

Extraordinarily High Carbon Filler-Incorporating and Dispersing Ability of 9,9-Diarylfluorene-based Polymers as Matrix Resins

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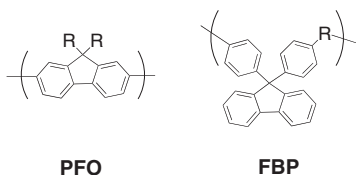
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Composite materials containing carbon fillers are well used in a variety of material fields including electronic and optical device fields. The carbon fillers are capable of endowing conductivity,¹ heat-releasing ability etc. to the composites.^{2–7} 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.⁸ 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.

Both polyfluorenes (PFO)^{9–11} and 9,9-diarylfluorene-based polymers (FBP, Structure 1) are interesting polymers as optical materials. In particular, FBP is actually used as lens materials.^{12–15} While PFO as matrix resin is known to have ability of dispersing nano-ordered fillers such as carbon nanotube (CNT),¹¹ much attention has recently focused on the filler-dispersing power of FBP.^{16–18} However, there is reported no study on the interaction between the carbon filler and matrix resin, the carbon filler-dispersing mechanism of FBP, and so on. In the recent study on polymer materials based on 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 paper, we would like to communicate 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.



EXPERIMENTAL

Materials and Methods

9,9-Bis(phenoxyethanol)fluorene diglycidyl ether (FBE, OGSOL-EG, Osaka Gas Chemical Co., Ltd.) and bisphenol-A diglycidyl ether (PBE, ADEKA RESIN EP-4520, Asahi Denca Co., Ltd.) were used as matrix resins (Structure 2). An amine compound (ADEKA HARDENER EH-458, Asahi DENCA Co., Ltd.), carbon black (CB, MA100, Mitsubishi Chemical Co., Ltd.), and multiwall carbon nanotube (CNT, Shenzhen Nanotech Port Co., Ltd.) were employed as hardener and fillers. Degree of dispersion of carbon filler in resin was evaluated with a spectrophotometer (Macbeth Color Eye, CE-3000), a FE-SEM (JEOL, JSM-7400F), and a Digital Microscope (VHX-100).

Preparation of Composite Material A typical procedure for FBE. To a solution of FBE (2.0 g) in tetrahydrofuran (2.0 g), were added a hardener (0.54 g) and a carbon black. The content of carbon used was 5 wt % (0.13 g) and 7 wt % (0.18 g) to the epoxy resin. The mixture was treated with an ultrasonic homogenizer for 30 s to obtain a composite material.

Preparation of Coated Material A coating film was prepared on a glass plate by spreading a tetrahydrofuran solution of FBE which contained an appropriate amount of CB so as to yield 0.3 mm thickness film by using a bar coater. The resulting wet film was dried at 60 °C for 3 h in a dry oven.

Preparation of CNT-Dispersed Composite Material Powdery CNT (0.5 g) was shaken in 14.0 g THF in the presence of 50.0 g zirconia's beads (diameter 30 μm)¹⁹ using a paint shaker for 3 h, giving a finely dispersed THF solution of CNT.

To a solution of a polymer (1.0 g) in a mixed solvent of THF and ethyl acetate (2.4 g and 1.6 g, was added 30.0 g of zirconia's bead¹⁹ and the mixture was stirred until all polymer was dissolved.

Coating solution containing 3 wt % of CNT in the composites was prepared by mixing 0.73 g of the CNT dispersion and 1.0 g of the polymer solution. The mixed solution was rotated with a paint shaker for 1 h, affording a composite mate-

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rial for coating.

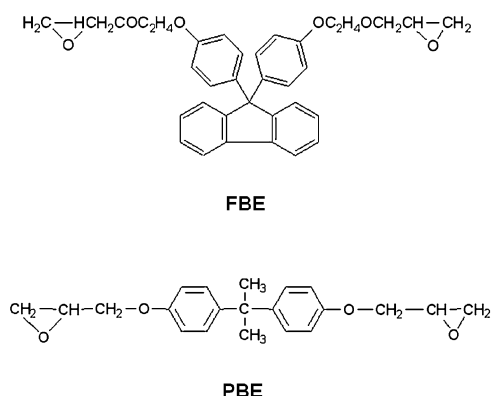
Preparation of Coated Film Coated film was prepared by coating a part of the solution prepared above on a PET film by a bar coater, and the film was dried at 120 °C for 30 min in a dry oven.

Method of Calculation With a model compound of the resin (EPF or bisphenol-A-based model) and a model of carbon black or CNT (graphite C96), energy minimization for their interaction was optimized using Cerius2-Minimizer with the force field of COMPASS.

RESULTS AND DISCUSSION

Affinity between fluorene-based epoxy resin (FBE) and carbon black (CB) was first investigated. Surprisingly, FBE resin could easily form the molded product with CB even in high CB content over 40 wt %. The unusually high CB-incorporating ability of FBE strongly suggested the relation to the high CB-dispersing power of FBE, indicating usefulness of FBE as the potent matrix resin.

To evaluate the CB-dispersing ability of FBE, bisphenol-A-based epoxy resin (PBE), a typical epoxy resin, was chosen for comparison. Coating film of the composite material was prepared by curing a mixture of an epoxy resin, CB, and a hardener.



Degree of dispersion of CB in the epoxy resins was evaluated by the measurement of “L” value, which is known as a parameter of colorimetry to measure the color intensity of an object with an appropriate spectrophotometer. The value $L = 0$ means complete black, whereas $L = 100$ indicates complete white. As shown in Figure 1, L value of FBE/CB composite film was much lower than that of PBE/CB composite film at a CB content of either 5 wt % and 7 wt %.

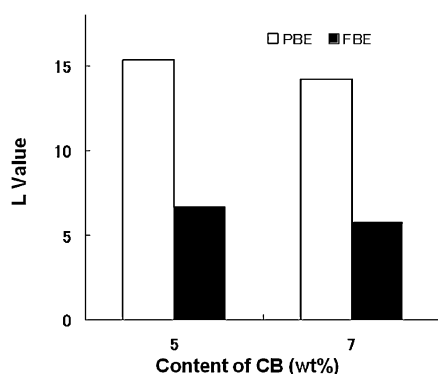


Figure 1. L value for the PBE and FBE resin-coated films containing CB measured by colorimetry.

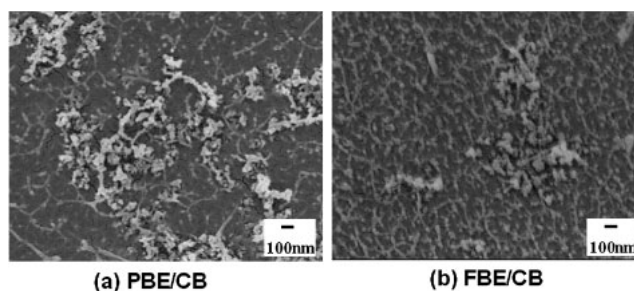
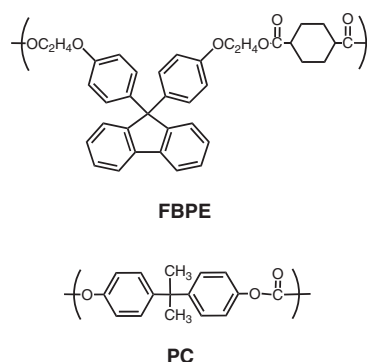


Figure 2. FE-SEM images of the CB-containing epoxy resin films: (a) PBE/CB and (b) FBE/CB.

The results clearly suggest that the degree of blackness of FBE/CB much higher than that of PBE/CB are undoubtedly resulted from the fine dispersion of CB in FBE resin. This was well supported by the FE-SEM results (Figure 2). The big difference between the two dispersion states of CB in the matrix resins containing CB (7 wt %) was observed. While large CB aggregates was appeared in everywhere of the PBE/CB composite (Figure 2(a)), no or less CB aggregate was found in the FBE/CB composite.

Thus, it is concluded that the FBE resin has ability to disperse CB much finer than PBE resin does, giving the composite with the excellent quality of blackness, in addition to its highly CB-incorporating power.



In relation to the marked CB-incorporating and dispersing power of FBE, filler-dispersing power of another fluorene-based polyester (FBPE, structure 3) was examined using carbon nanotube (CNT). From the microscope observation of the composite materials (Figure 3), the dispersion of CNT in FBPE (a) was much finer than that in polycarbonate (PC) (b), a typical matrix resin for CNT.²⁰

To explain the reason for the above mentioned unusually high dispersion of carbon fillers into FBPs, the authors noticed a special π - π interacting ability of 9,9-diarylfuorene moiety toward π -face of the carbon fillers such as CB. The π - π interaction was evaluated by the structure calculation of several

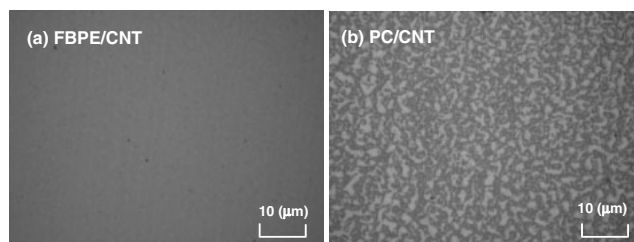


Figure 3. Digital microscope images of CNT-containing composite resins: (a) FBPE/CNT and (b) PC/CNT.

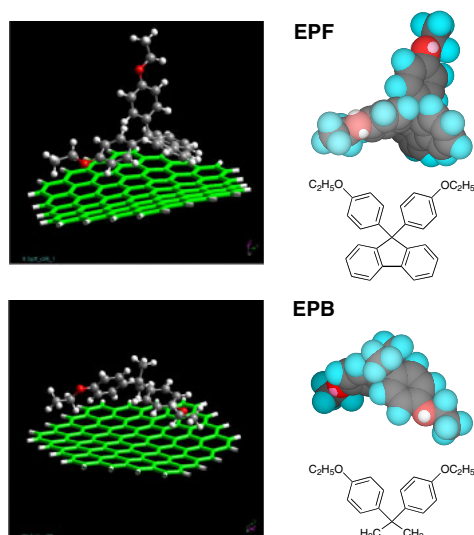


Figure 4. Optimized stable bimolecular structures (left) between model compound EPF (top) or EPB (bottom) and graphite(96), and chemical and MM2-calculated structures of EPF and EPB.

models using graphite (96) plane as the CB model. Figure 4 shows a typical π - π interaction model among the optimized stable structures where 9,9-bis(4-ethoxyphenyl)fluorene (EPF) as a model of FBP and graphite (96) can take a good π -face to π -face interaction. Namely, the fluorene pseudoplane including one 9-phenyl group is placed almost parallel to the graphite plane. It was impossible to obtain such a stable bimolecular association when a bisphenol-A-based resin model was used instead of EPF (10 kJ/mol energy difference). The strong interaction may depend largely upon the 9-phenyl group-containing fluorene skeleton, but not the fluorene skeleton alone.

In addition to the theoretical calculation, a model study on the π - π interaction was examined with a compound containing both the fluorene and C_{60} moieties. The UV-vis spectral study revealed the occurrence of the π - π interaction between the two chromophores,²¹ from the decrease in peak intensity of the typical C_{60} absorption peak around 330 nm.²²

In summary, it has been found that FBP resins have ability to incorporate much amount of carbon fillers such as CB and to disperse them quite finely, giving the composites with the excellent quality, in the present study. Theoretical and model studies have suggested that the 9,9-diarene-substituted fluorene moiety has extraordinary large affinity to unmodified carbon fillers containing π -skeleton. Therefore, FBPs can be regarded as the effective matrix resins possessing strong attractive interaction toward π - π interactive fillers such as CB and CNT. The extremely high carbon filler-dispersing power of the fluorene-based polymers will be utilized in a variety of composite material fields.

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20. It was found that the FBPE resin has an excellent pigment dispersing power, from the FE-SEM observations of the composites of FBPE and PC with pigment Disperse Blue 3.
21. Interaction between a FBP model compound and [60] fullerene: To evaluate the interaction between the FBP and carbon filler, UV-vis spectra of a FBP-graphite model compound consisting both 9-aryl-fluorene and [60]fullerene moieties were measured. The absorbance decrease around the [60]fullerene absorption (330 nm) was confirmed, showing that two moieties can interact each other via the π - π interaction at high concentration like in the composite. Thus, it can be considered that the occurrence of the attractive interaction between the FBP and carbon filler causes the extraordinarily high dispersion of the carbon filler in the FBP matrix.
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