COMPARATIVE STUDY OF CARBON-BASED NANO-FILLERS/POLYANILINE HYBRIDS REINFORCED POLYMER COMPOSITES

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ABSTRACT

Graphene oxide(GO), multi-walled carbon-nanotube(MWCNT) and fullerene(C60) were selected to make the carbon/PANI hybrids reinforced polymer composites. The doping action, dispersion state, thermal abilities, electrical conductivities, thermal conductivities and mechanical properties were characterized and compared. The doping action in three systems are different and the PANI/Carbon hybrids appear as a uniform network structure. GO/PANI and C60/PANI sample have higher decomposition temperature and lower thermal loss, while the MWCNT/PANI hybrids reinforced composites have lower decomposition temperature and thermal loss, which means MWCNT is not effective to improve the thermal stability of the PANI composites. The electrical conductivity of MWCNT-PANI/PDVB agrees well with the law of Landauer model, and Voigt-Reuss model can explain the modulus'change of the composites.

1. INTRODUCTION

Functional polymer composites are at the forward position of materials science research because of the large number of applications that have been developed utilizing their interesting and unique features integrating the good mechanical, electrical [1], and thermal properties [2]. Polyaniline (PANI) is one of the most promising polymers for industrial application mainly for its easy preparation, low cost, excellent electrical, optical, magnetic properties and environmental stability [3-5]. However, due to poor mechanical properties and poor process performance, blending PANI with other carbon nanofillers has been shown to be a good strategy to develop functional polymer composites [6-8].

Some attempts have been done to add all kinds of conductive fillers into matrix, researchers indicate that the Young's modulus of graphene oxide (GO) is as high as 207.6 GPa [9]. A different type of carbon nanofillers with high modulus is MWCNT, with the modulus range from 270 to 950 GPa [10]. Another carbon nanofiller is C60 with the high modulus of 874 GPa [11]. These carbon nanofillers also have special electrical and thermal conductivities. And the composites usually demonstrated different electrical and thermal conductivity [12]. Graphene oxide (GO) is an attractive nanomaterial because of its low cost, mass production and solution processability. It is established that graphene can help to get a better dispersion of other additives in the polymer matrix by synergetic effects due to its extremely high aspect ratio and surface area [13-15]. Carbon nanotubes (CNT) possess exceptionally high electrical and thermal conductivity [16, 17], making them ideal fillers for polymer matrix composites for electrical functional applications [18]. Fullerene(C_{60}) is a 60-atom carbon molecule, and the strong phonon scattering of C_{60} molecule can decrease the thermal conductivity by amplifying the randam oscillation of C_{60} [19].

Our group has reported three Carbon/PANI polymer composites with high mechanical and special functional properties made by a simple single step method [1, 6-8, 20-23]. However, the comparative study and the theoretical analysis of three different carbon/PANI hybrid system remain to be discussed until now.

Herein, GO/PANI, MWCNT/PANI and GO/PANI hybrids reinforced polymer functional materials were compared and analyzed. The doping action, dispersion state, thermal abilities, electrical conductivities, thermal conductivities and mechanical properties were characterized and compared. The doping action, dispersion state, thermal ability, electrical conductivity, thermal conductivity and mechanical properties in three systems are compared and the related theoretical models were chosen to explain the properties of composites.

2. EXPERIMENTAL

Materials and preparation process were reported in our previous papers[6-8].

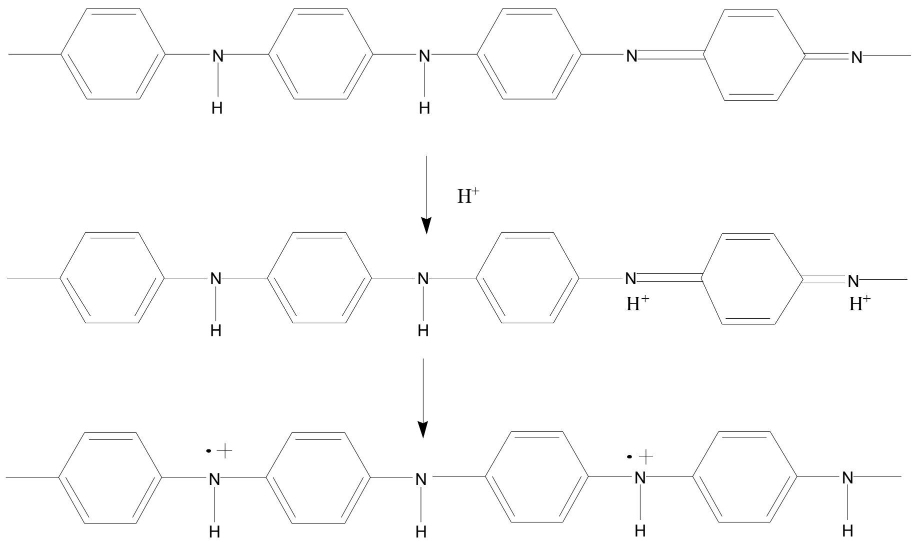
PANI Powder, supplied by Regulus Co. Ltd., Tokyo, Japan; DBSA, Kanto Chemical Co. Inc., Tokyo, Japan; DVB, supplied by Sigma-Aldrich Co., St. Louis, USA. PANI in emeraldine base form was used, and then doped with DBSA to make emeraldine salt. The conductivity of the prepared emeraldine salt was in the range of 10-20 σ/cm. GO was synthesized based on Hummers method [24]. The detailed process was reported elsewhere [25]; MWCNT with 10–30 um in length and 10-20 nm in diameter are obtained from Chengdu Organic Chemistry Company; C60 (purity >95%) with the density of 1.61 g/cm3, was bought from Xiamen Funano New Material Technology Co. Ltd. The content of GO is 0.45%, content of MWCNT is 0.6%; The volume fraction of C_{60} is controlled in 1.05vol%.

Typically, carbon nanofillers were added into DVB separately, and then dispersed by a sonicator. PANI(DBSA) paste with the weight ratio of 30:70 was prepared according to the procedure we reported before [1, 7], which were then mixed with the carbon/DVB solution. The weight fraction of PANI is set as 15%. Secondly, the suspension was poured into the mould and cured in a 120 ℃ hot-press machine for 2 h.

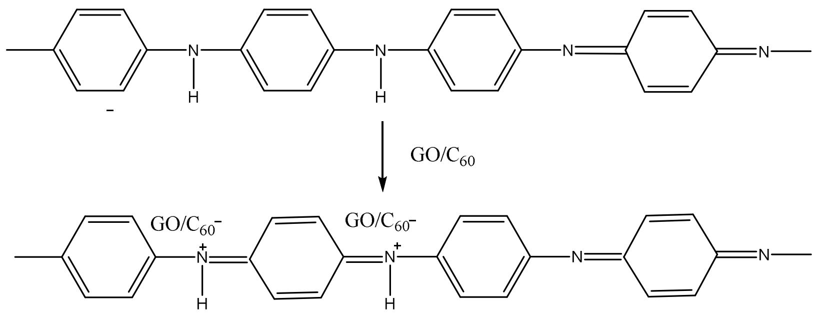
3. COMPARATIVE STUDY OF THETHREE HYBRID SYSTEM

Doping Action in 3 hybrid systems

The doping action of Reaction. 1 in Fig. 1 happened in all this system. But among the three carbon nanofillers, only GO and C60 were reported to be capable of doping with polyaniline as shown in Reaction. 2. That's why the GO/PANI and C60/PANI system have better dispersion state which will be discussed in the SEM results. The electrical enhancement of GO/PANI and C60/PANI system are different with MWCNT system. In GO/PANI and C60/PANI systems, not only the high electrical properties of carbon nanofillers but also increase of Reaction 2-based doped PANI account for the improvement of the conductivity of PANI composites.



Reaction. 1 The doping action of PANI with acid



Reaction. 2 The doping action of PANI with carbon nanofillers

Fig.1 Doping mechanisms of PANI and PANI/Carbon hybrids

Morphology comparison of 3 hybrid system

In order to check the change of the microstructure after the addition of carbon nanofillers, the morphology of PANI and PANI with different carbon nanofillers was observed by SEM.

As shown in Fig.2, a lot of big PANI–DBSA particles are observed in PANI system. In contrast, the PANI/Carbon hybrid systems appear as a uniform network structure as shown in Fig.1, which clearly indicates that both MWCNT, GO and C60 can improve the dispersity of conductive PANI particles.

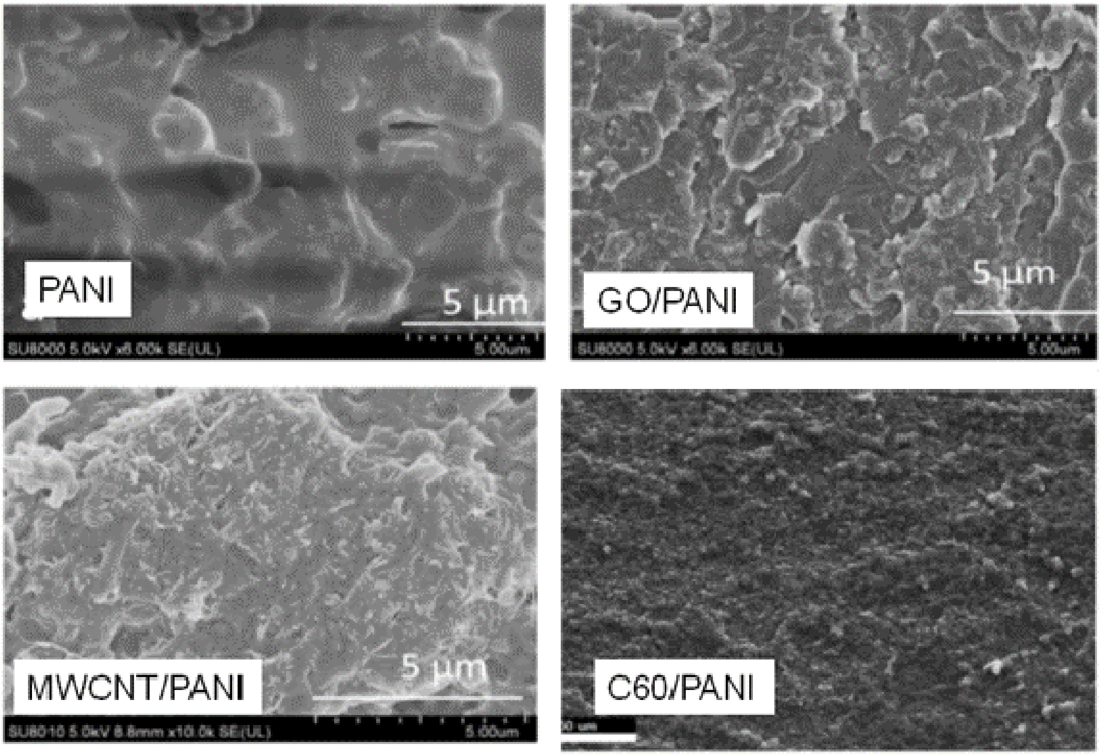


Fig.2 SEM image of PANI and PANI/Carbon hybrids.

Comparison of Flory-Huggins parameter

The Flory-Huggins parameter χ parameter and the binary interaction parameter a_{ij} were calculated and compared [6]. GO has a smallest χ parameter compared to MWCNT and C60. Table 1shows the calculation results of binary interaction parameters. This is probably because GO has a sheet-like structure composed of hexagonal carbon, it attempts to take a structure in which hexagonal mesh structures are piled up by π-π interaction. MWCNT and C60 have a graphene rounded structure, and the π-π interaction is hard to work, the cohesive energy becomes larger than that of graphene, and the χ parameters become bigger than that of graphene.

Table 1The calculation results of binary interaction parameters.

Materials	χ parameter	a_{ij}
PANI/MWCNT	3.331	35.885
PANI/GO	0.739	27.416
PANI/C_{60}	3.648	36.922

Thermal Stability of the 3 hybrid system

The thermal stability of nanocomposites with nanofillers were calculated and compared. In Table 2, the GO/PANI and C_{60}/PANI sample have higher decomposition temperature and lower thermal loss, while the MWCNT/PANI hybrids reinforced composites has lower decomposite temperature and thermal loss, that means MWCNT can not improve the thermal stability of the composites. Because the addition of MWCNT is very low, so if the MWCNT can not affect the whole structure of the PANI or the polymer, it can not improve the thermal stability. However, the introduction of GO and C60 can dope with PANI, this behavior makes the formation of a more stable 3D PANI network inside the nanocomposites, which can improve the thermal stability.

Table 2 The TGA results of composites with different nanofillers

Material	Decomposition Temperature(℃)	Thermal Loss(%)
PANI/PDVB	310	70
GO-PANI/PDVB	330	63
MWCNT-PANI/PDVB	315	68
C60-PANI/PDVB	325	65

Analysis of Electrical Conductivity

The conductivity comparation of Carbon/PANI hybrids reinforced polymer were presented in Table 3. According to Table 3, we can see that the pure DVB has very low electrical conductivity, but the doped PANI has high conductivity. Doped PANI can improve the electrical conductivity definitely. Also the disperse state can also have effect on the conductivity of the composites conductivity.

According to LANDAUER model [26], for the composites with different mixtures, there is no single theory can explain all situation. Among this, the most frequently used in the literature is shown in equation (1),

$$\rho_c = \rho_1 V_1 + \rho_2 V_2 \tag{1}$$

Where ρ_c is the resistivity of the composites. ρ_1 is the resistivity of component 1, ρ_2 is the resistivity of component 2, V_1 is the volume fraction of component 1, V_2 is the volume fraction of component 2. In this model, the components in the composites are supposed as dispersed at random. Therefore, This equation supply an upper limit for the resistivity, indicating the lower limit of the conductivity in as shown in equation (2).

$$\frac{1}{\sigma_c} = \frac{V_1}{\sigma_1} + \frac{V_2}{\sigma_2} \tag{2}$$

Where σ_c is the electrical conductivity of the composites. σ_1 is the electrical conductivity of component 1, σ_2 is the electrical conductivity of component 2,

The alternate hypothesis results in the following equation.

$$\sigma_c = \sigma_1 V_1 + \sigma_2 V_2 \tag{3}$$

This equation gives the maximum upper limit of the simple mixture of the composites. LANDAUER believes that these two expressions are the upper and lower limits of the conductivity of the mixed system [24].

In PANI/PDVB system, PDVB is supposed as component 1 and PDVB is supposed as component 2; In GO-PANI/PDVB, MWCNT-PANI/PDVB and C60-PANI/PDVB systems, PANI/PDVB system is supposed as component 1 and the carbon nanofillers is supposed as component 2. According to the above formulations,

The upper and the lower limit of the composite's conductivity are obtained in the Table 3.

Table 3 The electrical conductivity of material and composites

Electric Conductivity	Lower limit by Calculated (S m-1)	Upper limit by Calculated (S m-1)	Experiment (S m-1)
DVB	—	—	10^{-9}
GO	—	—	0.14
MWCNT	—	—	10^{6}
C60	—	—	10^{-3}
PANI(DBSA)	—	—	10^{3}
PANI/PDVB	$1.25*10^{-9}$	220	22
GO-PANI/PDVB	8.58	21.78	40
MWCNT-PANI/PDVB	22	8021	78
C60-PANI/PDVB	0.099	21.78	63.7

According to the calculation results, we can find that only PANI/DVB and MWCNT-PANI/PDVB systems can fit the law of LANDAUER model. The electrical conductivity of PANI/DVB system is 22 S m-1 which is between the lower limit ($1.25*10^{-9}$ S m-1)and the upper limit(220 S m-1). The electrical conductivity of MWCNT-PANI/PDVB is s 78 S m-1 which is between the lower limit (22 S m-1)and the upper limit(8021 S m-1). However, the electrical conductivities of GO-PANI/PDVB and C60-PANI/PDVB systems can not fit the law at all. The electrical conductivities of both systems are much higher than the upper limit calculated by the LANDAUER law. This also confirms that the doping action happen inside the system and the introduce of GO or C60 can improve the disperse of PANI. It can not be supposed as simple mix in this two systems.

Comparison of Thermal Conductivity

Because the thermal conductivities of graphene and carbon nanotube have been reported to possess similar values (3000 W/mK) [27]. The doped PANI and C60 have been reported with low thermal conductivity of 0.08 W/mK [28] and 0.16 W/mK [29]. So the thermal conductivity may be improved by GO and MWCNT, reducing by PANI and C60. In this part, the thermal conductivity of composited were calculated according to Prof.Hiroshi Hatta [30]. Then compared with the experiment results.

In the case of completely random distribution, the thermal conductivity can be expressed as formula. MWCNT can be considered as short fiber, GO can be supposed as short fiber with wired crosssection, so the system for MWCNT and GO reinforced polymer composites, the theremal conductivity can be expressed as

$$K_{11} = K_{33} = K^m\left(1 - \frac{V_f\left(K^m - K^f\right)\left[\left(K^f - K^m\right)(2S_{33} + S_{11}) + 3K^m\right.}{3\left(K^f - K^m\right)^2(1 - V_f)S_{11}S_{33} + K^m\left(K^f - K^m\right)R + 3\left(K^m\right)^2}\right) \quad (4)$$

where K_{11}, K_{33} is the thermal conductivity of the composites in different direction, K^m is the thermal conductivity of the matrix, K^f is the thermal conductivity of the fillers, V_f is the volume fraction of the fillers. S_{ij} is tensor and depends on the shape of the filler.

PANI and C60 are regarded as spheres, and the thermal conductivity can be expressed as follows:

$$S_{11} = S_{33} = \frac{1}{3} \quad (5)$$

$$K_{11} = K_{33} = K^m\left\{1 + \frac{V_f}{\frac{(1 - V_f)}{3} + \frac{K^m}{K^f - K^m}}\right\} \quad (6)$$

In the case of GO, the formulation for penny shape inclusion is used.

$$S_{11} = S_{22} = \frac{\pi a_3}{4a_1} \quad (7)$$

$$S_{33} = 1 - \frac{\pi a_3}{2a_1} \quad (8)$$

where *a* is the length in three direction.
In the case of MWCNT, the aspect ratio is defined as

$$\alpha = \frac{a_3}{a_1} \quad (9)$$

S can be calculated using the following equations.

$$S_{11} = S_{22} = \frac{a_1^2 a_3}{2\left(a_3^2 - a_1^2\right)^{\frac{3}{2}}}\left\{\frac{a_3}{a_1}\left(\frac{a_3^2}{a_3^2} - 1\right)^{\frac{1}{2}} - \cosh^{-1}\frac{a_3}{a_1}\right\} = \frac{\alpha}{2(\alpha^2 - 1)^{\frac{3}{2}}}\left\{\alpha(\alpha^2 - 1)^{\frac{1}{2}} - \cosh^{-1}\alpha\right\} \quad (10)$$

$$S_{33} = 1 - 2S_{22} \quad (11)$$

According to equations (4)-(11), the calculated results of the composite's conductivity were summarized in Table 4.

Table 4 Thermal conductivities by experiment and theoretical calculated modulus

Thermal conductivity	Experiment(W/mK)	Calculated(W/mK)

PDVB	0.58	_
Doped PANI	0.08	_
PANI/PDVB	0.43	0.45
GO	3000	_
MWCNT	3000	_
C60	0.16	_
GO-PANI/PDVB	0.42	0.427
MWCNT-PANI/PDVB	0.43	0.427
C60-PANI/PDVB	0.16	0.426

According to the calculated results. The calculated results of PANI/DVB has the perfect consistent with the experiment results. After the addition of GO and MWCNT, the calculated results also have perfect consistence with the experiment results. But for the calculated result after the addition of C60, it introduce a huge difference with the experiment results. That means the introduce of C60 take something change, which maybe can due to the change of dispersion state of doped PANI happened or the doping action happened between C60 and PANI happened.

Comparison of Mechanical Properties

Before applying the models, the mechanical properties of the matrix and the nanofillers are checked and showed in Table 5 Graphene is one of the strongest materials with the Young's modulus of E = 1.0 TPa. Researchers indicate that the Young's modulus of graphene oxide (GO) decreased, but it still as high as 207.6 GPa [9]. The other carbon nanofillers with high modulus is MWCNT, with the modulus range from 270 to 950 GPa [10]. Another carbon nanofillers is C60 with the high modulus of 874 GPa [11].

Micromechanical modeling comes from the properties of various components of the composite and their arrangement is a very useful method for understanding and predicting the composite behavior. The known Voigt-Reuss model [31] is used to calculate the theoretical Young's modulus of the composites with short random fibers. The expression is shown in formula 12. In our system, MWCNT is considered as the micro fibers, while the GO can be supposed as the fibers with line crosssection, C60 is supposed as the fibers with the same value of length and diameter. Under the hypothesis of this, the results were shown in Table 5.

$$E_c = \frac{3}{8}[V_f E_f + (1 - V_f)E_m] + \frac{5}{8}\left[\frac{E_f E_m}{E_f(1-V_f) + E_m V_f}\right] \quad (12)$$

Where, E_c is the modulus of the composites, E_f is the modulus of the fillers, E_m is the modulus of the matrix.

Table 5 Experimental and theoretical calculated modulus

Elastic Modulus	Experiment (GPa)	Calculated (GPa)
GO	207 [197]	
MWCNT	610 [198]	
C60	874 [199]	
PANI/PDVB	5.20	
GO-PANI/PDVB	5.90	5.55
MWCNT-PANI/PDVB	6.19	7.48
C60-PANI/PDVB	6.215	8.63

For GO-PANI/PDVB, there are hardly differences between Voigt-Reuss model and experimental values. However, in the systems of MWCNT-PANI/PDVB and C60-PANI/PDVB, great divergence exist between the theoretical model and the experiment data. This can be ascribed to difference of the materials.

4. CONCLUSION

The doping action in three systems are different and the system of PANI/Carbon hybrid system appear as a uniform network structure. GO has a smallest χ parameter than MWCNT and C60. GO/PANI and C_{60}/PANI sample have higher decomposition temperature and lower thermal loss, while the MWCNT/PANI hybrids reinforced composites has lower decomposite temperature and thermal loss, that means MWCNT can not improve the thermal stability of the composites. The electrical conductivity of MWCNT-PANI/PDVB can fit the law of LANDAUER model. However, the electrical conductivities of GO-PANI/PDVB and C60-PANI/PDVB systems can not fit the law at all. The calculated results of PANI/DVB has the perfect consistent with the experiment results. After the addition of GO and MWCNT, the calculated results also have perfect consistence with the experiment results. But for the calculated result after the addition of C60, it introduce a huge difference with the experiment results. Voigt-Reuss model were chose to explain the modulus change. For GO-PANI/PDVB there are hardly differences between Voigt-Reuss model and experimental values. However, in the systems of MWCNT-PANI/PDVB and C60-PANI/PDVB, great divergence exist between the theoretical model and the experiment data

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