

EXFOLIATED GRAPHITE NANOPATELET -VINYL ESTER NANOCOMPOSITES

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Abstract

Recent research at Michigan State University has shown that it is possible to exfoliate natural graphite into platelets having thicknesses of less than 10nm and diameters of any size from sub-micron to 15 microns or greater. Since graphite is one of the stiffest materials found in nature (Young's Modulus = 1060 GPa), having a modulus several times that of clay, and also has excellent electrical and thermal conductivity, the addition of these nanographite platelets to polymers can impart a combination of desirable mechanical, electrical, thermal and barrier properties to the resulting nanocomposite. We have investigated the addition of exfoliated graphite nanoplatelets (xGnP) to a vinyl ester resin to achieve a nanocomposite with an optimum combination of conductivity and mechanical properties. It was found that the flexural modulus increased with increasing the content of xGnP regardless of the dimensions of the particle. The flexural strength decreased with increases in the content of xGnP dependent on the size of xGnP. The impact strength of the nanocomposite reinforced with xGnP having a diameter about 1 micron (xGnP-1) increased compared to the nanocomposite reinforced with xGnP-15. The electrical impedance (resistivity) of the xGnP reinforced vinyl ester nanocomposite and particularly the percolation threshold depended strongly on the size of xGnP. The nanocomposite reinforced with xGnP-1 has a higher percolation threshold and resistivity compared to the one reinforced with xGnP-15. It will be shown that by blending xGnP-1 and xGnP-15 it is possible to obtain a combination of good mechanical properties as well as resistivity.

Introduction

Nanocomposites composed of polymers reinforced with exfoliated clays and carbon nanotubes are being considered for applications such as interior and exterior accessories for automobiles application [1,2]. Graphite, a layered material, can also be used to produce nanoplatelets and nanocomposites if the layers can be separated [3]. Graphite not only has a high in-plane modulus but it also has excellent electrical and thermal conductivity similar to carbon nanotubes. Thus, with the appropriate treatment, exfoliation and dispersion of graphite in polymer matrix results in a nanocomposite with excellent mechanical, electrical and thermal properties, which can be used for structural applications in automotive application as well as non-structural applications such as electromagnetic shielding and to allow plastics to be coated by electrostatic painting.

Epoxy matrix nanocomposites have been successfully fabricated using exfoliated graphite nanoplatelets (xGnP) of various diameters and at various concentrations up to 3 vol%. A flexural modulus of ~3.9 GPa could be attained with the xGnP which was significantly greater than nanocomposites reinforced with carbon fibers (CF), vapor grown carbon fibers (VGCF) and particulate carbon black (CB) at the same concentrations [4]. The key to have a nanocomposite with excellent mechanical thermal and electrical properties is to exfoliate the graphite nanoplatelets. Recent research at Michigan State University has shown that it is feasible to exfoliate natural graphite into platelets having thicknesses of less than 10 nm and diameters in broaden size [4-6]. xGnP has the potential to be a platelet nanoparticle to reinforce polymer matrices to form nanocomposites with super physical properties. In this research, we are

focusing on the mechanical properties and electrical conductivity of xGnP reinforced vinyl ester nanocomposites.

Experimental

Materials:

15 micro size exfoliated graphite nanoplatelets (xGnP-15) and 1 micro size exfoliated graphite nanoplatelets (xGnP-1) were made in Composite Materials and Structures Center at Michigan State University according to the previous method [4-6]. Vinyl ester resin 411-350 was supplied by Ashland specialty chemical, Division of Ashland INC (Columbus, OH). Butanone peroxide, N,N-Dimethylaniline, Cobalt Naphthenate, and 2-4-Pentanedione were obtained from Sigma Aldrich (St. Louis, Mo).

Nanocomposite preparation

Mixing of the vinyl ester 411-350 resin solution with different percentages of xGnP was conducted in a glass beaker under stirring for less than 24 hours. Then the mixture of xGnP and vinyl ester was continuously sonicated with 100w output for less than 30 min. 1% butanone peroxide, 0.1% 2-4-Pentanedione, 0.1% N,N-Dimethylaniline, and 0.2% Cobalt Naphthenate were added to the mixed vinyl ester resin solution in order and mixed for 10 min. The above mixed resin solution was stirred for 2 min with a Speedmixer at 3000 RPM. The xGnP vinyl ester resin solution was poured into a 6'×6'×0.125' plaque mold, which was mounted on a vibration plate to accelerate the viscous resin flow to the bottom of the mold. Finally, resin solution was cured at 80°C for 3 hours and post-cured at 120°C for 2 hours. Coupons for testing of the cured xGnP reinforced vinyl ester nanocomposites were cut with a diamond saw to obtain specimens to measure the mechanical properties and resistivity.

Mechanical properties

The flexural properties of xGnP reinforced vinyl ester nanocomposites were measured with a United Testing System SFM-20 according to ASTM D790. System control and data analysis were performed using Datum software. The notched Izod impact strength was measured with a Testing Machines Inc. 43-02-01 Monitor/Impact machine according to ASTM D256.

Resistivity measurement

The electrochemical AC impedance spectrum over a range of frequencies of these xGnPTM reinforced nanocomposites were measured with a Gamry instrument under FAS2TM Femtostat plug system and potentiostatic mode. Equation (1) can be used to calculate the resistivity of the sample.

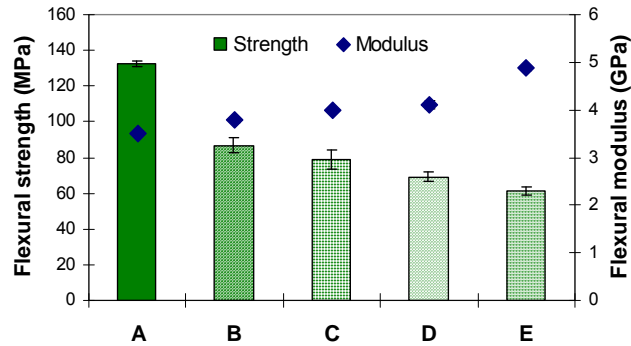
$$R = I \frac{S}{T} \quad (1)$$

Where I is the impedance value at 1Hz, R is the resistivity, S is the intercept surface area, T is the thickness of the sample.

Results and discussions

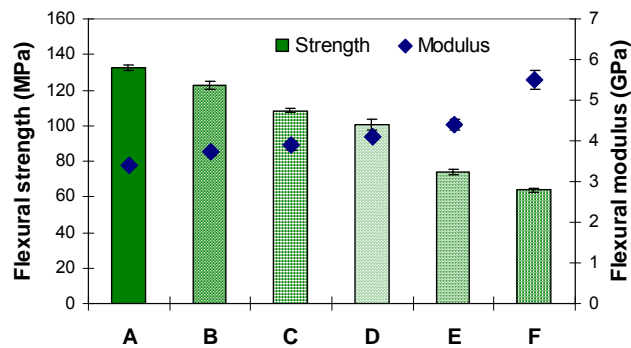
Mechanical properties of xGnP-reinforced vinyl ester nanocomposite

The flexural properties of xGnP-15 reinforced vinyl ester nanocomposites are shown in Figure 1. It was found that the flexural modulus of xGnP-15 reinforced vinyl ester nanocomposites improved with increasing content of xGnP-15. However, the flexural strength of xGnP-15 reinforced vinyl ester nanocomposites decreased with increasing the content of xGnP-15. This maybe due to the fact that xGnP-15 causes stress concentrations or xGnP-15 may reduce the crosslinking density of vinyl ester by interacting with the free radical curing mechanism. The flexural properties of xGnP-1 reinforced vinyl ester nanocomposites are shown in Figure 2. The flexural modulus increased and strength decreased with increasing the content of xGnP-1 in the vinyl ester nanocomposites in the same manner as xGnP-15.



A= Vinyl Ester (VE)
B= 0.5 wt.% xGnP-15/VE nanocomposite
C= 1.0 wt.% xGnP-15/VE nanocomposite
D= 2.0 wt.% xGnP-15/VE nanocomposite
E= 4.0 wt.% xGnP-15/VE nanocomposite

Figure 1. Flexural properties of xGnP-15 reinforced vinyl Ester nanocomposite



A= Vinyl Ester (VE)
B= 0.5 wt.% xGnP-1/VE nanocomposite
C= 1.0 wt.% xGnP-1/VE nanocomposite
D= 2.0 wt.% xGnP-1/VE nanocomposite
E= 5.0 wt.% xGnP-1/VE nanocomposite
F= 10.0 wt.% xGnP-1/VE nanocomposite

Figure 2. Flexural properties of xGnP-1 reinforced vinyl ester nanocomposite

The rule of mixture (ROM) is applied to predict the modulus of the nanofiller reinforced nanocomposites. Here, equation (2) is used to depict the modulus results of xGnP reinforced vinyl ester nanocomposites.

$$E_c = KV_f E_f + V_m E_m \quad (2)$$

Where E_c is the modulus of nanocomposite, K is the filler efficiency factor of nanocomposite modulus, E_f is the modulus of filler, V_f is the volume fraction of filler, E_m is the modulus of matrix, V_m is the volume fraction matrix. Equation (3) was used to calculate the volume fraction of filler.

$$V_i = \frac{W_i / \rho_i}{\sum W_i / \rho_i} \quad (3)$$

Where V_i , W_i , and ρ_i are the volume fraction, weight fraction and density of component i in the nanocomposites.

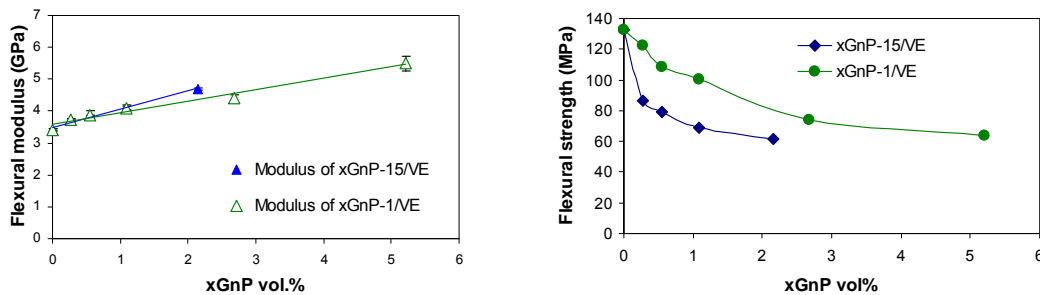


Figure 3. The plot of flexural properties vs. xGnP vol% of xGnP-reinforced nanocomposite

The plots of nanocomposite modulus vs. volume fraction of xGnP in the nanocomposites are in shown [Figure 3](#). It was found that the slope of xGnP-15 reinforced nanocomposite was higher than that of xGnP-1 reinforced nanocomposite. This indicates that xGnP-15 has higher filler reinforcement efficiency factor than xGnP-1. Therefore, it can be concluded that xGnP-15 is much more effective in improving the modulus of xGnP reinforced vinyl ester nanocomposite compared to xGnP-1. The plots of nanocomposite strength vs. volume fraction of xGnP are shown in [Figure 3](#). It was found that the rate at which xGnP-1 reduces the strength of the nanocomposite is lower than that of xGnP-15. xGnP-1 reinforced vinyl ester nanocomposites had better flexural strength than xGnP-15 reinforced one at a given xGnP content. Based on this result, the smaller sized xGnP-1 produces a nanocomposite with higher strength but xGnP-15 is better for higher modulus. A combination of xGnP-1 with xGnP-15 might be useful to obtain a balance between modulus and strength in the vinyl ester nanocomposite.

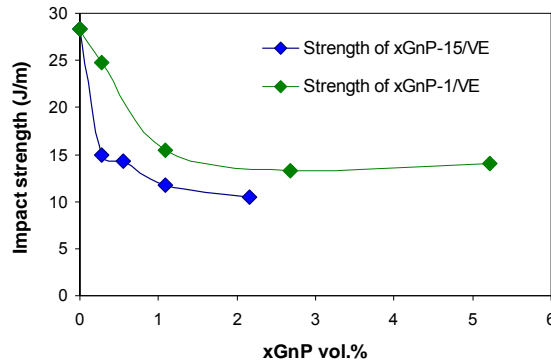


Figure 4. The notched Izod impact strength of xGnP-reinforced nanocomposite

Impact strength of a material shows the energy required to break the specimen and the value of impact strength reflects the ability of material to resist impact, namely toughness. Notch Izod impact strength emphasizes the energy to propagate a crack under high speed impact load. The notch Izod impact strength of xGnP reinforced vinyl ester nanocomposites is represented in Figure 4. It was found that both of xGnP-1 and xGnP-15 lowered the impact strength of vinyl ester, but the xGnP-1 reinforced nanocomposites had better impact strength than xGnP-15 reinforced one.

Resistivity of xGnP-reinforced vinyl ester nanocomposite

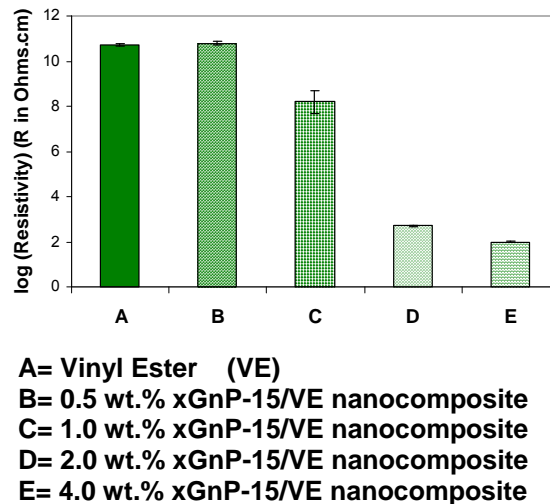
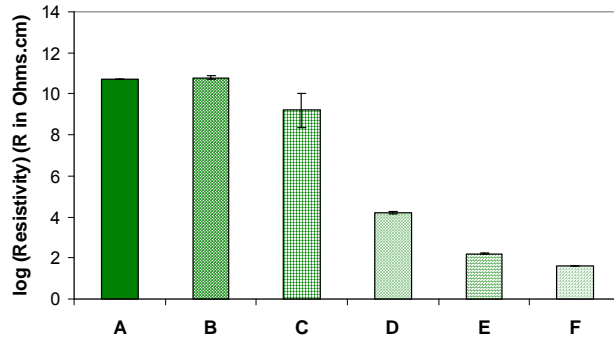


Figure 5. Resistivity of xGnP-15 reinforced vinyl ester nanocomposite

The resistivity of xGnP-15 reinforced vinyl ester nanocomposites is shown in Figure 5. It was found that the resistivity of the nanocomposite did not change when 0.5 wt% xGnP-15 was added to the vinyl ester. The addition of 1.0 wt% xGnP-15 reinforced vinyl ester nanocomposite has a resistivity in the range of semi-conductive materials. The addition of 2.0 wt% xGnP-15 produces a reinforced nanocomposite which is a conductive materials. When 4.0 wt% xGnP was used, the nanocomposite resistivity is about 200 ohms.cm. Therefore, it appears that a percolated network starts to form around 0.5 wt%.

The resistivity of xGnP-1 reinforced vinyl ester nanocomposites is shown in Figure 6. The 0.5 wt% xGnP-1 reinforced nanocomposite is not conductive. 1.0 wt% xGnP-1 reinforced

nanocomposite starts to be conductive. 2 wt% and 5 wt% xGnP-1 reinforced nanocomposite are both conductive. When xGnP-1 content around 10 wt%, the resistivity is around 40 ohms.cm.



- A= Vinyl Ester (VE)**
- B= 0.5 wt.% xGnP-1/VE nanocomposite**
- C= 1.0 wt.% xGnP-1/VE nanocomposite**
- D= 2.0 wt.% xGnP-1/VE nanocomposite**
- E= 5.0 wt.% xGnP-1/VE nanocomposite**
- F= 10.0 wt.% xGnP-1/VE nanocomposite**

Figure 6. Resistivity of xGnP-1 reinforced vinyl ester nanocomposite

For the purpose of finding a percolation threshold for resistivity and comparing the resistivity between xGnP-1 and xGnP-15 reinforced nanocomposite, the resistivity was plotted as the volume percentage of xGnP as shown in Figure 7. For xGnP-15 reinforced vinyl ester nanocomposite, the percolation threshold is around 0.3 vol. %. For the xGnP-1 reinforced vinyl ester nanocomposite, the percolation threshold is 0.5 vol. %. It is also found that xGnP-15 is more effective to reduce the resistivity of its reinforced vinyl ester nanocomposite compared to xGnP-1.

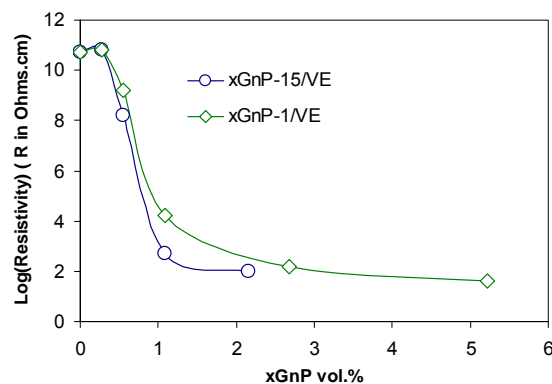


Figure 7. The plot of resistivity vs. xGnP vol.% of xGnP-reinforced nanocomposite

Helsing and Helte [7] proposed an approach to determine the critical concentration of a percolating system. Their approach is based on calculating the average effects of the random resistor network by approximating a binary heterogeneous mixture of insulator and conductor as a homogenous effective medium. According to this theory, the percolation threshold of the conductive filler in the insulator system can be described in the equation (4).

$$C_{per} = 1.18\varepsilon \quad (4)$$

where C_{per} is the percolation threshold, ε is the reciprocal of the aspect ratio of the thin and flat ellipsoids.

Since the percolation threshold could be found in the experiment, the thickness of the exfoliated graphite nanoplatelets could also be estimated. According to above theory, the thickness of the xGnP-15 nanoplatelets is 25 nm and the xGnP-1 is 4 nm. This difference probably results from the ball milling during processing of xGnP-1.

Mixing effect of xGnP

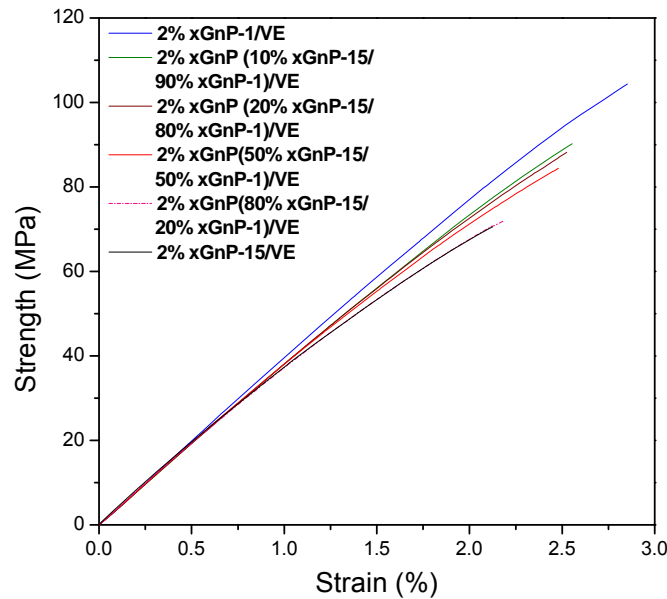


Figure 8. Stress-strain curves of xGnP-reinforced nanocomposite

Since xGnP-15 can provide a good contribution on resistivity, xGnP-1 provides good contribution on mechanical strength; a combination of xGnP-15 with xGnP-1 could have benefits to obtain nanocomposite with better resistivity and balanced mechanical properties. The stress-strain plot of the mixed xGnP reinforced vinyl ester nanocomposite with total 2 wt% xGnP in flexural properties test is shown in Figure 8. It was found that the strength was really dependent on the xGnP-1 fraction in the total xGnP content. With increases in the content of xGnP-15, the strength continuously went down. The modulus of these nanocomposites almost the same.

The plots of flexural strength and resistivity vs. xGnP-1 fraction in total xGnP are shown in Figure 9. Both resistivity and flexural strength of the mixed xGnP reinforced nanocomposite (totally 2 wt% xGnP) increased with increases in the content of xGnP-1. Therefore, a mixture of was more effective at producing a balance of properties. A mixture increases the mechanical strength and lowers the resistivity. It is feasible that mixed xGnP reinforced nanocomposite can have balanced mechanical properties and better resistivity.

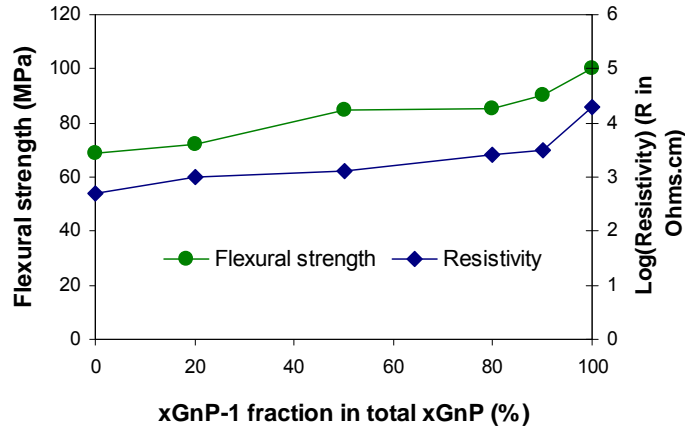
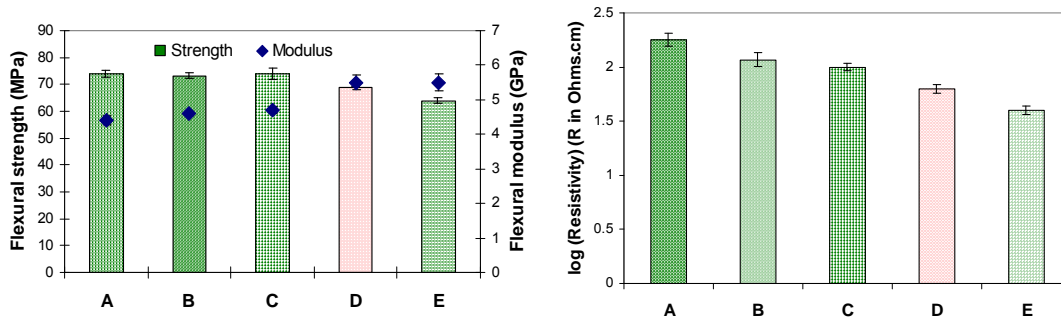


Figure 9. Plots of flexural strength and resistivity vs. xGnP-1 volume fraction in total xGnP

The flexural properties of mixed xGnP reinforced nanocomposite with the xGnP content above 5 wt.% are shown in Figure 10. The flexural strength of 5 wt% xGnP (20%xGnP-15) reinforced nanocomposite are almost the same as that 5 wt% xGnP-1 reinforced nanocomposite, but the modulus is improved. In addition, the flexural strength of 7.5 wt% xGnP (13%xGnP-15) reinforced nanocomposite had flexural strength almost same as 5% xGnP-1 with a modulus similar to 10% xGnP-1. The resistivity of 5 wt% xGnP (20%xGnP-15/80%xGnP-1) reinforced nanocomposite was around 100 ohms.cm, which is lower than that of 5% xGnP-1. Also, the resistivity of 7.5 wt% xGnP (13%xGnP-15/87%xGnP-1) was around 60 ohms.cm, which is close to the 10 wt% xGnP-1. This demonstrates that mixed xGnP reinforced nanocomposite can achieve better mechanical properties as well as better conductivity.



- A= 5.0 wt.% xGnP-1/VE nanocomposite**
- B= 5.0 wt.% xGnP (10xGnP-15/90%xGnP-1)/VE nanocomposite**
- C= 5.0 wt.% xGnP (20xGnP-15/80%xGnP-1)/VE nanocomposite**
- D= 7.5 wt.% xGnP (13xGnP-15/87%xGnP-1)/VE nanocomposite**
- E= 10.0 wt.% xGnP-1/VE nanocomposite**

Figure 10. Flexural strength and resistivity of xGnP-reinforced nanocomposite

Conclusions

Exfoliate graphite nanoplatelets (xGnP) reinforced vinyl ester nanocomposite have been fabricated and characterized for mechanical properties and resistivity. It was found that the flexural modulus increased with increasing the content of xGnP regardless of the dimensions of the particle. The flexural strength decreased with increases in the content of xGnP dependent on the size of xGnP. The electrical impedance (resistivity) of the xGnP reinforced vinyl ester nanocomposite and particularly the percolation threshold depended strongly on the size of xGnP. The nanocomposite reinforced with xGnP-1 has a higher percolation threshold and resistivity compared to the one reinforced with xGnP-15. Mixing xGnP-1 and xGnP-15 in the vinyl ester matrix can achieve a combination of good mechanical properties as well as resistivity. For example, 7.5 wt% xGnP(1%xGnP-15/6.5%xGnP-1) reinforced nanocomposite had a flexural strength 69 MPa, flexural modulus of 5.6 GPa and resistivity of 60 ohms.cm (AC impedance). The formation of nanocomposites by combining nanoparticle of different sizes is a viable route to optimize strength, stiffness, impact and electrical properties.

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