

## NOVEL MATERIAL DESIGN OF IMMISCIBLE POLYMER BLENDS WITH LOCALIZED DISTRIBUTION OF CARBON NANOTUBES

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### **Abstract**

*The migration phenomenon of multi-walled carbon nanotubes (CNTs) is detected from isotactic polypropylene (PP) to polycarbonate (PC) during annealing procedure in the molten state. After cooling process, the piled sheet composed of PP/CNT and PC sheets can be separated without any difficulty. This technique provides a polymer sheet showing low level of surface resistivity with a considerably small amount of CNTs, because the conductive CNT network is formed only in the thin surface layer. On the contrary, the CNT transfer from PC to PP does not occur, indicating that the transfer is determined by the interfacial tension with CNTs. These experimental results suggest that CNT localization in a polymer blend can be achieved by employing an appropriate immiscible system, which provides a new type of material design of a conductive polymer composite.*

### **1 Introduction**

As increasing the demand for electronic application of polymeric materials, a polymer with good electrical conductivity has been desired and investigated intensively these days. Especially, carbon nanotubes (CNTs) are widely used as one of the high-performance modifiers because of the unique properties such as high stability, high electric and thermal conductivity, and large aspect ratio. As the filler content increases, the composite exhibits a transition from an electrical insulator to a conductor due to the formation of a conductive network.

It was previously reported that CNT-filled polymer composites without post-processing annealing procedure would be a thermodynamically non-equilibrium system, in which conductive network formation depends on the temperature and residence time [1,2]. Consequently, redistribution process of conductive fillers takes place, which is known as dynamic percolation [2-5].

According to Mamunya [6], the distribution of conductive fillers in an immiscible polymer blend is determined by interfacial tension. Moreover, he demonstrated that carbon black is localized at the interface between both polymers at the specific condition. Meanwhile, Sumita

et al. [7] and Duvdevani et al. [8] reported that carbon fibres or carbon blacks in an immiscible blend immigrate during melt-mixing from one phase to another. In their cases, two basic requirements must be fulfilled to form a conductive network throughout the composite: (1) a three-dimensional filler network is achieved in a filler-rich phase, and (2) the filler-rich phase exists continuously in a blend. In this study, CNT migration behaviour is studied to propose a new material design of conductive polymer nanocomposites by localization of CNTs.

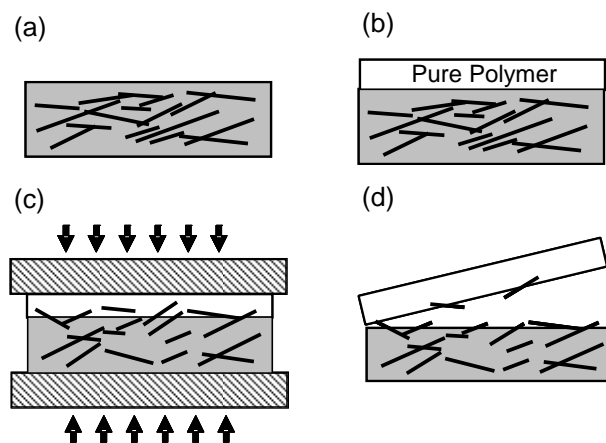
## 2 Materials and testing methods

### 2.1 Materials

Polycarbonate (PC), poly(ethylene terephthalate) (PET), and polypropylene (PP) were used as polymers. The compounds of 20 wt% of multi-walled carbon nanotubes (CNTs) in PC and PP matrix were prepared by melt-mixing. Typical diameters of employed CNTs are from 40 to 80 nm, while the lengths are between 10 and 20  $\mu\text{m}$ . The density is approximately 2300 kg/m<sup>3</sup>.

### 2.2 Transfer in piled sheets

The polymer composites with 20 wt% of CNTs and corresponding pure polymers (PC and PP) were compressed into flat sheets using a compression-moulding machine. Each specimen was heated at 200 °C for 4 min and then quenched at 30 °C. In case of pure PET, the compression-moulding was performed at 280 °C. The laminated sheets were prepared by placing the pure polymer sheet on the sheet of a polymer composite with 20 wt% of CNT. Furthermore, annealing operation was performed in a compression-moulding machine at 300 °C for 2 and 15 min. After annealing, the sheets were cooled and then separated to observe the morphology of the surface of the pure polymer by a scanning electron microscope (SEM). The detail in the experimental method was described in Figure 1. In case of the piled sheets of PP – PP/CNT and PC – PC/CNT, an aluminium foil was sandwiched between the sheets to confirm the boundary. Then, the morphology of the cross-sectional area was observed by SEM without separating sheets.



**Figure 1.** Experimental procedure of CNT transfer [1]; (a) a CNT-filled polymer sheet, (b) place a pure polymer sheet on the CNT-filled sheet, (c) anneal the laminated sheet at 300 °C, and (d) separate the sheets after cooling.

### 2.3 Transfer during melt-mixing

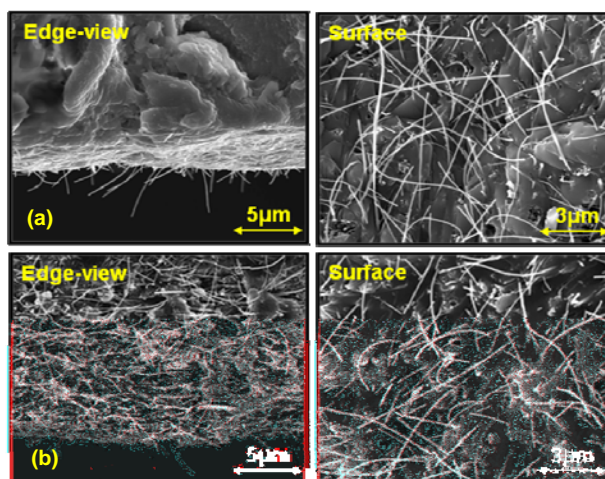
Melt-mixing was carried out using PC/CNT(80/20) and PET in an internal mixer at 280 °C for 5 min. The blade rotation speed was 50 rpm, and the weight content of PC in the blend was

44 %. After mixing, the samples were compressed into flat sheets and then annealed at 120 °C for 4 hours to crystallize the PET fraction. As reference samples, sheets of PC/PET(50/50) without CNT and pure PET were prepared by the same method. Finally, the sheets were immersed into chloroform for 48 hours at room temperature.

### 3 Results and discussion

#### 3.1 Transfer in piled sheets

Figure 2 shows SEM pictures of the PC sheet after peeled off from the laminated sheet annealed at 300 °C for 2 and 15 min. Since PC is immiscible with PP, it is not difficult to separate the sheets after cooling. As seen in these figures, CNTs are localized at the surface of PC, demonstrating that CNT transfer occurs from the composites during the applied annealing procedure. It should be noted that a conductive polymer sheet with a significantly small amount of CNTs is obtained employing the CNT transfer technique. Moreover, it is apparent that the prolonged annealing procedure enhances the migration of CNTs. Correspondingly, the surface resistivity of PC decreases with the annealing time. On the contrary, it is found that CNT transfer does not occur from the PC/CNT (80/20) composite to pure PP. This is reasonable because the compatibility of CNTs with PC is better than that with PP in accordance with the studies by Pötschke et al. [9,10].



**Figure 2.** SEM images of (left) cross-section and (right) surface of PC sheet after peeling off from PP/CNT (80/20) annealed at 300°C for (a) 2 min and (b) 15 min.

Interestingly, it is found that CNT transfer is not detected from PP/CNT to PP and from PC/CNT to PC in the experimental condition. The result suggests that the driving force of the migration of CNTs is the difference in the compatibility between CNTs and the polymer.

#### 3.2 Transfer during melt-mixing

The CNT transfer is also detected from PC to PET in the piled sheets. Furthermore, CNT transfer experiments are carried out in the blend using the system.

Figure 3 shows the sample sheets after immersing in chloroform. It is confirmed from the weight measurements and IR spectra that most PC is removed by chloroform even for the blend composed of PC/PET/CNT (44/44/11). On the contrary, the PET fraction is not dissolved in chloroform, which is confirmed by IR measurements of the insoluble part. This is presumably owing to the crystallization of PET by the annealing process.

As seen in the picture, the solution containing a PC/PET/CNT sheet is fairly transparent, although it contains 11 wt% of CNTs in the sample. On the other hand, the PC/CNT solution is black, because the sample is dissolved into the solution perfectly. The result indicates that CNTs exist in PET phase not in PC. In other words, the CNT transfer from PC to PET occurs during the melt-mixing process.



**Figure 3.** Photographs of the immerse experiments in chloroform; (left) PC/PET/CNT (44/44/11), (middle) PC/PET (50/50), and (right) PC/CNT (80/20).

#### 4 Conclusions

It is demonstrated that localization of CNTs at the surface of a polymer sheet is attained using the CNT transfer technique. The CNT migration occurs from PP phase to PC during annealing procedure beyond the melting point. Furthermore, the laminated sheets are separated easily after cooling because PC is immiscible with PP. The migration of the CNTs can be assigned to much more favourable interaction between CNTs and a polymer matrix, because it does not occur from PC to PP.

CNT transfer from PC to PET takes place in both piled sheets and blend as far as the system is beyond the melting point of PET. In case of melt-mixing of the blend, most CNTs originally mixed with PC immigrate to PET phase.

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