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Comparative Study of the Electrical, Thermal and Mechanical Properties of Polypyrrole/VGCNF and Copper Nano Powder Reinforced Polyester Hybrid Composites

Asma Iftikhar[1], Sumaira Nosheen[2], Farzana Habib[2], Muhammad Irfan[2], Bilal Waseem[2]

[1]Department of Physics, University of Lahore, Pakistan - 54000
[2]PCSIR Laboratories Complex, Ferozepur Road, Lahore, Pakistan - 54600
sumera_pcsir@yahoo.com

ABSTRACT

The present research work based on Synthesis and characterization of Polypyrrole coated CB (carbon black), Copper, and VGCNF (vapor grown carbon nanofibers) hybrid composite. Two approaches were used comprising in situ polymerization of Polypyrrole/CB composite. The resulting composite was dispersed in with the measured quantity of Cu nano Powder and VGCNF in polyester at very high rate of dispersion to produced hybrid composite. The resulting composites were characterized by FTIR, electrical conductivity, mechanical properties, thermal analysis and UV visible spectroscopy.

Keywords: Polymer, Composite, Hybrid, Mechanical, Thermal

INTRODUCTION

Polymers is a big class of materials have very diversity in nature due to having some unique properties they are helpful in the synthesis of idyllic materials which can have easy processing lightweight, and wanted mechanical properties. Therefore, these high temperature withstanding resins has wide application in aeronautical industry. The main advantage of developing hybrid composites is to enhance the properties of composites and to make them more functional for diversified applications. Several researchers developed hybrid composites and reported improved properties of resulting composites. E.g, raza et al. [1] reported graphite nano platelet /carbon black (CB) /epoxy composites. They reported improvement in mechanical and electrical properties by incorporation of CB. They also reported that the good dispersion and high loading %age of fillers lead to increase the thermal stability.

Nano composites is an extensive class of composites which consist of multiphase solid materials in which at least one component is in nano scale (i.e. in the range of zero to 3D with the length of less than 100nm). Nanocomposites not only show remarkable difference from the conventional materials but also differ from the individual component used in the synthesis of these composites. That's why they show improved mechanical, electrochemical, optical, thermal stability, corrosion protection, enhanced Chromium absorption ability, and many more due to high surface to volume ratio. [2] More over CNTs also effect on the mechanical properties of polymer especially when it dispersed into the polymer matrix to form composite [3, 4]. A polymer nanocomposite is a polymer matrix with a reinforcing phase consisting of particles with one dimension in the nanosized regime. In the past decade, extensive research has focused on polymer nanocomposites in hopes of exploiting the unique properties of materials in the nanosized regime [5-10]. Polymers with extended conjugated carbon¬-carbon double bonds can be named as electrically conducting polymers [4]. In terms of their properties the conducting polymers are recognized as new materials. The first conducting polymer was investigated in nineteenth century. Henry Lethe prepared poly aniline in 1862 by electrochemical method, which not only shows the conduction but also exhibit electro chromic behaviour [11-13]. Poly acetylene as a black powder was synthesized by Natta et al. in 1958 and it was found to be semiconductor with the conductivity ranges from 10 -11 to 10-3 depends upon the process ability of the polymer. [11]. The doped poly acetylene was reported in 1977 as a first ICP [2]. After the preparation of poly acetylene by Sirakawa and coworkers a new field of research was actually launched by the group led by MacDiarmid and Heeger who discovered that the doping method cannot only helps us to increase the electrical conductivity, but also used to monitor the martial properties in response to their electrochemical properties [12]. This electro active class of polymers gains more importance in the field of science when Nobel Prize was awarded in the field of chemistry to Shirakawa and his coworkers in 2000 [11-12]. The composition of any material is very useful to establish the electrical properties in a certain material. The band theory is most useful way to describe the electronic structure of any electrically conducting materials. Quantum mechanism shows that the electrons have quantized energy level which forms bands. The highest and outer most occupied band is called as valance band while highest and the lowest unoccupied levels termed as the conduction bands. These ICPs specially used as hetero junction polymeric materials, polypyrrole coated n-type silicone based solar cells have been synthesized by electrochemical method. Similarly, the electrodes for rechargeable batteries had also been reported [11-17].

The conductivity of these polymers can be enhanced by introducing highly conductive fillers at very high loading as high as 80% by weight with the polymer matrix such as silver, gold and graphite powders to meet the requirements of electronic industry. A part from these benefits, there are copious disadvantages also exist with these polymers for example there high-cost wear and tear environmental stability and many other properties of the polymer [20]. The PP/PPy and PP/CB composites and pure PP were synthesized by melt mixing while pure PPy is prepared by chemical method. They observed that the composites which are synthesized by melt mixing exhibit good electrical properties then the composite which is prepared by the chemical method. More over even the small amount of PPy if introduce in the polymer matrix it is sufficient to enhance the electrical properties of the PP/PPy composite was reported. Hence this property will also be affected by the processing conditions used to synthesize this composite [21].

EXPERIMENTAL SECTION

(PPy was synthesized by using pyrrole monomer (sigma Aldrich). About 8.65ml along with 25ml DI water was taken in the round bottom flask assisted with overhead mechanical stirrer. The mixture was stirred for 10 minutes. Then 2.5M $FeCl_3$ was added drop wise which acted as an oxidizing agent. The polymerization started immediately which was observed from the formation of black particles in the solution. [22]. The weighted amount of the CB was dispersed in the solvent along with continuous stirring. The 25% aqueous ethanol was found to be the most effective solvent for well dispersion of the CB. The solution containing CB was stirred on a disperser machine at the rate of 600 rpm for 20 min and then this solution was ultrasonicated for 30 min. The pyrrole monomers was added into it and disperse for 10min so that monomer diffused onto the surface of CB and 2.5M$FeCl_3$ was added drop wise. This solution was allowed to stir for 24 hours so that the Pyrrole monomer polymerized on the surface of CB. The resultant composite was filtered to remove $FeCl_2$ indicated in the form of green color from the final product by washing it with de ionized water and ethanol, respectively, till the green color discharged. Then finally the filtered composite dried in vacuum oven at 70°C for 10 hours. After drying the yield of the prepared composite was calculated. The same recipe was used for the synthesis of this composite with different %ages of CB (3, 5, 10, 15, and 20 wt %).

Synthesis of PPy /CB with polyester composites

Polypyrrole coated carbon black was mixed with polyester resin by high shear mixer at speed of ~ 6,000 rpm for 10 min. The composites were prepared by mixing PPy coated CB at 3, 5, 7 wt. % ages respectively. After mixing filler in polyester resin cobalt Naphthalate and methyl-ethyl ketone peroxide was added as curing agent and the mixture was immediately poured into custom made moulds for curing purpose. The curing procedure was completed in vacuum oven at room temperature

Synthesis of PPy coated CB/Cu nano powder/polyester hybrid composites

The PPy coated CB and copper powder was dispersed in polyester resin to produce composite. 5% PPy coated carbon black was used for development of hybrid composite. The composites were prepared at 5, 10, 15, 20 wt% of Cu nano powder. The Cu nano powder was dispersed into polyester by high shear mixer at speed of ~ 6,000 rpm for 10 min. The curing procedure is same as described in PPy/CB polyester composite.

Synthesis of PPy coated CB/Cu nano powder/ VGCNF polyester hybrid composites

The PPy coated CB/Cu/VGCNF hybrid composites were produced by dispersing all of these nano fillers in polyester by high share mixing at speed of ~ 8,000 rpm. The time of mixing for each filler was 10 min. The composite was prepared at 5, 7, 10, 12 wt% of VGCNF. Due to high speed of mixing the dispersion temperature increased significantly. This dispersion was then cooled in ice after the mixing of each filler and also prior to the addition of curing agent. The curing procedure is same as described in PPy/CB polyester composites. The pure polyester composite was also prepared by the same method.

RESULTS AND DISCUSSION

The FTIR spectra (Fig 1) show the comparative analysis of pure PPy and PPy/CB composite. The presence of a strong signal at 3612 cm^{-1} is due to the presence of N-H in the pyrrole ring. Composite also shows the same vibration in that region. In the fig 4.1 (b) some new peaks has been noticed in the regions of 500-600 cm^{-1} 2250-3000 cm^{-1} and weak signals also seen in the region of 1000-1400 cm^{-1} which indicated that the polymer has strong attraction with CB due to the presence of some functional groups on the surface of CB. The peaks characterized in the existing work are quite similar with the data presented in literature that confirms the synthesis of polymer.

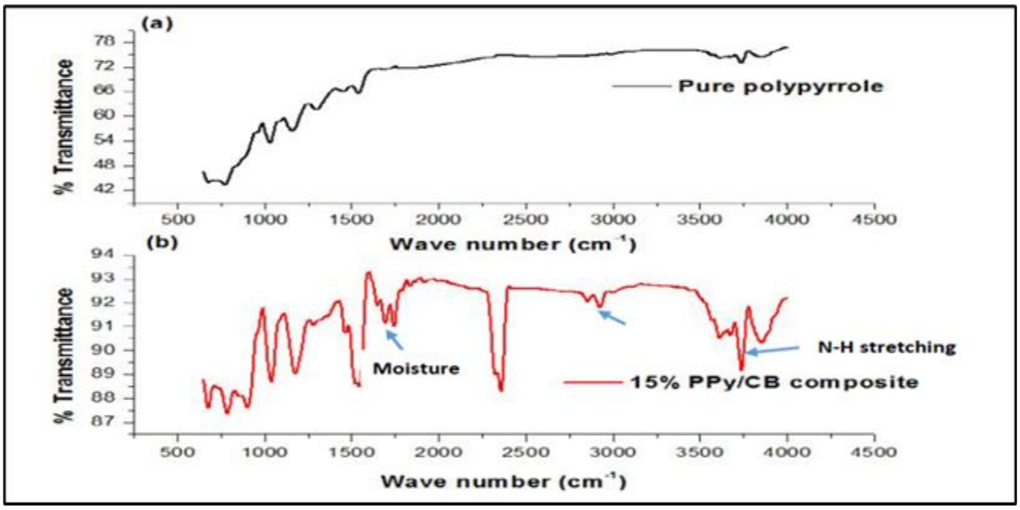
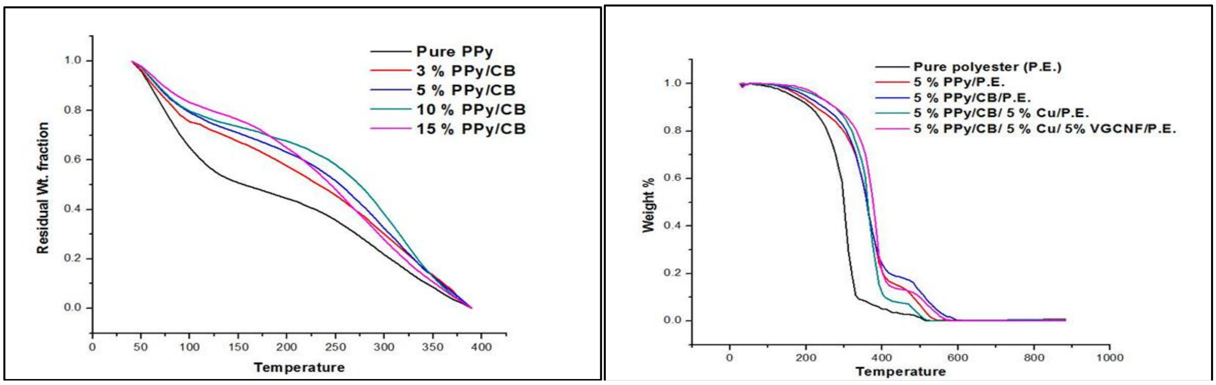


Figure 1: *FTIR Spectra of prepared samples*

THERMO GRAVIMETRIC ANALYSIS

Thermogravimetric analysis has been shown in Figure which displays that all these components impart good thermal stability to the Polyester. TGA behaviour of these hybrid composite interprets that by the incorporation of PPy and PPy/CB composite to the polyester do not shows significant effect comparatively as they retain the 80% and 81% mass at the temperature of 320℃ and 340℃ respectively. But when the Cu nano particles were added to the system it causes to increase the thermal stability and shows TGA at 360℃ with the loss of 18% mass which is a good effect just at 5% loading of Cu nano particles. Similarly, the introduction of VGCNF at 5 % loading imparts very good effects that it becomes stable even at 400℃ and retains 87% mass and then shows rapid decomposition and finally all these materials decomposed at 900℃.



(a) (b)

Figure 2: *(a) TGA comparison of pure polypyrrole and composite with various percentage of carbon (b) TGA comparison of polyester and Hybrid composites*

ELECTRICAL CONDUCTIVITY

As Copper nanoparticles should impart good electrical properties but their behaviour is negligible. The reason behind that although these particles are conductive in nature but they reduce the conductivity in composite of polyester because they lose their entire contact with each other as if some of them are coated with polyester and this also indicates that quality of dispersion is very good. Table 1 presents the conductivity of hybrid composites showing that all the materials which are used in the synthesis of these hybrid composites are conductive in nature hence its conductivity must be higher but it is not. Rather it shows the conductivity level even less than that. It may be due to synthesis mode of this hybrid composite as various fillers with different conductivity encounters with each other might be due to the evolution of gasses during the process of curing some voids also left behind which also tend to kept apart the fillers and reduced the conductivity. The second is the good dispersion and coating of polyester on the surfaces of these fillers also suppressed the conductivity and the main cause to reduce the contact with each other.

Table 1: Conductivity of various fabricated hybrid composites

Composites (5% loading)	Conductivity S/m
Polyester + PPy	1.24×10^{-2}
Polyester + (PPy+C)	1.54×10^{-2}
Polyester + Cu	0.27×10^{-3}
Polyester + (PPy+C) +Cu	5×10^{-6}
Polyester + (PPy+C) +Cu + VGCNF	8.27×10-2
Pure polyester Highly resistive	Highly resistive

SCANNING ELECTRON MICROSCOPY

The SEM studies were carried out to get the information of surface morphology of synthesized materials. The synthesis of pure polypyrrole is confirmed after taking the image (a) its results are comparable with the literature [23]. The image (b) indicates the carbon nano particles are coated with Polypyrrole. It also shows some agglomerates while image (c,d) shows the images of hybrid composites in which it is clearly seen the formation of agglomerates which is the main area can produce the cracks due to reduce in attraction between the filler and matrix. Spike like out growths confirms the presences of VGCNF and also demonstrate the good dispersion of VGCNF moreover it also shows that some of VGCNF are also coated with polyester that is the symbol of the good interaction between VGCNF and polyester Apart from these the presences of some voids due to the elimination of gases while curing which may affect on the net properties of the resultant material.

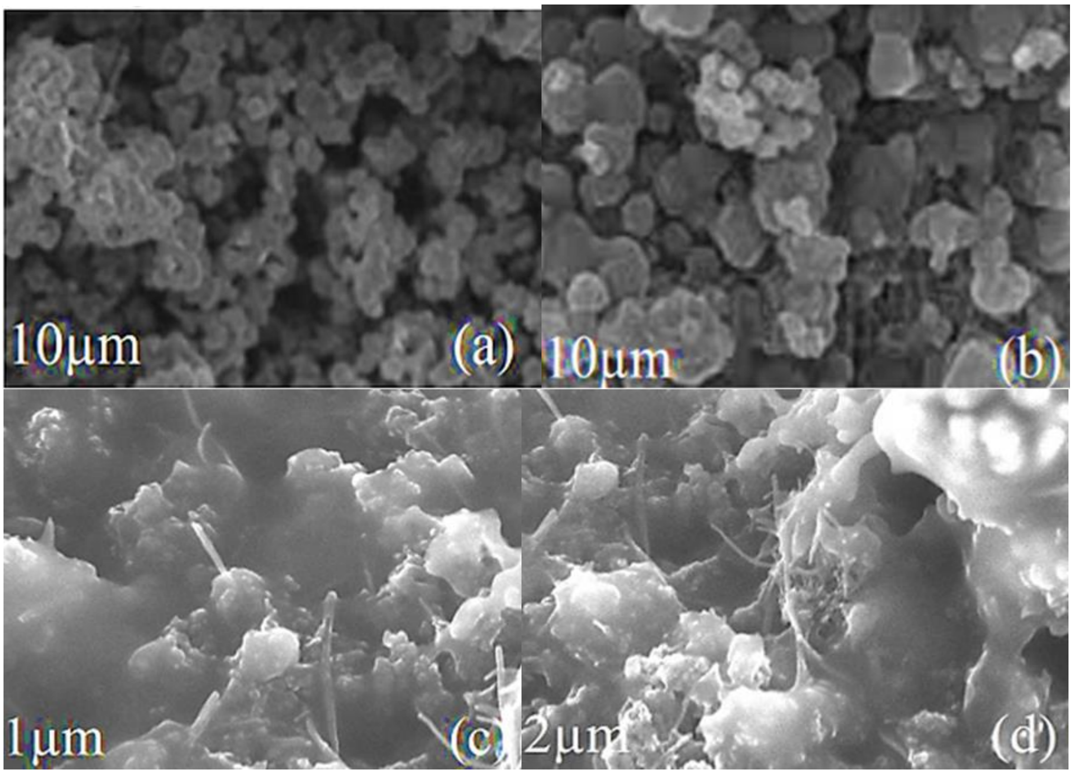


Figure 3: *SEM images of (a) polypyrrole (b) Composite PPy/CB (c,d) Hybrid composites*

OPTICAL MICROSCOPY

The optical images of hybrid composites are shown in Fig. 4.6. Many voids and holes were seen on the surface and these voids initiated cracks as clear from optical micrographs. Moreover, some golden shiny spots indicate the presences of agglomerates of Cu nanoparticles and also indicates that the quality of dispersion of Cu nanoparticles is not as much good as it should be.

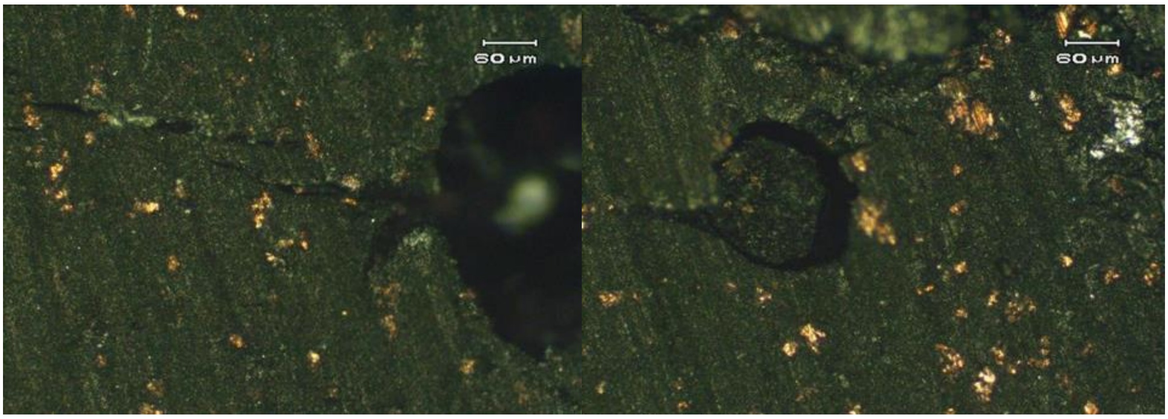


Figure 4 *Investigation of 5% VGCNF/15%Cu particles /5%PPy/CB/P.E. hybrid composite under optical microscope*

COMPRESSION TESTING

The samples were also assessed by their compressive values to judge if composites are hard enough to be used in certain other applications. Table 2(a) shows that the addition of various concentration of PPy coated carbon black composite in the pure polyester affect the compressive strength of the polyester. It is noticed that by adding 2 % of PPy coated carbon black composite its strength has been decreased but increased gradually by raising the concentration and when it is raised up to 7% it tends to raise the strength up to 20 % of pure polyester this effect can also see in the figure 5.Table 2(b) indicates that cu nano particles imparts good mechanical properties to polyester and if its concentration raised up to 20% along with the 5% PPy /CB composite the resultant hybrid composite is ~59% more stronger than pure polyester fig 5. While to check the combined effect of composite, VGCNF and 5% Cu nano particles on the mechanical properties of polyester, the hybrid composites of 12, 10 , 7 and 5 % were assessed for compression testing which indicated theta although the 12% loading of VGCNF imparts ~15% more strength than polyester but this is value is much less than that of Cu nano particles alone the reason behind due to the huge interaction of Different particles their association with the polyester suppressed due to which some primary cracks or voids are left behind during the process of curing (Table 2c). Hence when the load applied on these samples they start breaking from these spots as they can be clearly seen in the optical microscopy images.

Table 2(a): Compressive strength of (PPy+C) + polyester hybrid composite

Sr. No.	Sample ID with various %age PPy/CB in polyester	Compressive strength (MPa)
1	2%	14.76
2	5%	22.786
3	7%	228.451
4	Pure polyester	57.741

Table 2(b): Effect of Cu Nano particles on Compressive strength of hybrid composite

Sr. No.	Sample ID with various % age of Cu Nano particles (PPy/CB) in polyester	Compressive strength (MPa)
1	20%	97.132
2	15%	72.492
3	10%	60.669
4	5%	22.774
5	2%	17.8090

Table 2(c): Combined effect of VGCNF Cu Nano particles on hybrid composite

Sr. No.	Sample ID with various %age of VGCNF and Cu nano particles (PPy/CB) in polyester	Compressive strength (MPa)
1	12%	65.899
2	10%	45.36
3	7%	30.101
4	5%	13.566

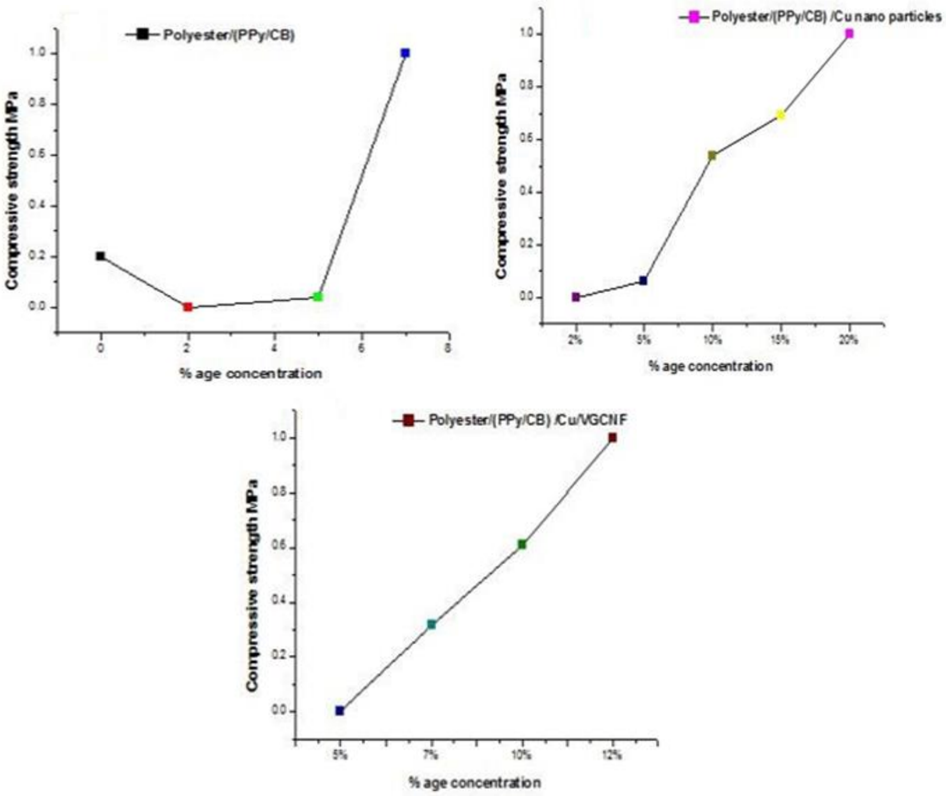


Figure 5: *Results of Compression testing of different hybrid composites*

CONCLUSION

FTIR analysis clearly indicates that the resultant product of PPy is successfully synthesized via chemical route. Moreover, it also confirms the coating of polypyrrole on carbon black. Electrical conductivity data indicate that by the successive addition of fillers may effects its electrical conductivity as polyester is nonconductive in nature but by the addition of PPy coated carbon black its conductivity improves which became maximum by the addition of VGCNF which make it more conductive due to its good electrical properties. TGA analysis indicates that the resultant hybrid composites show good thermal stability which is a good sign for their use in the electric appliances even at high temperature places due to their good thermal stability. SEM images confirms the synthesis of PPy and PPy coated carbon black composites, moreover these also show the good dispersion of carbon fibres, Cu nanoparticles and composite in polyester but some agglomerates and voids has also been noticed. Optical microscopy shows the formation of some primary cracks and holes while the dispersion of Cu nanoparticles was not good as can be seen from agglomerates of cu nanoparticles. The compression testing indicated that Cu nanoparticles and composite imparts good strength to the polyester but as we add VGCNF into it its strength value has been decreased as compare to Cu based hybrid composites. The reason behind is the formation of crack and aggregates during fabrication in hybrid composites are the main hindrance for improving strength in VGCNF based hybrid composites.

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