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Anomalous transfer phenomenon of carbon nanotube in the blend of polyethylene and polycarbonate

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ABSTRACT

A contradict interphase transfer of multi-walled carbon nanotubes (MWCNT) is detected in the immiscible polymer pair of polyethylene (PE) and polycarbonate (PC). When laminated sheets composed of PE with MWCNTs and PC are annealed in the molten state of both polymers, MWCNTs are found to move from PE to PC. This transfer phenomenon is originated from the difference in the interfacial tension with the aid of Brownian motion. On the contrary, MWCNTs prefer to reside in the PE phase in the blend of PE, PC and MWCNTs, even when MWCNTs are first dispersed in PC. This result indicates that MWCNTs transfer from PC to PE. The opposite direction of the transfer is attributed to the PE molecules being adsorbed on the surface of MWCNTs, which are generated during mixing.

1. Introduction

Carbon nanotubes (CNTs) have been investigated in many research fields ever since their discovery by Iijima in 1991 [1]. Due to their high aspect ratio (100–1000) and specific surface area, the electrical and mechanical properties of a polymeric material can be improved by adding CNTs [2–4]. Based on the above characteristics, it is appropriate to employ CNTs as a conductive filler in polymer composites for many applications in the manufacturing such as electrostatic dissipation, interference shielding, and so on [5–7]. Of course, the electrical properties of polymer composites are affected by the dispersion of CNTs in the material, therefore it is important to understand and control the CNT dispersion [8].

Sumita et al. described the concept of double percolation, in which the amount of carbon blacks (CBs) is beyond the critical value for percolation in one continuous phase of an immiscible blend [9,10]. This method makes it possible to prepare a conductive composite with a small amount of CBs. Sumita et al. also revealed that CBs selectively reside in polyethylene (PE) phase in the blend of PE and poly(methyl methacrylate) (PMMA), although PE is a non-polar polymer [10]. Furthermore, Wu et al. found that the addition of PE reduces the percolation threshold of the composite with vapor-grown carbon fibers (VGCFs) in PMMA [11]. They explained that it is attributed to the self-assembled conductive network constructed by selective adsorption of PE on the end part of the VGCF filament. Later, they explained that this phenomenon is attributed to the flexibility of PE chains, which leads to the preferential adsorption at the rough ends of VGCF by entropic favor [12]. Similarly, Pötschke et al. prepared a conductive blend using polycarbonate (PC) and PE with MWCNTs and found that MWCNTs act as a bridge between two polymers by the adsorption of chain ends [13]. Though, Mamunya et al. reported that the selective localization of conductive fillers in an immiscible polymer blend can be predicted by the interfacial tension between polymers and conductive fillers [14]. Typically, CNTs immigrate from a polymer with high interfacial tension to another with low interfacial tension through the boundary between the phases, because CNTs show high surface tension (45 mN/m) [15]. Besides, Gubbels et al. demonstrated that the selective localization of CBs at the interphase between PE and polystyrene (PS) in the co-continuous blend can greatly reduce the content of CBs required for the percolation threshold [16]. This selective localization occurs at the specific balance of interfacial tension among polymers and fillers.

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Recently, the imprinting technique of nanofillers from one polymer to another has been developed to modify the surface properties of polymers [17–20]. Doan et al. conducted the annealing procedure using laminated sheets composed of pure PE and polypropylene (PP) containing nanofibers of poly(butylene terephthalate) (PBT) [19]. They found that PBT fibers are transferred from molten PP to PE, which results in the surface-modified PE sheet after separation of the laminated sheets. Similarly, nanofibers of polytetrafluoroethylene (PTFE) in a molten poly(lactic acid) (PLA) are transferred from PLA to PP during the annealing procedure, although PTFE does not transfer from PP to PLA [19]. These results indicate that the localization phenomenon is attributed to the compatibility with nanofillers. Furthermore, they reported that silica nanoparticles preferentially migrate from poly(styrene-*co*-butadiene) (SBR) to poly(butadiene) (BR) phase during annealing beyond their glass transition temperatures [20]. Nevertheless, the migration from BR to SBR does not occur, demonstrating that the interfacial tension between silica and BR is lower than that between silica and SBR, i.e., the compatibility between silica and a rubber is the main driving force for the transfer.

In the previous paper in our research group [21], it was found that the interphase diffusion of MWCNTs from PP to PC occurs during the annealing treatment of laminated sheets composed of PP/MWCNT and PC, leading to a conductive film of PC with a significantly small amount of MWCNTs. In contrast, the transfer is not detected at all from PC to PP. The results directly indicate that the interfacial tension between PC and MWCNT is lower than that between PP and MWCNT. Since the Brownian motion is required for the interphase diffusion, the annealing time and temperature are critical conditions for the transfer.

In this study, however, a contradict phenomenon of the MWCNT transfer from PC to PE phase was detected during melt-mixing process. Considering that MWCNTs move from PE to PC in laminated sheets composed of PE/MWCNTs and PC, these results should be noted. This study will provide the useful information on the material design using PE and carbon fillers with understanding of the driving force of PE adsorption on the fillers. Furthermore, it will be applicable to obtain high-performance polymer blends reinforced by CNTs. Since the enhancement of mechanical properties, especially rigidity, is greatly required in the field of automobiles and aircrafts, intense interest has been focused on composites with CNTs. In these applications, for example, CNTs should be localized in a matrix of rubber-modified plastics with sea-island structure.

2. Experimental

2.1. Materials

The polymers used in this study were commercially available bisphenol A polycarbonate (PC) (Panlite L-1225Y, Teijin Co., Ltd., Japan, MFR = 11 [g/10 min]) and high-density polyethylene (PE) (HJ590N, Japan Polyethylene Corp., MFR = 40 [g/10 min]). The number- and weight-average molecular weights, characterized by a size exclusion chromatograph (SEC) (Tosoh Corp., HLC-8020) using chloroform as an eluent, of PC are 1.9×10^4 and 9.7×10^4, respectively, as a polystyrene standard. Moreover, M_n and M_w of PE were also characterized by SEC using 1,2,4-trichlorobenzene at 140 °C and found to be 0.87×10^4 and 4.9×10^4, respectively as a polyethylene standard. The density of PE is 960 [kg/m^3] at room temperature.

MWCNTs were produced by a catalytic chemical vapor deposition method using a floating reactant method and subsequent thermal treatment up to 2600 °C [22,23]. Typical diameters of the MWCNTs are ranging from 40 to 80 nm as shown in Fig. 1, while the lengths are between 10 and 20 μm. The density is approximately 2300 [kg/m^3].

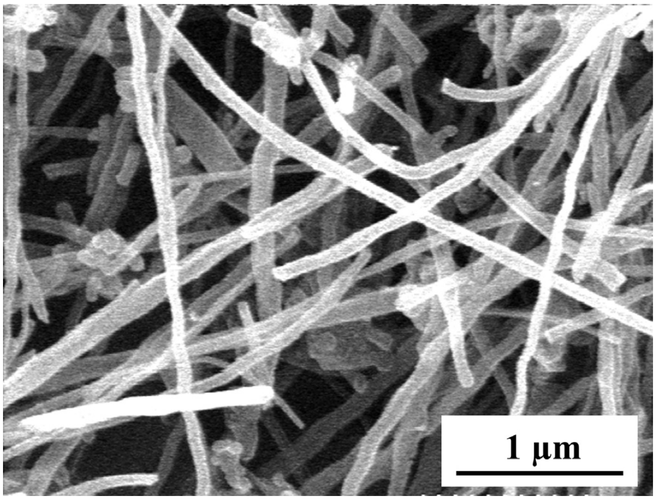

Fig. 1. SEM image of MWCNTs.

Two types of composites with 20 wt% of multi-walled carbon nanotubes (MWCNTs), i.e., PC/MWCNT and PE/MWCNT, were kindly provided by Hodogaya Chemical Co., Ltd. (Japan) as a pellet form.

2.2. Sample preparation

Pure PC and its composite with 20 wt% of MWCNTs were dried at 120 °C for 8 h in a vacuum oven before processing.

A composite of PC/MWCNT (80/20) was mixed with pure PE in the molten state using a 30 cc internal mixer at 250 °C for 10 min at a blade rotation speed of 50 rpm. The blend ratio of PC/MWCNT and PE was 80:20 in weight fraction, i.e., PC/MWCNT/PE = 64/16/20. In addition, another blend composed of pure PC and pure PE at a blend ratio of 76/24 (=64/20) was also prepared under the same condition without MWCNTs. The obtained samples were compressed into flat sheets with a thickness of 1 mm using a laboratory compression-molding machine (Table-type test-press, Tester Sangyo Co., Ltd., Japan) at 200 °C under 10 MPa for 3 min.

Flat sheets of PE, PC, PE/MWCNT (80/20) and PC/MWCNT (80/20) were also prepared using the compression-molding machine at 200 °C under 10 MPa for 3 min. Then, the sheets with 1 mm thickness were subsequently cooled at 25 °C. The transfer experiments in the laminated sheets were conducted by placing a pure PC sheet on a PE/MWCNT (80/20) sheet (PC − PE/MWCNT). After the annealing treatment at 250 °C for 10 min, the sheets were immediately cooled and separated. The same experiment was performed using a pure PE sheet and a PC/MWCNT (80/20) sheet (PE − PC/MWCNT). This procedure was also described in detail in our previous paper [21].

2.3. Measurements

The flat sheets of PC/PE and PC/MWCNT/PE with a thickness of about 1 mm were immersed in chloroform to remove PC fraction at room temperature for three days. Then, the insoluble part in chloroform was immersed into hot-xylene to remove PE fraction at 140 °C for 6 h. The chloroform and xylene solutions with dissolved polymers were collected and subsequently dried up to characterize the dissolved parts. Furthermore, the insoluble part was dried and weighed to determine the soluble fraction *S*, defined by equation (1).