanoparticles used are montmorillonite, carbon nanotubes, SiC, graphene, graphite nanoflakes, SiO₂, Fe₃O₅, carbon nano-wires and so on [40–46]. There are lot of research works published regarding incorporating fillers with PA [47–50]. There are rigorous studies being performed on the carbon-based nanomaterials [49–56]. The graphene possesses very high thermal conductivity, tensile strength and modulus making it necessary to use it with polymers. One more literature studied the thermal, mechanical and rheological behavior of graphene nanosheet/PP composite but not GNPs [57]. Incorporation of lower wt. % of graphene nanosheet into PA6/acylonitrile butadiene styrene (ABS) blends, improved the tensile strength significantly [58]. However, there is a need for such studies on the mechanical properties of graphene with thermoplastics. There is a potential need for work to be carried out regarding the mechanical properties of PA66 + TCE blend with GNPs.

This research investigation aims to seek the role of SCFs and GNPs and the dispersion of SCFs and GNPs in significantly enhancing the mechanical properties of the newly framed two-phase matrix material combination (PA66/TCE). The efforts have put in this study to discuss the role of MAPE in improving interfacial adhesion. The mechanical properties such as density, hardness, tensile, flexural and impact strength were investigated according to the governing ASTM standards.

2. Materials and methods

2.1. Materials

PA66 and TCE were procured from DSM India Pvt. Ltd. Pune, India. The density of PA66 was quoted to be 1.14 g cm⁻³ and TCE to be 1.29 g cm⁻³. The combination of PA66 and TCE was used as the matrix material. PAN-based carbon fibers (SIGRAFIL), which were sized with polyurethane material, were supplied by Fine organics, Mumbai, India. Sizing mass content on carbon fiber was 2.7 % by wt. Short carbon fiber content in composites was kept constant at 20 % by wt. The material data as per the manufacturer (SIGRAFIL) are as follows: diameter 7 μm, length 100 μm. weight density 1.80 g cm⁻³, tensile strength of 4000 MPa, tensile modulus of 240 GPa and elongation at break was 1.7 %. The secondary reinforcements were selected to be GNPs, were procured from Sigma Aldrich Ltd, India. The GNPs were structured of 3–6 layers. The density of the material was 0.2–0.4 g cm⁻³. The available surface area was 750 m² g⁻¹.
2.2. Fabrication

The hybrid composites were fabricated with the employment of extrusion followed by an injection molding process. The twin-screw extruder was used for the process (Make: CMEI, Model: 16CME, SPL, Chamber size of 70 cm³). The PA66 and TCE were blended with a proper agitation in a known proportion with the help of 2 wt. % of polyethylene grafted maleic anhydride (MAPE) as a compatibilizing agent to blend matrix material. The matrix material thus prepared was again mixed thoroughly along with the SCFs and GNPs in a high-speed mechanical stirrer, followed by preheating to a temperature of around 160 °C for 4 h. Selected compositions were mixed and extruded in Brabender co-rotating twin-screw extruder. The twin screw extruder chamber consists of five heating zones to heat the material to melt mix uniformly. The L/D ratio of the screw was 40:1. The mixing speed of 100 rpm was maintained for all the compositions. The temperature maintained in all these zones were 220, 230, 245, 260 and 270 °C respectively. The ingredients were mixed while passing through different melt zones by a rotating screw, and finally extruded out as strands through hardened steel die. The extrudates were cooled with water and chopped by pelletizer to get PA66/TCE blend composite pellets. The obtained composite pellets were dried in an oven at preheating temperature of 160 °C for 4 h.

The dried pellets were fed to the injection moulding machine (Make: DGP Windsor, 50 Ton). The solid pellets were transferred from hopper to nozzle of molding machine by rotating screw through different zones with a temperature profile of 190 °C, 230 °C and 260 °C respectively. The steel mold temperature was 70 °C. The melt was injected to the steel mold and cooled to obtain the various mechanical test coupons as per ASTM standards. Table 1 presents the description of the composites and total weight of the composite prepared. Figure 1 portrays the fabrication process in transitory.

2.3. Test procedure

The examination of the physico-mechanical properties was initiated with the density test. The specimens were cut to 6 mm × 6 mm × 3.5 mm. The density was measured using Mettler Toledo, model AX205 balance in accordance with the Archimedes principle. The experimental density and the theoretical density were calculated and compared to get the total void content in the composites. The experimental density of the specimens was

| Sl. No. | PA66 (wt%) | TCE (wt%) | SCFs (wt%) | GNPs (wt%) | Total Weight of composite (g) | Designation |
|--------|------------|-----------|------------|------------|------------------------------|-------------|
| 1      | 75 (3750 g) | 25 (1250 g) | —          | —          | 5000                         | SR-1        |
| 2      | 80 wt% SR-1 (4000 g) | 20 (1000 g) | —          | —          | 5000                         | SR-2        |
| 3      | 79 wt% SR-1 (3950 g) | 20 (1000 g) | 1 (50 g)   | —          | 5000                         | SR-3        |
| 4      | 78 wt% SR-1 (3900 g) | 20 (1000 g) | 2 (100 g)  | —          | 5000                         | SR-4        |
| 5      | 77 wt% SR-1 (3850 g) | 20 (1000 g) | 3 (150 g)  | —          | 5000                         | SR-5        |

Figure 1. Fabrication process employed in the present investigation.
tested abiding by the procedure mentioned in ASTM D 792 [59]. The average of five readings was considered as the experimental density of the respective composites.

The Shore-D hardness test was exercised to seek the hardness of the composite. ASTM D 2240 was the governing standard for the test [60]. The Durometer was indented at various locations (minimum at 20 indentation points per specimen) on the composite (three specimens in each series) to get the collective results.

The tensile test was more habitually performed on the flat and dumb-bell shaped specimen. The dimensions of the specimens were 70 mm × 12 mm × 3.5 ± 0.05 mm. The test was accomplished using Kalpak Instruments 100 kN UTM at the crosshead speed of 5 mm min⁻¹ according to ASTM D 638 at 23°C. Five specimens were tested to affirm the results [61]. The load versus displacement curve was obtained to find the modulus.

The flexural test was performed according to ASTM D 790 [62]. The test length employed was 60 mm, a width was 12 mm and with a thickness of 3.5 ± 0.05 mm. The crosshead speed was maintained to be 1 mm min⁻¹. The tests were carried out at 23°C. The load versus deflection curve was obtained to find the flexural modulus. Five specimens were tested to affirm the consistency in the value.

Impact test was performed on Avery Duison impact tester according to governing ASTM D 256 standard [63]. The dimensions of the specimens were 60 mm × 12 mm × 3.5 mm. The specimens were notched until 10.16 mm of width was obtained. The hammer was released and the impact was made with the velocity of 3.46 m s⁻¹. Five specimens were tested to affirm the value.

The above said mechanical tests have repeated for five times for each series of specimens and the mean of the results have been considered for discussion.

3. Results and discussion

3.1. Dispersion of reinforcements in composites
The uniform distribution of the constituents of the composite enhances the properties of the material. In this regard, the material SR-5 was analyzed for the proper dispersion of the SCFs and GNPs because it has the highest amount of GNPs included in it. Figure 2(a) portrays the SEM micrograph of the SR-5 composite. To analyze the dispersion of the constituents, the element mapping with the help of energy dispersive analysis of X-rays (EDAX) has been done. Figures 2(b)–(d) show the element mapping of carbon, oxygen and nitrogen. The density of the carbon is very high and the high density can be attributed to the presence of GNPs, SCFs and carbon in polymer chain. However, the density of oxygen and nitrogen are relatively lesser. The oxygen is present in the polymer.
chains of PA66, TCE and MAPE. The nitrogen can be traced only in the polymer chain of PA66, hence the element density is still lesser when compared to that of oxygen. The density of the oxygen and nitrogen at the center is lesser because we can observe the GNPs and a few SCFs which reflects on to the carbon mapping. The uniformity in the carbon mapping can be taken as a witness to affirm the good dispersion. Bijwe et al have employed the similar procedure to analyze the element mapping of wear surface [64]. Zhou et al has discussed the uniform distribution using the element mapping of porous graphene in polyaniline composites [65].

### 3.2. Void content in composites

The voids in the composites are inevitable because of the challenges in the fabrication process. The theoretical density to experimental density comparison has a percentage deviation called void content. The density calculated theoretically and measured experimentally are tabulated in Table 2. Figure 3 shows the pictorial representation of the voids in the composites. The density of the SR-2 is greater than the SR-1 because the density of the SCFs is higher than the host matrix. Similarly, densities of SR-3, SR-4 and SR-5 are lesser in relation with SR-2 because GNPs replaces by the amount equivalent to wt. % of matrix blends. The void content is the number of empty spaces in the composites under study. The theoretical density is greater than that of the experimental density. Upon observation, the percentage of void content in hybrid composite has less void than the SR-1. The nano-sized GNPs have a capability of filling the voids to some extent. However, with GNPs inclusion, the void content increased, because the GNPs may form aggregates and these aggregates when come closer creates the empty space restricting the polymers flow into them leading to void. The void content have severe effects on the flexural modulus and impact strength which is discussed in this article in the further sections. Jeong has proved experimentally the decrement in interlaminar shear strength with void content [66].

| Specimen | Theoretical Density (g cm$^{-3}$) | Experimental Density (g cm$^{-3}$) | Void Content (%) |
|----------|----------------------------------|-----------------------------------|------------------|
| SR-1     | 1.174                            | 1.15                              | 2.04             |
| SR-2     | 1.262                            | 1.254                             | 0.634            |
| SR-3     | 1.236                            | 1.223                             | 1.052            |
| SR-4     | 1.211                            | 1.196                             | 1.238            |
| SR-5     | 1.188                            | 1.172                             | 1.346            |

Figure 3. The void content representation in the composites.
Zhu et al have investigated the effect of void content on the tensile property and found that tensile strength decrease with an increase in void content [67].

3.3. Hardness of composites
The composites were tested for the hardness on Shore-D scale. The circular plate of 100 mm in diameter was cut out of composite to measure the hardness values. The indentations were considered at 20 different locations, keeping the specimen on the flat table. The arithmetic mean of the hardness was considered for the discussion.

The hardness of the composites increased with filler loading till SR-4 but for SR-5 hardness value decreases. However, the hardness value of SR-5 is collectively higher than the SR-1, SR-2 and SR-3. Figure 4 shows the variation of hardness for different composite specimens. The host SR-1 has 60 shore D hardness number, with SR-2 the hardness increased by 8.33 %, with SR-3 hardness increased by 21.66 % finally with SR-4 the increment was about 30.55 %. Even though the hardness of SR-5 reduced in accordance with SR-4, the value is still greater than SR-3. During indentation on the thermoplastics, the region of indentation undergoes plastic deformation hence, the hardness of the hybrid composites is dictated by the amount of dispersion of reinforcements in the matrix material. The dispersion makes fillers and fibers available for the indentation and offers resistance to the indentation.

Suresha et al observed the increase in the surface hardness of the PA66/PP composites and concluded that the uniform distribution of the fillers and fibers was one of the reasons responsible for the higher hardness than the matrix and at the time of indentation the matrix, fibers, and fillers together will offer resistance for the compressive load of the Durometer [68].

As the percentage of GNPs increases, there is a probability that GNPs concentration at the surface and at the core of composite is different. A similar discussion was found in the work by Liu et al [69].

3.4. Tensile properties of composites
The purpose of incorporating reinforcement is to enhance mechanical properties. The SCFs and GNPs have served the purpose which can be observed in figure 5. Upon incorporation of SCFs alone, tensile strength was increased by 131.14 % with respect to SR-1. Similarly, the tensile strength showed an increasing trend with GNPs loading. The highest value of tensile strength was observed in SR-5. The percentage increment was about 144.4 % with SR-1 and 5.66 % with SR-2. However, a tensile property is not concluded without considering Young’s modulus. The modulus of SR-2 was increased by 168.54 % in accordance with SR-1. The GNPs incorporation also led to an increase in Young’s modulus. Young’s modulus of SR-5 in relation to SR-1 had increased by 189.1 %. However, the increment of 7.66 % was identified when compared SR-5 with SR-2, this was not as significant as observed with SR-1. At a lower percentage of GNPs loading, GNPs acted as space fillers and property was boosted by a small amount. With GNPs loading there was an improvement in tensile strength and modulus. However, even at the 3 wt. % loading of GNPs we observed the mild enhancement in the properties. These findings are in correlation with the findings of earlier investigations [58, 70–72]. Tang et al have discussed the reason for a feeble improvement in the tensile property. Firstly, the weak interfacial interaction of graphene...
with a polymer. Second, the structure of graphene which has weak Van der Waals force of attraction and lastly, the curvature effect of graphene loaded in the polymers \[73\]. The improvement in tensile property is due to the substantial filler dispersion and firm interfacial adhesion between reinforcements and elastic matrix \[74\]. As the reinforcements/matrix adhesion increases the effective load transfer happens to the reinforcements through the matrix. The fibers generally will have highest strength among matrix/fiber combination and graphene has also proved it’s strength as a promising filler to improve the properties \[50, 51\]. Cai and Song discussed that effective stress transfer leads to improvement in properties \[52\]. However, the good dispersion will reduce the void content which increases the availability of the surface to distribute the applied load uniformly. Similarly, the uniformity in the dispersions can be found in the section 3.1. The sudden increment in the tensile strength and modulus can be attributed with a reason that SCFs have higher strength and higher modulus upon combining with the matrix beneﬁts to increase the strength. Fu et al have compared the tensile property of polypropylene (PP) with both SCFs and SGFs. They also studied the effect of fiber loading and concluded that with an increase in fiber loading the tensile strength will increase \[30\]. Rezaei et al have also proved that the strength of SCFs reinforced PP composites is guided by the SCFs loading \[39\].

The elongation at fracture for various composites are depicted in figure 6 for SR-1 is 24.44 mm. It is evident from figure 7 that for about first 6 mm displacement duration there was a linear trend with loading and the matrix started to elongate without significant enhancement in load. At this stage, the predominant elastic nature increases in the longitudinal dimension with a decrement in lateral dimension. Further, with the inclusion of 20 wt. % SCFs the elongation decreased drastically from a value of 24.44 mm to 9.618 mm. However, with GNPs loading, the value started achieving a consistent decrement. Finally, for SR-5 the elongation at fracture was 7.252 mm. The GNPs loading has reduced the elasticity leading to the brittleness of the hybrid composites.
Deshmukh and Joshi have attributed that the inter flake shear strength and inter flake stress transfer was responsible for the decrement in elongation at fracture and increment in other tensile properties [74]. From figure 7 it is clear that upon adding the SCFs and GNPs to SR-1, elastic nature was reduced and the brittle nature was predominant making them fail at a lower value of elongation with increase in load carrying capacity. The encircled part was exaggerated and shown on the right segment of figure 7.

Figures 8(a)–(c) depict the scanning electron microscope images of tensile fractured PA66/TCE blend and their composites. It can be noted from figure 8(a), that the fragmented layers can be observed with the PA66 matrix material during separation, however, inclusion of TCE with PA66 resulted in the formation of fibrils and enhanced the ductility of the PA66/TCE blend under tensile loading. Conversely, it failed to withstand the higher tensile load, which is evident from figure 7. chains of SCFs resulted in a significant improvement in the tensile strength of SR-2 composites. Further, the presence of MAPE as compatibilizer has provided fair interfacial adhesion of polymer and the fiber resulting in the increase in tensile strength and modulus of the composite. Few fiber pullout and TCE fibrilar structures can be noticed in the figure 8(b) of SR-2 composite.

Inclusion of 2 wt% GNPs has improved the tensile properties very marginally. Good interfacial adhesion between the polymers and the fibers and very few fiber pullout can be witnessed in figure 8(c). This has made the SR-4 composite to exhibit better tensile properties in the study group.

3.5. Flexural properties of composites
The composites were examined under a three-point bend test. Figure 9 shows the variation in flexural strength and flexural modulus. The unfilled blend i.e. SR-1 had a very low flexural strength and modulus, but upon the incorporation of the SCFs, the flexural strength and modulus was increased by 370.7 % and 494.45 % respectively. However, GNPs were not beneficial in improving flexural properties. The integration of GNPs enhanced the brittleness of the hybrid composite as observed in figure 10. From figure 11 we can observe a few fiber pullouts and fiber de-bonding in SR-4 which is not observed with SR-2. These also collectively affects the strength of the material under the flexural loading. Sheshmani et al have employed the GNPS with PP and wood flour and found the decrement of the flexural strength beyond 0.8 wt. % and quote it to be the limiting value for incorporating GNPs [75]. One more reason that can be attributed is the percentage void content in the specimen which definitely have a role on governing flexural strength. Liu et al have experimentally determined that the void content affects the tensile, flexural and inter laminar shear property [69].

Flexural modulus improved with GNPs loading up to 2 wt. % and decreased at 3 wt. % even though the flexural strength was under decrement. The flexural modulus was increased by 494.45 % in SR-2 in accordance with SR-1. The loading of GNPs though increased modulus, the increment was not as substantial as increment between SR-1 and SR-2. The increment of 2 % between SR-2 and SR-3, 10.99 % between SR-2 and SR-4 and 7.67 % between SR-2 and SR-5. The results are somewhat correlated with the finding of Julia et al [76]. Sheshmani et al got similar results, the flexural modulus of 1 wt. %, 2 wt. % 4 wt. % and 5 wt. % is greater than that of unfilled PP/wood flour composites [75]. From figure 10, we can easily find the reason for the increment in the flexural modulus even though there is a decrement in the strength. The slope is more for SR-4 than any
other composites. Hence, the modulus turns out to be the highest. It was observed while testing, all the specimens except SR-1 were fractured. The spring-back effect was observed with SR-1 whereas, rest of the specimen fractured affirming the fact that the incorporation of the fiber and fillers will lead to brittle failure.

**Figure 8.** SEM images of tensile fractured PA66/TCE composites, (a) SR-1, (b) SR-2 and (c) SR-4.

**Figure 9.** The variation of flexural strength and flexural modulus of the composites.
Surface morphology of the specimens failed due to threepoint loading are depicted in figure 10. Good interfacial adhesion between the polymers and the fiber reinforcements can be witnessed over the SCF surface as indicated in figures 11(a), (b). When the material is affected by external force, the matrix can transfer it effectively to the interface between fibers and matrix and lead to the increase of the flexural strength and modulus of the composites. This has resulted in higher flexural strength and modulus of SR-2 and other hybrid composites compared to SR-1. The SR-2 composite had shown the better flexural strength in the study group, however inclusion of 2 wt. % GNPs in SR-4 composite had demonstrated the better modulus in the study group. The presence of GNPs cannot be witnessed with the lower magnification as indicated in figure 11(b).

3.6. Impact strength of composites
The specimens were tested to determine their ability to absorb the impact energy during the propagation of the crack. Figure 12 shows the impact strength of composites. It is a well-known fact that the utilization of fillers will enhance the impact resistance of the material. Eventually, we observed the increased impact strength in SR-4 and suddenly decreased at SR-5. The impact strength increases from 27.08 kJ m⁻² to 46.64 KJ m⁻² with SCFs reinforcement to PA66/TCE. The loading of GNPs led to increment in impact strength. This increment can be attributed for superior dispersion of GNPs within the composite. This restricts the crack flow in the direction transverse to the fiber. The decrement in the impact strength with SR-5 might be due to the formation of GNPs clusters. The results of the impact strength can be related to the void content also. Yang et al have shown the improvement in the impact strength of the poly(arylene ether nitrile) composite even till 20 wt. % of the GNPs employed [77]. However, we can see that the 3 wt. % GNPs have reduced impact strength which means 2 wt. % is
the optimum loading with the present material system. Sreekala et al have discussed that impact properties depend on the interfacial and inter laminar strength and further discussed that at higher fiber loading fiber-fiber contact increases leading to higher impact strength [78]. Similarly, in short fiber composite system, we can improve fiber-fiber contact by considering GNP s in the composite material combination. This Fibers and fillers interaction led to enhancement in strength by paving no avenue for the crack to propagation. Suresha et al have discussed that interfacial areas provided resistance for the crack propagation [68]. Hemanth et al discussed that the longer chain polymers have higher impact strength than particle filled composite as fillers act as a stress concentration zone which eventually curtails the impact strength of the composites [79].

Figures 13(a)–(c) depicts the SEM images of impact failed samples of SR-1, SR-2 and SR-4 composites. Traces of TCE, TCE fibrils and separation TCE can be witnessed in figure 13(a) of SR-1 composites. Inclusion of 20 wt. % SCFs has enhanced the impact strength of SR-2 composites. Good interfacial adhesion between matrix and SCF is evident in figure 13(b). Fiber pullout indicates the subsequent energy absorption and dissipation by the matrix to the fiber on application of impact load. Further, inclusion of 2 wt. % of GNP s has significantly increased the impact strength, which is out pacing in the study group. Earlier studies have revealed that the impact properties of polymers can be increased by inclusion of nano sized particles, which reduces the stress concentrations near their edges resulting in consumption of more impact energy for failure. However, GNP s presence could not have been traced with lower magnification of SEM image as shown in figure 13(c).

3.7. Role of MAPE in composite fabrication
In this work, polyethylene grafted maleic anhydride (MAPE) was utilized in 2 wt. % to blend PA66 and TCE uniformly. The anhydride functional group bonds with amide group thereby producing a stable interfacial adhesion with polyamides. PA66 possess the amine group which reacts with anhydride group of MAPE resulting in the formation of co-polymer [80, 81]. In this study, during fabrication process, soft phase material MAPE was blended with PA66 and TCE. Later SCFs and GNP s were introduced to make a quaternary phase material with good interfacial bonding. Similar observation was made by Dayma and Satapathy with PA6 and low density polyethylene grafted maleic anhydride [82]. The MAPE forms a covalent bond with the SCFs surface which enable the fibers adhere to polymers substantially. Youssef et al have observed similar behavior with the lignocellulosic fibers [83]. Also Meng et al reported that the cross-linking of polymers generally improves their properties such as dimensional stability, resistance to thermal deformation, stress cracking, etc. particularly at high temperature [84]. In this work the MAPE employed was beneficial in improving interfacial adhesion between PA66/TCE/SCFs, which improved the mechanical properties. Figure 14 depicts the mechanism involved in blending the two or more polymer by MAPE.

4. Conclusions
In this article, the investigation was performed on mechanical properties of GNP s and SCFs reinforced PA66/TCE composites and portrayed an improvement in mechanical properties upon reinforcement.
Upon incorporating reinforcements with SR-1 the void decreases. It is observed that the void content becomes less than 1 % with SCFs loading. However, the void content starts increasing with loading of GNP s. Increment in void content with SR-3 is 1.66 times the SR-2 and that of with SR-5 is 2.12 times the SR-2.

The hardness of composites in the current study increases with increase in fiber/filler loading. There is 8.33 % increment in hardness between SR-2 and SR-1 and 30.55 % increment between SR-4 and SR-1. The SR-4 specimen showed the highest hardness.

The tensile property showed a drastic increment with fiber loading about 131.14 %, but there was a mild increment in tensile properties with GNP s (SR-5) loading of about 5.66 % with SR-2. The main agenda of this investigation was fulfilled by the SCFs but the expected improvement in the tensile properties was undergone by GNP s loading.

The GNP s loading was not beneficial with the flexural strength point of view because of inherent brittleness that was induced in the material upon incorporation of GNP s. There was a huge increment in the flexural strength by 370.7 % and modulus by 494.45 % with SCFs loading alone. Even though the GNP s failed to enhance the flexural strength it continued to enhance modulus by 10.21 % in relation with SR-2.

Figure 13. SEM images of tensile fractured PA66/TCE composites, (a) SR-1, (b) SR-2 and (c) SR-4.
Impact strength of the hybrid composites (SR-4) is almost 2.5 times that of the SR-1 and 1.4 times of the SR-2 presenting a superficial crack resistance. A direct relationship can be developed between the hardness and impact strength.

It is notable that SR-4 performed excellently among all the combinations of the composite which can be considered as the best suitable filler loading for the fiber and matrix combinations considered. However, the improvement in the mechanical properties of the PA66/TCE with SCFs were substantial but GNP-filled hybrid composite though managed to improve properties further, it failed to portray the enhancement as it was expected during the formulation. MAPE was found to be beneficial for enhancement in interfacial adhesion which is in good agreement with past literature.

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Conflicts of Interest

The authors declare no conflict of interest.

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