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# High Dispersion Power of Cardo-Typed Fluorene Moieties on Carbon Fillers

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## 1. Introduction

Composite materials containing carbon fillers are well used in a variety of material fields including electronic and optical device fields. The carbon fillers are capable of endowing conductivity, heat-releasing ability etc. to the composites. Property indispensable for such matrix resins, as expected for most matrix resins, is to perform high dispersion of the fillers. Surface modification of fillers is one of the straightforward approaches to produce the excellent composite materials. However, if the matrix resin itself can possess good carbon filler dispersing power, it can simply achieve the fine dispersion of a variety of carbon fillers including non-surface modified fillers, making the composite fabrication easy.

Currently, much attention has recently focused on the filler-dispersing power of fluorene moieties. In the recent study on polymer materials based on fluorene based polymer (FBP), we have found that FBP shows not only a much filler-incorporating ability but also an excellent filler-dispersing ability for carbon fillers, suggesting that FBP is a highly suitable matrix resin for carbon fillers.

In this chapter, we discussed the interesting nature of FBP as matrix resin that shows extremely high carbon filler-incorporating and dispersing powers to yield high quality composite materials, along with the investigation on the interaction based on the structural characteristics of 9,9-diarene-substituted fluorene skeleton of FBP.

## 2. Carbon filler

### 2.1 Allotrope of carbon

Atomic carbon is a very short-lived species and, therefore, carbon is stabilized in various multi-atomic structures with different molecular configurations called allotropes. The three relatively well-known allotropes of carbon are amorphous carbon, graphite, and diamond. Once considered exotic, fullerenes are nowadays commonly synthesized and used in research; they include buckyballs, [Samal, S. & Ebbesen, T.W.] carbon nanotubes, [Dresselhaus, M.S. et al] carbon nanobuds [Nasibulin, A. G.] and nanofibers. [Nasibulin, A. & Vieira, R.] In this paper, we will focus on two carbon filler in the market: carbon black and carbon nanotube.

## 2.2 Carbon black

Carbon black [C.A.S. NO. 1333-86-4] is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. Carbon black is a form of amorphous carbon that has a high surface-area-to-volume ratio, although its surface-area-to-volume ratio is low compared to that of activated carbon. Its physical appearance is that of a black, finely divided pellet or powder. Its use in tires, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, particle size and structure, conductivity and color.

In this paper we are focused on conductive carbon black, and evaluated dispersion power of fluorene moieties on conductive carbon black.

## 2.3 Carbon nanotube

**Carbon nanotubes (CNTs)** are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1,[ Wang, X. et al] significantly larger than any other material. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

### 2.3.1 Mechanical properties of carbon nanotube

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp<sup>2</sup> bonds formed between the individual carbon atoms.[ Yu, M.F.; Collins, P. G.; Jensen, K; Belluci, S.; Chae, H.G.; Meo, Michele; Sinnott, S.B.; Demczyk, B.G; ASTM; & Wagner, H. D. ]

	Young's modulus (TPa)	Tensile strength (GPa)	Elongation at break (%)
SWNT E	~1 (from 1 to 5)	13-53	16
Armchair SWNT T	0.94	126.2	23.1
Zigzag SWNT T	0.94	94.5	15.6-17.5
Chiral SWNT T	0.92		
MWNT E	0.2~0.95	11~150	
Stainless steel E	0.186 ~0.214.	0.38. ~1.55	15-50
Kevlar-29&149 E	0.06~0.18	3.6~3.8	~2

Table 1. Mechanical properties of carbon nanotube

### 2.3.2 Electrical properties of carbon nanotube

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given  $(n,m)$  nanotube, if  $n = m$ , the nanotube is metallic; if  $n - m$  is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair ( $n = m$ ) nanotubes are metallic, and nanotubes  $(6,4)$ ,  $(9,1)$ , etc. are semiconducting.[ Lu, X; Chen, Z. et al]

However, this rule has exceptions, because curvature effects in small diameter carbon nanotubes can influence strongly electrical properties. Thus, a (5,0) SWCNT that should be semiconducting in fact is metallic according to the calculations. Likewise, *vice versa*-- zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap (armchair nanotubes remain metallic). [Hong, S.H.; et al] In theory, metallic nanotubes can carry an electric current density of  $4 \times 10^9$  A/cm<sup>2</sup> which is more than 1,000 times greater than metals such as copper, [Takesue, I. et al] where for copper interconnects current densities are limited by electromigration. Multiwalled carbon nanotubes with interconnected inner shells show superconductivity with a relatively high transition temperature  $T_c = 12$  K. In contrast, the  $T_c$  value is an order of magnitude lower for ropes of single-walled carbon nanotubes or for MWNTs with usual, non-interconnected shells. [Pop, E. et al]

### 2.3.3 Thermal properties of carbon nanotube

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal conductivity along its axis of about  $3500 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ; [Sinha, S.L. et al] compare this to copper, a metal well-known for its good thermal conductivity, which transmits  $385 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about  $1.52 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , [Thostenson, E. et al] which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to  $2800^\circ\text{C}$  in vacuum and about  $750^\circ\text{C}$  in air. [Ando, W.]

By challenging on fine dispersion of CTNs in polymer matrix, polymer composites with promising mechanical properties, electrical properties and thermo-conductive properties can be expected.

## 3. Fluorene moieties

### 3.1 Basic properties of fluorene moieties

Fluorene is a member of polycyclic aromatic hydrocarbon (PAH). Two benzene rings are fused to cyclopentane ring. It emits violet fluorescent color. It is not synthesized commercially but is obtained from middle oil fraction of coal tar. It is insoluble in water; soluble in ether and acetone; melting point  $116\text{-}117^\circ\text{C}$ . It plays important part in metallocene catalysts as a ligand. It is used in the formation of polyradicals for resins. It is used in manufacturing antimalaria drugs and other pharmaceuticals. [Stephan, O. et al]

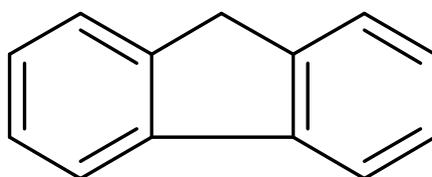


Fig. 3.1. Fluorene

Fluorene family compounds are base materials for dyes and optical brightening agents. They have useful functions such as light and temperature sensitivity, heat resistance, conductivity, emittability, corrosion resistance and detection of amino groups.

They are used in the applications of thermo and light sensitizer, liquid crystal chemistry, luminescence chemistry, spectrophotometric analysis, molecular chemistry, organometallic-complexes and biochemorphology industry.

### 3.2 Fluorene polymers

#### 3.2.1 Derived from 2,7-disubstituted fluorene

9,9-disubstituted and polymerized in 2,7 disubstituted fluorene-polymers had its promising photo-sensitive applications. The application areas of polymers derived from 2,7 disubstituted fluorene covers polarized photo- and electroluminescence materials [Grell, M.; Lim, E.; Morin, J.-F.; Jin, S. H.; Yang, R.; Mo, Y.; & Lee, P.I.], White-Light-Emitting Diodes by copolymerization with other functional unit. [Salim, T.]; Solar cell application of Polyfluorene Copolymer by blending with Poly(3-hexylthiophene) Nanofiber was also reported. [Teramoto, T.]

#### 3.2.2 Polymers derived from 9,9-bis(4-hydroxyphenyl)fluorene

Because 9 position of fluorene with its high reactivity, it was easy to be oxidized by oxygen, and convert to fluorenone. With further reaction with the compounds with aryl group, can design and achieve many kinds of 9,9-diaryl fluorene. [Teramoto, T.; Papava, G. S; Morgan, P. W.; Yamada, M.; Yamada, M.; Li, Y.J.; & Korshak, V.V]

These kinds of diaryl fluorene, because they have multiple aromatic rings in one molecule, fluorene unit and aryl group can had to be positioned in same planar due to high steric hindrance of them. The structure based on 9 position of fluorene similar to wings and body of butterfly so called cardo structure. [Sakurai, K. et al]

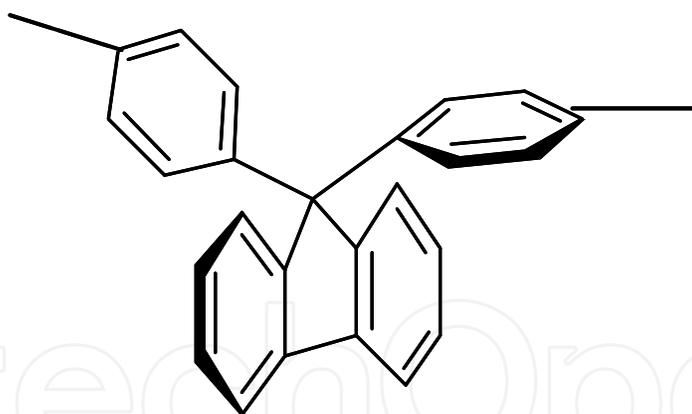


Fig. 3.2.2. *Cardo* structure of fluorene based compound.

#### 3.2.2.1 Polymers in commercial base

Fluorene based polyester (FBP) possess high refractive indices (1.64 in average) as well as extremely low birefringence, so they are used in high fidelity lens materials such as digital cameras and cell phones with cameras, and can also be used as promising optical film materials due to its high flexibility and low retardation.

In general, organic polymers like polycarbonate and polyethyleneterephthalate have their high refractive index due high ratio of aromatic unit in their molecular chain. But, if the aromatic chains in same plane, anisotropy of unit with high dielectricity will cause optical anisotropy in molecules, finally results in high birefringence of molecules. But in the case of

fluorene molecules with cardo-structure, even the molecule had many aromatic ring, due to the rings not in the same plane, anisotropy of entire molecule was reduced, finally the achievement the molecule with high refractive index and low birefringence. [Yao, K.]

Fluorene based polyester (FBP) with cardo structure in it, regardless of its polyester structure, they demonstrated as amorphous materials. FBP had its refractive index over 1.6 which was higher than polycarbonate, and lower birefringence than PMMA. Figure 3.2.2.1 shows injection molded polycarbonate, PMMA, and FBP under polarized plates. [Kawasaki, S. et al]

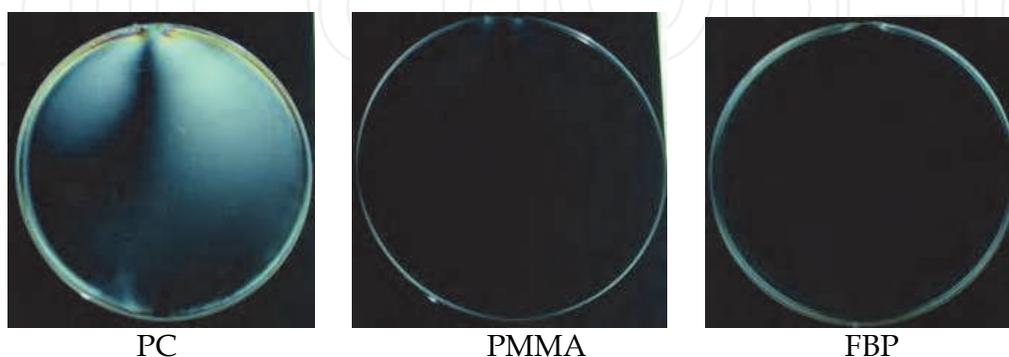


Fig. 3.2.2.1. Birefringence property of optical polymers.

Epoxy and Acrylates resin derived from 9,9-bis(4-hydroxyphenylfluorene) possess useful advantages such as high refractive indices and high heat resistance, and are used in hard coating materials and sealants and high refractive index coating films. [Liu, W. B.; Xiong, Y.Q.; & Dai, Z.]

FBP can also forming polymer alloys with commercial available polycarbonate and polyethylene naphthalene, and the final products with promising transparency and low birefringence compared to other alloys. [Kawasaki, S. et al]

### 3.2.2.2 Polymers in development

Except the polymers already available in the market, there are still many kinds of new applications on challenging by applying fluorene unit in the main chain. Polymers based on fluorene unit, like polyimide [Yang, C.P. et al], polyetheretherketone [Kawasaki, S. et al], polythioether [Hayashi, H. & Seesukphronrarak, S] were synthesized to increase solubility and process ability of high performance polymers; silicon contained polymers to increase heat resistance. [Seesukphronrarak, S et al] Spiro unit contained polymers to increase refractive index of fluorene polymers [Seto, R. et al] now under challenging too. Some nanocomposites based on organic-inorganic hybridization of fluorene with organic metallic compounds were also published recently. [Matsukawa, K.; & Suzuki, A.]

### 3.3 Potential power of fluorene moieties to disperse carbon filler

Since the first finding by Chen F. et. al that fluorene-based polymers are able to selectively wrap the single-walled carbon nanotubes (SWNTs) with certain chiral angles or diameters depending on their chemical structures, many report regarding selective dispersion of CNTs in fluorene based polymers were published in the world. [Chen, F.; & Ozawa, H.]

The polymers investigated in the research focused on 2,7-linked polymerization of fluorene diaryl substitutes. No report had been published before the finding of fine dispersion of

9,9-bis (4-hydroxyphenyl) substitute derivatives on carbon fillers. In chapter 4, detailed finding of 9,9-bis (4-hydroxyl phenyl) substituted fluorene derivatives on carbon filler dispersion will be discussed. [Inada, T.; & Kawasaki, S.]

#### 4. Dispersing power of carbon fillers in fluorene moieties

##### 4.1 Dispersing power of fluorene moieties on carbon black in fluorene moieties

###### 4.1.1 Introduction

Although the surface modification of carbon fillers is one of the established methods for producing excellent composite resins containing carbon fillers, a matrix resin that can disperse carbon fillers on its own will be a more efficient way to achieve high performance composite materials.

In this section, we compare the dispersion of carbon black (CB) in fluorene-based epoxy (FBE) resin with bisphenol-based epoxy (PBE) resin that does not contain a fluorene skeleton. The dispersity of carbon black in thermal plastic resin containing 9,9-cardo fluorene structure compared with the common thermal plastic resin polycarbonate are also discussed in this section.

###### 4.1.2 Composites of CB/FBE

It was found that the L value of CB/FBE composite decreased with an increase in the content of CB. For the CB/FBE composites, the L value was lower than that of CB/PBE composites in three cases (containing 3, 5, and 7 wt% of CB in CB/FBE resin), especially for the CB/FBE composite containing high CB content in them (Figure 4.1.1).

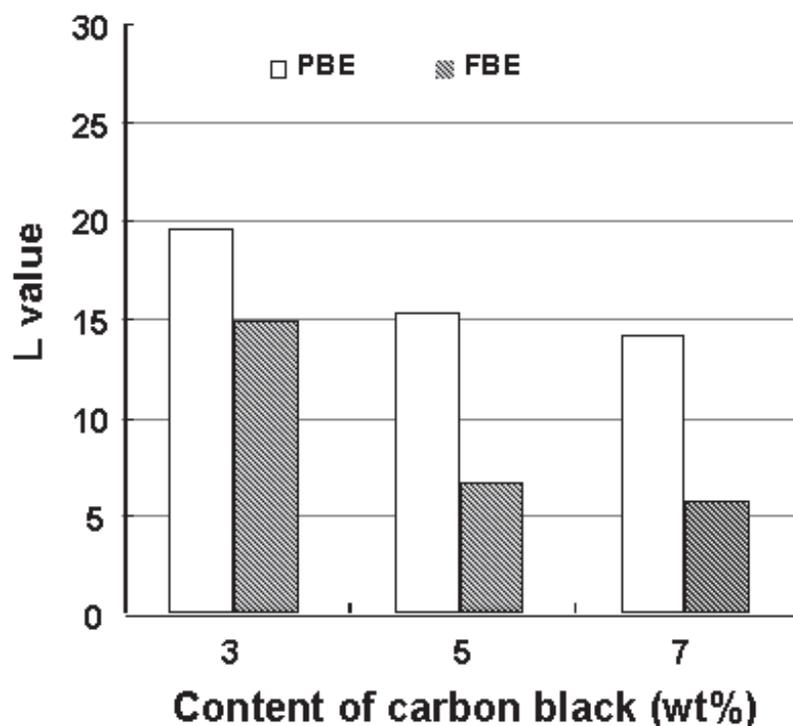


Fig. 4.1.1. Colorimetric analysis of coating film in which carbon black was dispersed in the epoxy resin.

The result of the reflectance between 400 nm and 700 nm was shown in Figure 4.1.2. The reflectance of CB/FBE composite was lower than PBE at either CB concentration. Generally, the optical density that was calculated from the degree of reflection was regarded as an index of the blackness. The optical density (OD) is defined in the equation,

$$OD = \log (1 / T)$$

where  $T$  is the transmittance.

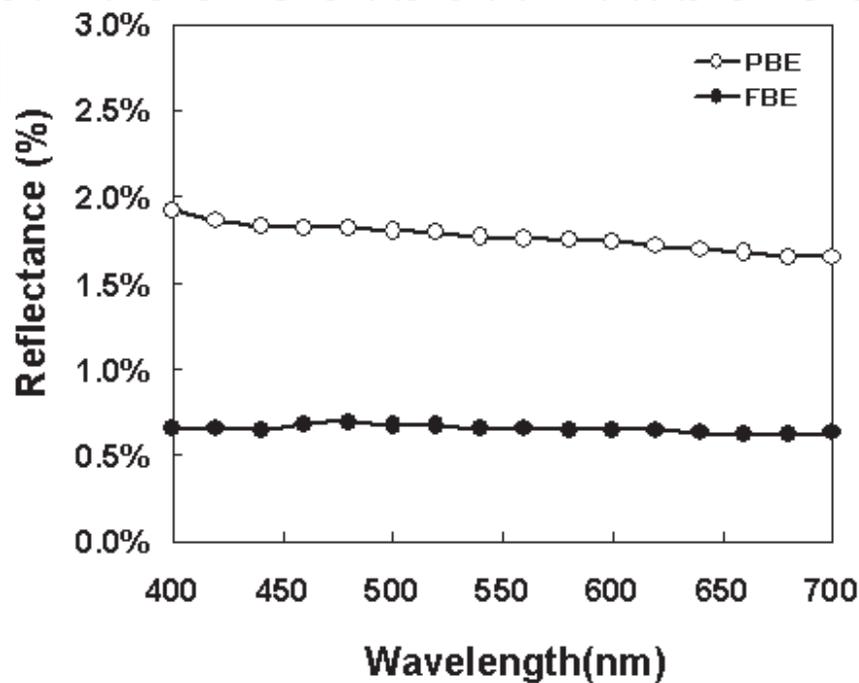


Fig. 4.1.2. Reflectance of CB/FBE composite sheets and CB/PBE sheets containing 7 wt% of CB in the composites.

In the case of CB/FBE composite containing 7 wt% content of CB, the optical density of the composite was 2.18, on the other hand, the optical density of CB/PBE composite was 1.75. This means that the degree of blackness of CB/FBE composite was higher than that of CB/PBE composite.

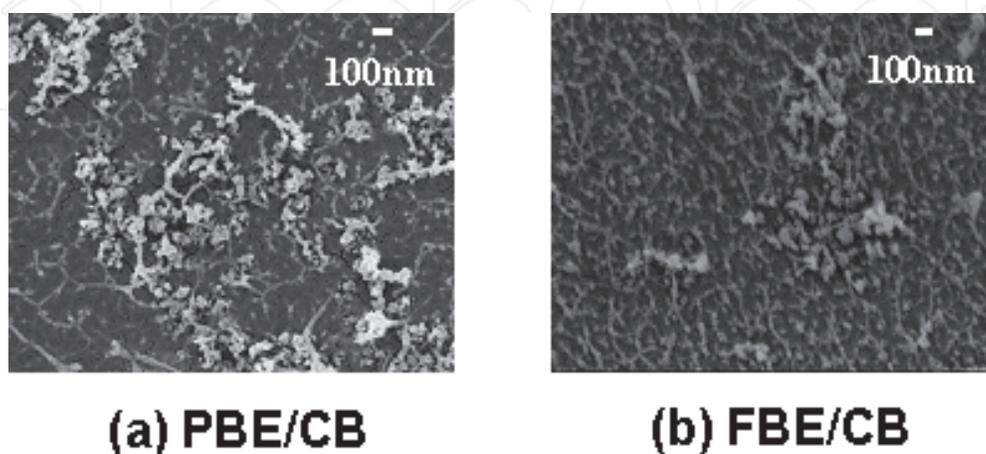


Fig. 4.1.3. FE-SEM images of the epoxy resin film (containing CB, 7 wt%).

The dispersion state of CB observed by FE-SEM is shown on Figure 4.1.3. In the case of CB/PBE composite, there are large aggregations of CB observed. On the other hand, in the case of CB/FBE composite, aggregate size was much smaller than in the CB/PBE composite.

#### 4.1.2 Fine dispersion of CB in FBP

Even a 50% addition of carbon black (CB) was possible for the CB/FBP composite. High amount of CB in FBP did not cause a reduction in the efficiency of FBP. On the other hand, for the CB/PC composites only 10 wt% CB was available to be dispersed into the PC matrix. High dispersion amount of CB in FBP is obvious evidence for the high compatibility of FBP with CB.

##### 4.1.2.1 Effect of CB addition on the mechanical properties and thermal properties of FBP

The effect of CB addition on CB/FBP composites is shown in Table 4.1.1. Storage modulus of CB/FBP composites was increased with the addition of CB in the composites. Enhancing ratio of CB on FBP was about two times above the PC. It means that CB interacted more strongly with FBP than with PC.

	FBP	PC
Without CB(A)	$1.9 \times 10^9$ Pa	$2.2 \times 10^9$ Pa
With 5wt% CB(B)	$4.9 \times 10^9$ Pa	$3.4 \times 10^9$ Pa
Effect of CB on CB/Polymer composites (B/A)	2.6	1.5

Table 4.1.1. Results of Dynamic Mechanical Analysis

The softening point of FBP was increased to about 22°C by the addition of CB; however, the effect of this addition was quite low on PC (about a 4°C increment). This was the other evidence supporting the high interaction between CB and FBP compared with the low interaction of CB and PC.

As shown in Figure 4.1.1, the degree of blackness for the CB/FBE composite was much higher than that of the CB/PBE composite. The aggregation of CB in the CB/FBE composite was much smaller than that in CB/PBE composite. According to the results shown above, it is obvious that the dispersion of CB in the CB/FBE composite was much finer than in the CB/PBE composite.

In addition, CB had a fine dispersion in FBP when compared with PC. With the same amount of CB addition, enhancement of mechanical properties and the increase in the Tg of FBP is much higher than that of PC (Table 4.1.2)

All the above results indicate that 9,9-substituted fluorene may have a strong interaction with carbon black. The strong interaction results in the fine dispersion of CB in FBP and the enhancement of mechanical properties as well as an increase in Tg.

	FBP	PC
Without CB(A)	148°C	166°C
With 5 wt% CB(B)	170°C	170°C
Effect of CB on CB/Polymer composites (B-A)	22°C	4°C

Table 4.1.2. Results of Glass Transition Temperature

#### 4.1.3 Summarize of section 4.1

CB can be dispersed finely in CB/FBE composites. Compared with the aggregations of CB in PBE, there was no obvious aggregation in CB/FBE observed. The fine dispersion of CBs in FBE can be regarded as a result of strong  $\pi$ - $\pi$  interaction between CB and FBE molecules. Also, because of the strong interaction, FBP molecules are firmly held by CB molecules by finely dispersing in them. This restriction of FBP molecules appears as a result of an increase in the Tg of FBP.

### 4.2 High dispersion ability of fluorene-based polyester as polymer matrix for carbon nanotubes

#### 4.2.1 Introduction

The high electric conductivity of CNTs make them suited for use in electronic fields and makes it possible to prepare polymer composites using CNTs that have particular electric conductivity or electrostatic discharge properties. Although surface modification of carbon fillers is an established method for producing excellent composite resins, developing a matrix resin in which carbon fillers without such modification could be dispersed would provide a more efficient method of achieving high-performance composite materials.

The *cardo* structure of fluorene-based polymers, demonstrated in structure 1, makes it easy to achieve the fine dispersion of fillers such as carbon black, CNT and organic pigments. In a previous report, the fine dispersion ability of carbon black in FBP was proved.

This section discusses the fine dispersion of carbon fillers having a high aspect ratio in FBP. MWCNT was used as high aspect fillers for FBP. Commercially available polycarbonate (PC) was used for comparison.

#### 4.2.2 Surface resistivity of MWCNT/polymer composites

A fine dispersion of MWCNT in matrix polymer will result in a low surface resistivity. In contrast, a covering of the matrix polymer on the MWCNT, will disturb the electrical pathways between MWCNTs – thus MWCNT covered with matrix polymer should have a higher surface resistivity than uncoated or 'naked' nanotubes.

Figure 4.2.1 shows the surface resistivity of MWCNT/polymer composites prepared by the solution casting method. Both of the composites of MWCNT with PC and FBP had a low percolation ratio, of between 0.5 ~ 1.0 wt%. The high dispersion power of PC and FBP on

MWCNT induced the low surface resistivity of the composites, and due to the covering of FBP on 'naked' MWCNTs, a higher surface resistivity of MWCNT/FBP-HX was achieved than for MWCNT/PC. The reason for this phenomenon was the covering of FBP-HX on MWCNT. It resulted in both the higher surface resistivity in MWCNT/FBP-HX composites and the higher percolation ratio of MWCNT/FBP-HX composites when compared with the values for MWCNT/PC composites.

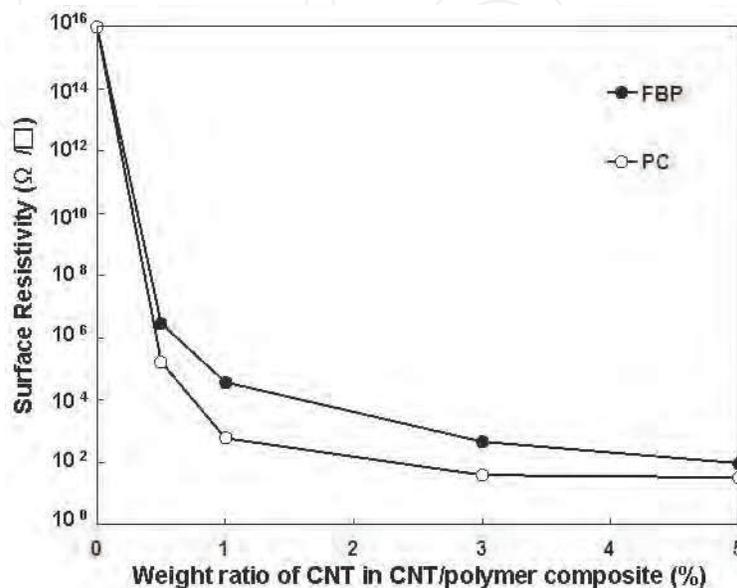


Fig. 4.2.1. Surface resistivity of MWCNT/FBP-HX composites prepared by solution casting, with different weight ratios of MWCNT (● MWCNT/FBP-HX composite, ○ MWCNT/PC composite).

#### 4.2.3 Fine dispersion of MWCNT in FBP-HX observed by SEM

MWCNTs in composite materials as prepared by the solution method showed significant differences in the PC and the FBP-HX polymer matrices. The fluorene structure of FBP-HX had a strong  $\pi$ - $\pi$  interaction with the graphite structure on the surface of the MWCNT. This improved the compatibility of MWCNT with the FBP-HX polymer through a process that is not yet clear. The MWCNTs were separated at the nanometer level in FBP-HXs. The fine dispersion of MWCNTs in FBP-HX and PC resulted in the low surface resistivity of both kinds of MWCNT/polymer composites, even those which contained low weight ratios (0.5 ~1.0 wt%) of MWCNT.

SEM observation of the cross-section of the MWCNT/FBP-HX composite indicated that the FBP-HX matrix polymer covered the surface of the MWCNTs (Figure 4.2.2b). However, this was not true for the MWCNT/PC composite, indicating that PC had a lower compatibility with the MWCNTs (Figure 4.2.2a, Figure 4.2.2c).

Figure 4.2.2a, 4.2.2b demonstrate the differences between the status of MWCNT in PC and FBP-HX. In figure 2b, almost none of the MWCNTs are separated from the matrix resin. In figure 4.2.2a, 'naked' MWCNT can be observed spilling out from the matrix resin.

The MWCNTs in FBP-HX, as observed by SEM, had diameters of 30 nm (Figure 4.2.2d). This was about 1.5 times that of the 'naked' MWCNTs (20 nm), providing more evidence for the fine dispersion of MWCNT in FBP-HX and the strong interaction between MWCNT and FBP-HX. It means that FBP-HX layer with 5 nm thick were covered on MWCNTs. The covered

layers of FBP-HX became swollen in chloroform. The diameters of the MWCNT covered with FBP-HX increased to 60-70 nm after becoming swollen in  $\text{CHCl}_3$  (Figure 4.2.2e).

All the above evidence shows that FBP-HX can cover the surface of MWCNT without further treatment. The fine dispersion of the MWCNT was the result of the strong interaction between the FBP-HX and the MWCNT.

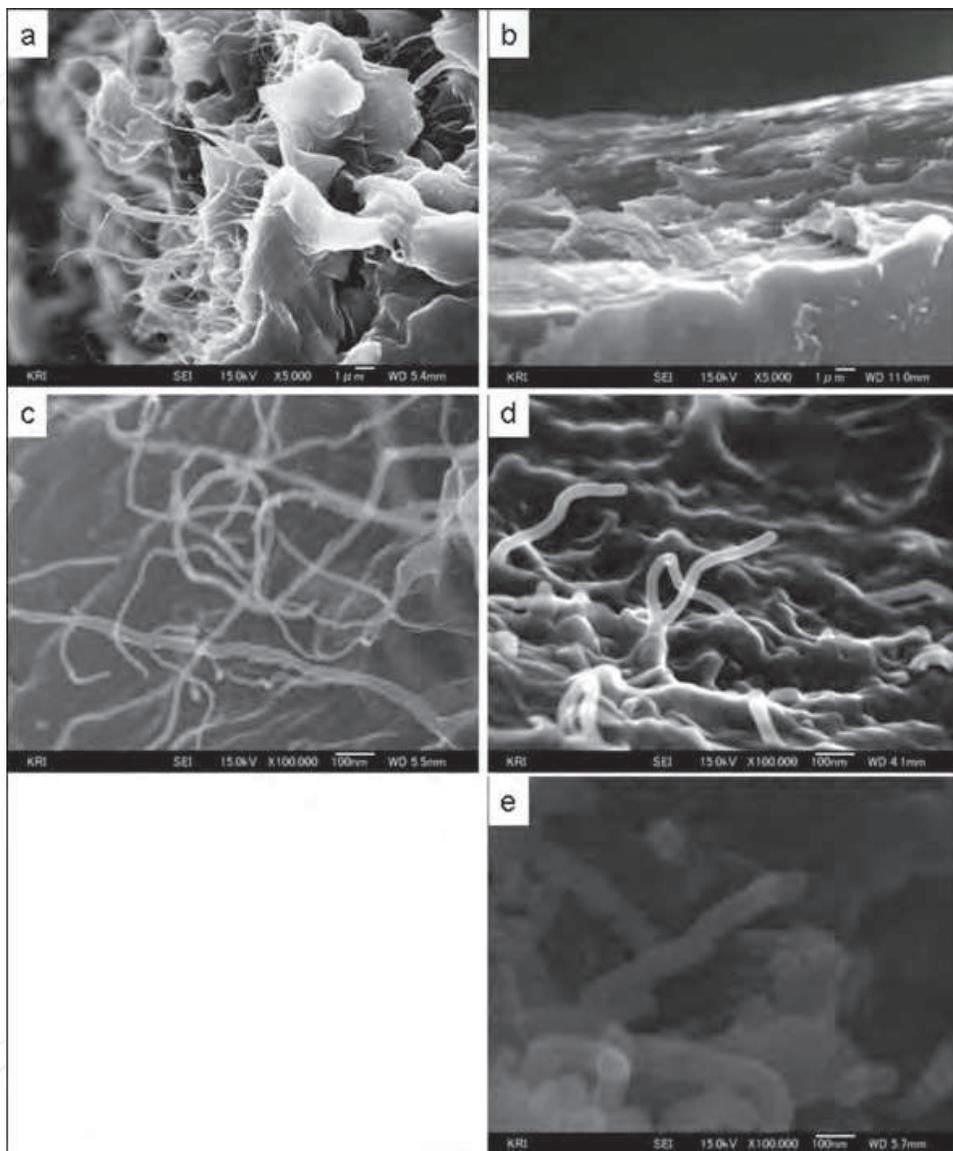


Fig. 4.2.2. Cross-sections of MWCNT/polymer composites observed by scanning electronic microscopy. a: MWCNT/PC composites with 3 wt% MWCNT,  $\times 5000$  magnification; b: MWCNT/FBP composites with 3 wt% MWCNT,  $\times 5000$  magnification; c: MWCNT/PC composites with 3 wt% MWCNT,  $\times 100000$  magnification; d: MWCNT/FBP composites with 3 wt% MWCNT,  $\times 100000$  magnification; e: swollen MWCNT/FBP composites with 3 wt% MWCNT,  $\times 100000$  magnification.

#### 4.2.4 Variation of glass transition temperature ( $T_g$ )

The glass transition temperature,  $T_g$ , is the temperature at which an amorphous solid, such as a glass or polymer, becomes brittle on cooling, or soft on heating. In polymers,  $T_g$  is often

expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. From this definition, we can see that the introduction of relatively stiff materials (such as carbon nanotubes) will interfere with the flow process and hence increase  $T_g$ . [IUPAC]

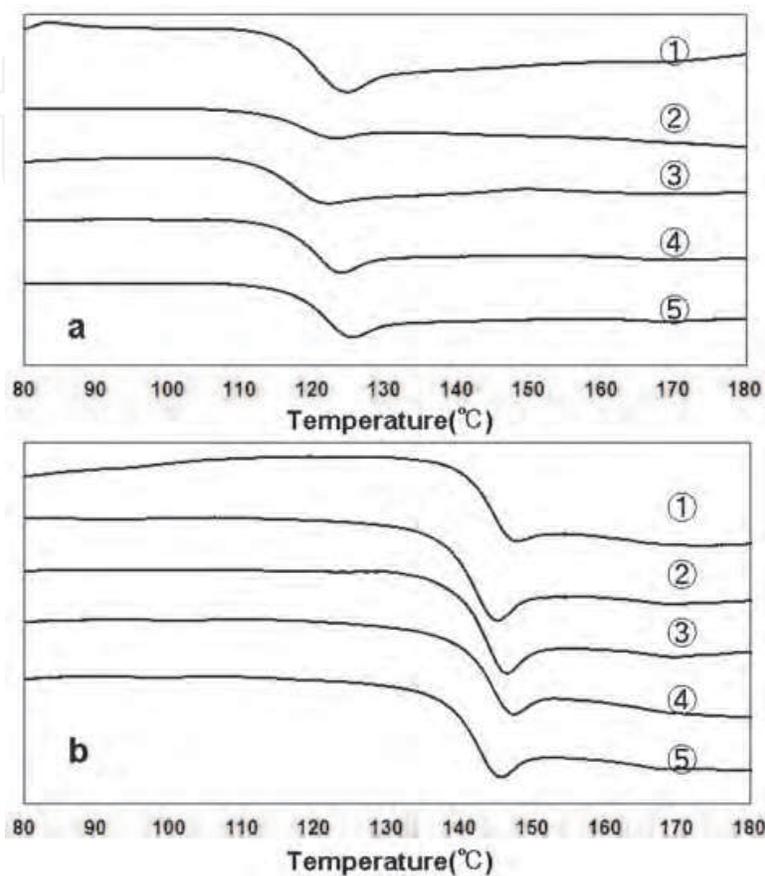


Fig. 4.2.3. Shift in the glass transition temperature of the matrix resin due to the addition of MWCNT. Figure 3a and 3b represent FBP-HX and PC composites with different amounts of MWCNT dispersed in them. ① Neat resin; ② composite with 0.5 wt% MWCNT in matrix resin; ③ composite with 1.0 wt% MWCNT in matrix resin; ④ composite with 3.0 wt% MWCNT in matrix resin; ⑤ composite with 5.0 wt% MWCNT in matrix resin.

It is shown in Figure 4.2.3 and Table 4.2.1 that the increase in  $T_g$  for FBP-HX in MWCNT/FPB-HX composites was due to the physical wrapping of the MWCNTs by the matrix resin. Although not the chemical modification of CNT, the immobilization of FBP molecules around CNT occurred. So, the matrix polymer (FBP-HX) was restricted by CNT. The reinforcements of the filler with high aspect ratio have been explained by the network forming method [Favier, V. et al]. According to Favier's theory, the incomplete nature of the network of the filler induces a reduction in the polymer's properties. This is reflected by the data we obtained at low additions (0.5~1.0 wt%) of CNT in polymer matrix. Above the ratio of network forming, the further addition of filler results in the greater reinforcing effect of the filler in the polymer matrix.

For the MWCNT/PC composites, the matrix polymer PC had a low interaction with the MWCNT. Therefore, it underwent only a minor change in its glass transition temperature.

Although the addition of MWCNT resulted in the improvement of the thermal dynamic properties for both the MWCNT/polymer composites, the driving force for the wrapping of MWCNT by PC and FBP is small. Therefore, the effect of MWCNT on the thermal dynamic properties was not that obvious, as demonstrated by the DSC data.

	T <sub>g</sub> (°C)	T <sub>gComposite</sub> /T <sub>gMatrix</sub>
PC	143.6	1
PC-CNT 0.5wt%	140.9	0.98
PC-CNT 1.0wt%	142.5	0.99
PC-CNT 3.0wt%	143.2	0.997
PC-CNT 5.0wt%	143.6	1
FBP-HX	119.4	1
FBP-CNT 0.5wt%	118.2	0.99
FBP-CNT 1.0wt%	116.2	0.973
FBP-CNT 3.0wt%	119.2	0.998
FBP-CNT 5.0wt%	120.7	1.011

Table 1. Variation of glass transition temperature of MWCNT/polymer composites

#### 4.2.5 Raman spectra of MWCNT/polymer composites

Raman spectra of MWCNT/polymer composites are shown in figure 4.2.4. For the MWCNT/PC composites (Figure 4.2.4a), a 1 wt% addition of MWCNT was enough to homogenize the mobility of the materials in the composites. A peak at around 1780 cm<sup>-1</sup>, which is known to result from the vibration of the carbonate groups of PC, disappeared due to the addition of MWCNTs in PC. The Raman spectra of MWCNT/PC composites with MWCNT weight ratios higher than 1.0 wt%, were similar to the spectrum of MWCNT alone (1340 cm<sup>-1</sup> for the defects of MWCNT and 1590 cm<sup>-1</sup> for the G-band of MWCNT). This shows that the MWCNTs in PC were separated out from the resin and mainly covered the surface of the composites, without a covering of PC on them.

In the case of MWCNT/FBP-HX composites (Figure 4.2.4b), a specific peak arising from the stretching of the phenyl groups on fluorene moiety was observed around 1450~1500 cm<sup>-1</sup>. The peak remained up till 3 wt% addition of MWCNT in FBP-HX. In the MWCNT/FBP-HX composites with a weight ratio higher than 5 wt%, this specific peak had disappeared. Because of the covering of FBP-HX on MWCNT, the mobility of the polymer and the MWCNT was almost the same; smaller amounts of 'naked' MWCNTs moved to the surface of MWCNT/FBP-HX composites. As per the increased diameter of MWCNT in FBP-HX compared to 'naked' MWCNT in PC, the Raman spectra provide more evidence for the fine

dispersion of MWCNT in FBP-HX because of the strong interaction between the FBP-HX matrix and the MWCNT filler.

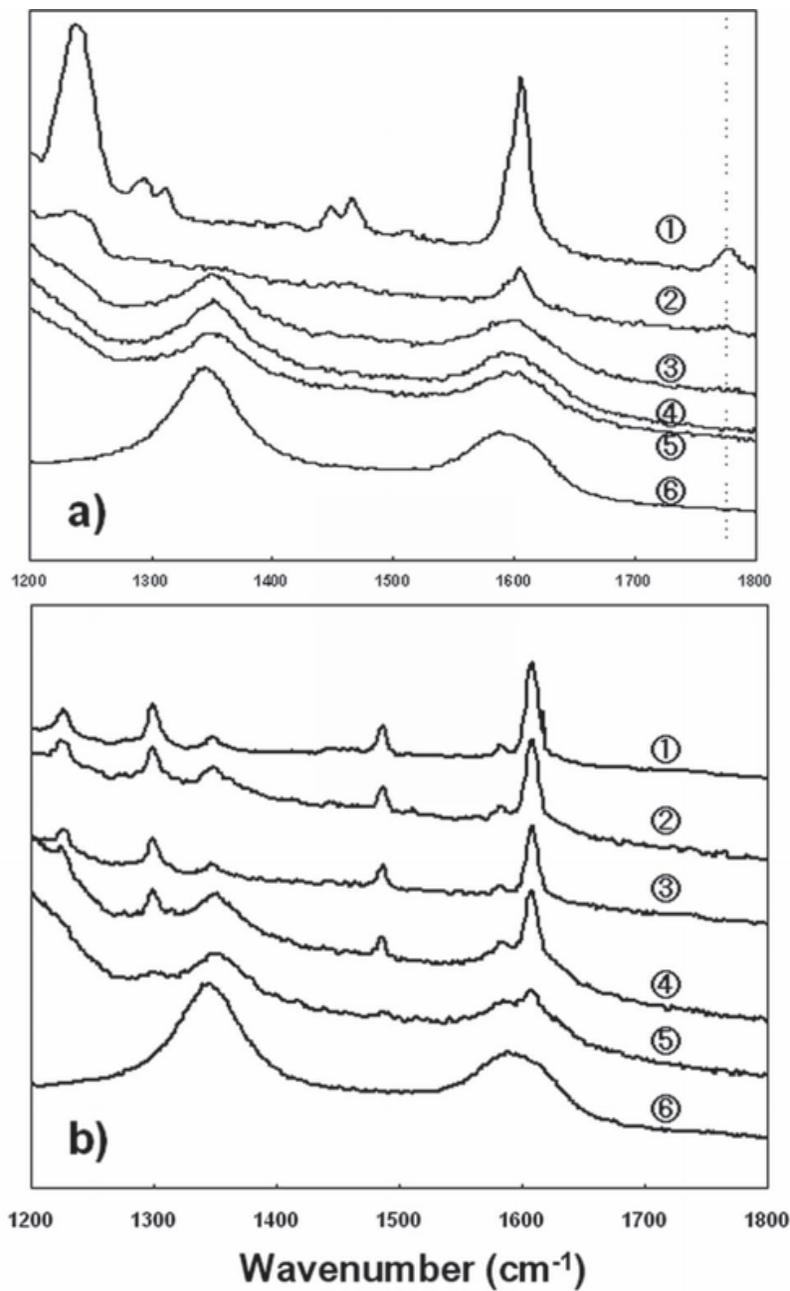


Fig. 4.2.4. Raman spectrum of MWCNT/polymer composites. Figure 4a and 4b represent PC and FBP-HX composites with different amounts of MWCNT in them. ① Neat resin; ② composite with 0.5 wt% MWCNT in matrix resin; ③ composite with 1.0 wt% MWCNT in matrix resin; ④ composite with 3.0 wt% MWCNT in matrix resin; ⑤ composite with 5.0 wt% MWCNT in matrix resin; ⑥ MWCNT.

#### 4.2.6 Summarize of Section 4.2

The fine dispersion of MWCNTs in FBP-HX and PC resulted in low surface resistivity of both kinds of MWCNT/polymer composites, even those containing low weight ratios (0.5

~1.0 wt%) of MWCNT. FBP-HX covered MWCNTs were observed in MWCNT/FBP-HX composites; however, for the MWCNT/PC composite, the MWCNTs remained separate from the matrix polymer. Because of that, a higher surface resistivity and a higher percolation ratio were achieved for the MWCNT/FBP-HX composites, compared with the values for the MWCNT/PC composites. The  $T_g$  of the matrix polymer was lower at lower concentrations of MWCNTs in polymer. At higher concentration ratios, that is above 5 wt% of MWCNT incorporated with the polymer, an increase in the  $T_g$  was observed. The relative increase in the  $T_g$  for FBP-HX was higher than that for PC for the MWCNT/polymer composites. Raman spectroscopy of MWCNT/polymer composite sheets with 3 wt% addition of MWCNT indicated that the MWCNTs in the MWCNT/PC composites covered the surface of the sheets in their 'naked' form, but the MWCNTs in MWCNT/FBP-HX sheets were distributed homogeneously in the bulk and were covered with FBP-HX.

## 5. Discussion of dispersing power of fluorene moieties on carbon fillers

All the results in section 4 indicate that 9,9-substituted fluorene may have a strong interaction with carbon black. The strong interaction results in the fine dispersion of Carbon Plate in FBP and the enhancement of mechanical properties as well as an increase in  $T_g$ . To prove our assumption, we performed computational simulations on both Carbon Plate (Carbon plate with C96 structure was designated to represent carbon filler). /FBE and Carbon Plate models to determine their respective stabilizing energy (Carbon Plate /FBE, Figure 5d) and Carbon Plate /PBE, Figure 5e)). It was shown that the most stable structure of FBE-M was more stable than that of PBE-M at about 10 kJ/mol. This indicated that the compound containing a fluorene skeleton was able to interact with the carbon compound more strongly than that containing bisphenol. This was one of the reasons for the high dispersion of the carbon compound in the epoxy resin containing fluorene structure. On the other hand, 9,9-substituted phenyl groups on fluorene moieties also interacted with Carbon Plate through  $\pi$ - $\pi$  interactions. This strong interaction was also related to the fine dispersion of Carbon Plate in FBE.

## 6. Conclusions

High dispersion power of *cardo*-typed fluorene moieties on carbon fillers was discussed in this chapter.

CB can be dispersed finely in CB/FBE composites. Compared with the aggregations of CB in PBE, there was no obvious aggregation in CB/FBE observed. The fine dispersion of CBs in FBE can be regarded as a result of strong  $\pi$ - $\pi$  interaction between CB and FBE molecules. Also, because of the strong interaction, FBP molecules are firmly held by CB molecules by finely dispersing in them. This restriction of FBP molecules appears as a result of an increase in the  $T_g$  of FBP.

MWCNTs covered with FBP-HX were observed in MWCNT/FBP-HX composites; however, for the MWCNT/PC composite, the MWCNTs remained separated from the matrix polymer. Because of that, lower concentration of MWCNT is sufficient to induce electrical conductivity in MWCNT/PC composites than MWCNT/FBP-HX composites. The  $T_g$  of the matrix polymer decreased in lower concentration of MWCNTs in polymer. At higher concentration ratio above 5 wt% of MWCNT incorporated with polymer, increasing of  $T_g$  is observed. The increase in  $T_g$  for FBP-HX was higher than that for PC in MWCNT/polymer composites. Raman Spectrum indicates that MWCNT in MWCNT/PC composites were

covered on the surface of composites sheets with naked state, compared to covered FBP-HX on MWCNT in MWCNT/FBP-HX composites.

Computer simulation of the graphene model combined with the FBE and PBE models also proved that the graphene/FBE model has a lower minimum energy than the graphene/PBE model. It means that fluorene carbon model had strong interaction than other without fluorene. It also resulted fine dispersion of carbon fillers in fluorene moieties.

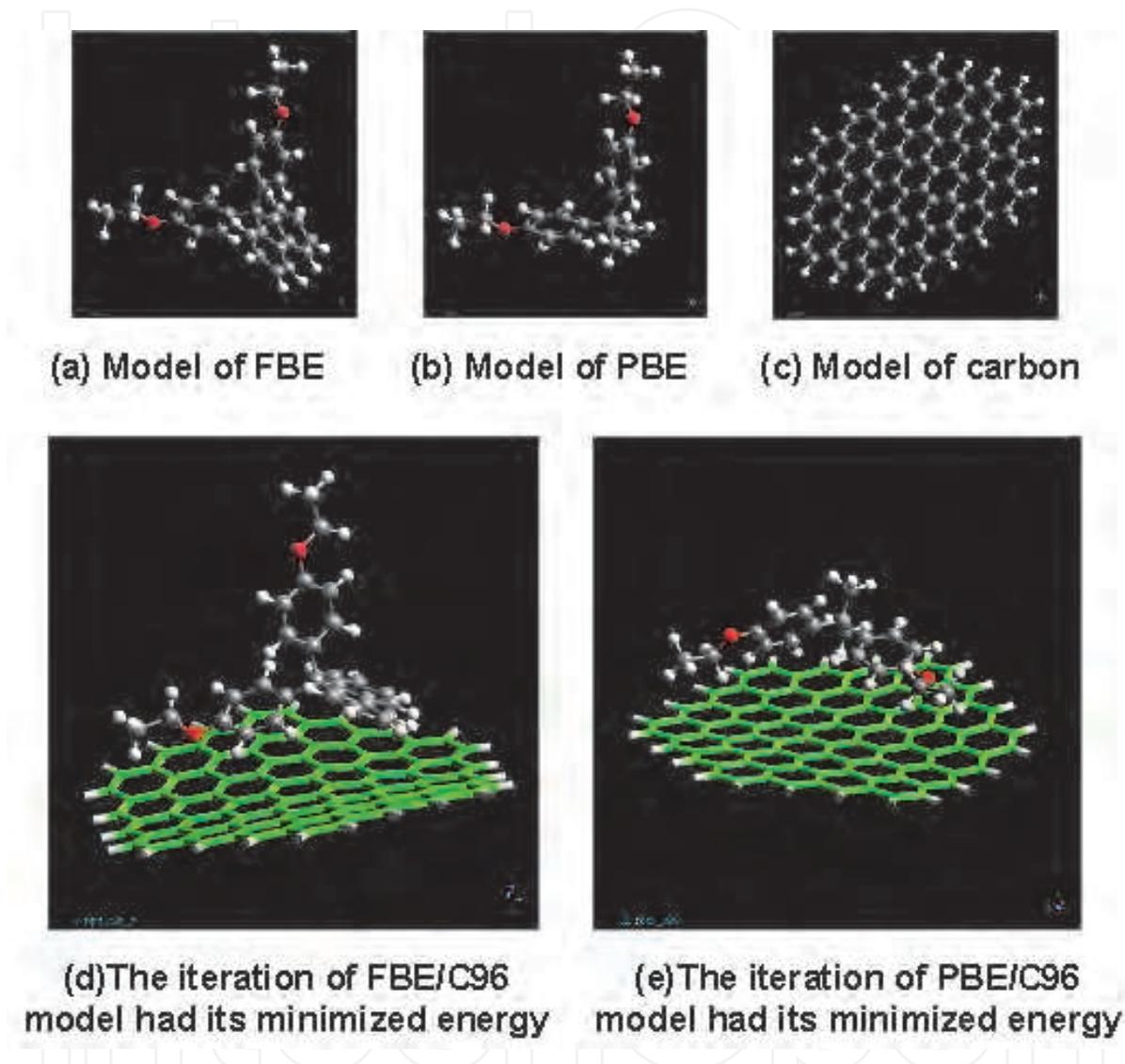


Fig. 5. Model structure and the iteration of FBE/Carbon plate and PBE/Carbon Plate models that have their minimum energy. Here, a, b, and c referred to the model of FBE, PBE, Carbon Plate (C<sub>96</sub>), respectively; d and e referred to the iteration of FBE/ Carbon Plate and PBE/ Carbon Plate model that has its minimum energy.

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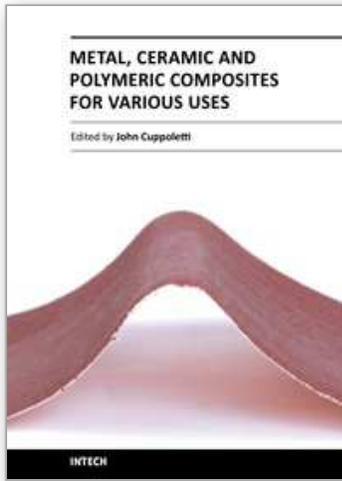
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