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Description	

Carbon nanotube imprinting on a polymer surface

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Abstract

Imprinting of multi-walled carbon nanotubes (CNTs) on the surface of a polymer sheet was demonstrated using interphase CNT transfer from one polymer to another. A pure polycarbonate (PC) sheet was placed on top of a sheet of a polypropylene (PP)/CNT composite and annealed at either 200 or 300 ºC. It was found that CNTs move from the PP/CNT composite to the PC during annealing. The sheets of PP/CNT and PC were easily separated because of the large interfacial tension between PP and PC. The formation of a thin CNT-rich layer on the surface of the separated PC sheet produces electrical conductivity. Consequently, a conductive sheet is obtained with 2 wt% of CNTs only in the thin surface layer. Since the CNT transfer is attributed to Brownian motion, the annealing conditions such as temperature and time are responsible for the diffusion. The polymer species decides the ability of the CNTs to transfer.

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. In particular, great attention has been focused on the composites of conventional insulating polymers with conductive fillers. The composite exhibits a transition from an electrical insulator to a conductor due to the formation of a conductive network, when the filler content exceeds a critical value, known as a percolation threshold [1]. For the purpose to obtain the conductive composite effectively, various studies have been carried out.

It is well known that the percolation threshold greatly depends on the filler species and shape. For example, the percolation threshold of conductive fillers decreases with aspect ratio as demonstrated theoretically by several researchers [2-5]. Therefore, the discovery of carbon nanotubes [6] (CNTs) attracted the interests of researchers in both academia and industries.

Further, mixing and processing techniques of composites with conductive fillers have been also studied to a great extent. Especially, the recent trend is to reduce the amount of the conductive fillers in the composites. It has been known in rubber industries for a long time that uneven distribution of carbon blacks (CBs) often occurs in multiphase blends [7,8], which depends on the mixing protocol and the difference in the interfacial tension with CBs. Moreover, precise control of the uneven distribution leads to conductive composites with a small amount of conductive fillers, because a conductive path is formed by the network of conductive fillers only in a continuous phase. This idea was proposed by Sumita et al. and called as "double percolation" [9,10]. For example, they revealed that CBs selectively exist in polyethylene (PE) phase in the blends of PE and poly(methyl methacrylate) (PMMA). As a result, the conductive composite of PE/PMMA/CB is obtained by a small amount of CBs as compared with PE/CB system. Furthermore, Wu et al. revealed that the percolation threshold of the composite of PMMA with vapor-grown carbon fibers (VGCFs) is greatly reduced by the addition of 1 – 5 wt% of PE [11]. They suggested that this phenomenon is attributed to the self-assembled conductive network composed of selective adsorption of PE on VGCFs. Moreover, they clarified that the surface roughness on the carbon particles such as CB and VGCF decides the interaction due to van der Waals force and then concluded that the flexibility of polymer chains determines the localization in a multiphase polymer blend [12]. On the contrary, Mamunya reported that the distribution of conductive fillers in an immiscible polymer blend is determined by the interfacial tension [13]. Further, he demonstrated that a lot of CBs are localized at the interface of phase-separated blends at specific conditions [13]. A similar result was reported by Gubbels et al. employing PE/polystyrene/CB system [14]. Moreover, compression-molding of polymer chips or particulates coated with conductive fillers enables to provide a conductive composite [15], which is actually employed in electrostatic dissipative floor tile. Chan et al. [16] and Zhang et al. [17] also employed a similar technique using ultra-high molecular weight polyethylene (UHMWPE) powder. Finally, CNT imprinting technique using solvent was proposed recently to illustrate the conductive pattern on the material [18]. However, it is not available in industries at present, because the method requires the solvent evaporation process.

In this article, a novel method to localize CNTs on the surface of a polymer sheet is proposed using interphase CNT transfer from a composite with CNTs to a pure polymer, which provides a conductive sheet with a significantly small amount of CNTs. This concept is applicable to co-extrusion process of film or sheet processing.

Further, it should be noted that this technique is completely different from the recent works by Hua et al., in which they employed CNTs as a template for a polymer imprinting technique [19,20].

2. Experimental

2.1 Materials

The polymers employed were isotactic polypropylene (PP) (Prime Polypro J108M, Prime Polymer, Japan; MFR= 45 [g/10min]) and polycarbonate (PC) (Panlite L-1225Y, Teijin Chemicals Co., Ltd., Japan; MFR= 11 [g/10min]). The zero-shear viscosities of the polymers at 300 ºC are 99 [Pa s] for PP and 126 [Pa s] for PC. Two types of composites with 20 wt% of multi-walled carbon nanotubes (CNTs), such as PP/CNT and PC/CNT, were provided by Hodogaya Chemical Co., Ltd. (Japan) as a pellet form. The CNTs employed were produced by a catalytic chemical vapour deposition method using a floating reactant method, and subsequent thermal treatment up to 2600 ºC [21,22]. Typical diameters of the CNTs are ranging from 40 to 80 nm, while the lengths are between 10 and 20 μm. The density is approximately 2.3 [g/cm^3].

2.2 Preparation of Composites

PC/CNT (80/20) was diluted by the pure PC in a molten state using a 30 cc internal batch-type mixer with kneading disks (IMC-1891, Imoto Co., Ltd., Japan) at 280 ºC for 5 min. The blade rotation speed was 50 rpm. The obtained composites with 0, 1, 3, 6, 10, and 20 wt% of CNTs were compressed into flat sheets using a compression-molding machine (Table type test press, Tester Sangyo Co., Ltd., Japan) at either 200 or 300 ºC for 2 min.

2.3 CNT Imprinting

A pure PC sheet that was dried in a vacuum oven at 120 ºC for 8 h was placed on top of a PP/CNT (80/20) sheet. Then the piled sheets were heated in the compression-molding machine with a slight pressure at either 200 or 300 ºC for various residence times. After cooling the sheets at 30 ºC for 2.5 min, the sheets were separated. The procedure is illustrated in Figure 1. Moreover, the same experiment was performed employing a pure PP sheet and a PC/CNT (80/20) sheet at 300 ºC.

[Figure 1]

2.4 Measurements

The distribution of CNT on the surface of the PC sheets was observed by means of a scanning electron microscope (SEM) (Nova Nano200, FEI Company, USA). Furthermore, the distribution along the thickness direction was evaluated employing the samples fractured in liquid nitrogen. All the specimens were coated with Pt-Pd by a sputter coating machine.

Electrical resistivity was measured on the surface of the separated PC sheets using a constant-voltage supplied resistivity meter (MCP-HT450, Dia Instruments Co. Ltd., Japan) at room temperature. The measurements were performed five times for each sample, and the average value was calculated.

3. Results and Discussion

3.1 Conductivity of PC/CNT composites

Prior to the experiments on CNT imprinting, electrical conductivity of PC/CNT composites is studied to comprehend the threshold content of CNTs. Figure 2 shows the surface resistivity (ρ_s) plotted against the CNT content in PC. It is shown that the surface resistivity of the pure PC sheet is over the limit of the machine ($>10^{15}$ Ω/sq.), which is a typical value for a conventional polymer without doping conductive materials, whereas that of the composite having 20 wt% of CNTs is 10^2 Ω/sq.

[Figure 2]

It is apparent that the surface resistance falls off sharply around 1 wt% for the PC/CNT sheets compressed at 300 ºC, suggesting that the percolation threshold of this system is approximately 1 wt%. The content roughly corresponds with the values obtained by previous studies employing PC/CNT composites prepared by melt-mixing [23,24]. In the case of the sheets compressed at 200 ºC, however, the resistance decreases moderately with the CNT content. Apparently, the threshold is larger than those obtained at 300 ºC. The result demonstrates that the applied processing conditions affect the electrical conductivity to a great extent.

In order to investigate the effect of the annealing temperature on the dispersion state of CNTs in PC, the cut surface of the compressed sheet is observed by SEM employing PC/CNT (97/3) blends. Figure 3 demonstrates that CNTs align to one direction for the sample compressed at 200 ºC (Figure 3(a)). The orientation direction of CNTs is parallel to the flow direction, i.e., transversal direction to the compressive deformation. On the contrary, CNTs are randomly distributed in the sample compressed at 300 ºC. The results suggest that Brownian motion at 300 ºC overcomes the hydrodynamic force generated by the squeezing flow at the compression-molding. As demonstrated in the case of composites with carbon fibers, the distribution process of conductive fillers, leading to a conductive network, is called as "dynamic percolation" [25-27].

[Figure 3]

The rotational diffusion constant D_r of rigid rods dispersed in a viscous liquid was theoretically discussed by Doi and Edwards [28]. They derived the following equation;

$$D_r = \frac{k_B T}{\zeta} \tag{1}$$

where k_B is the Boltzman constant and ζ is the rotational friction constant in which hydrodynamic force is considered. Further, ζ is provided as,

$$\zeta = \frac{16\pi}{3}\eta_s a^3 \left(1 - \frac{1}{p^4}\right)\left[\frac{2p^2 - 1}{2p\left(p^2 - 1\right)^{1/2}} \ln\left(\frac{p + \left(p^2 - 1\right)^{1/2}}{p - \left(p^2 - 1\right)^{1/2}}\right) - 1\right]^{-1} \tag{2}$$

where η_s is the viscosity of the medium, $2a$ is the length of long axis of rigid rods, and p is the aspect ratio.

Since the aspect ratio of the CNTs is considerably large, equation (2) is approximated as,

$$\zeta = \frac{16\pi\eta_s a^3}{3\left[2\ln(2p) - 1\right]} \tag{3}$$

Therefore, the diffusion constant of the current system is proportional to temperature and the inverse of the viscosity of the PC.

The zero-shear viscosities of the PC are found to be 17,900 [Pa s] at 200 ºC and 126 [Pa s] at 300 ºC. As a result, the diffusion constant at 300 ºC is approximately 172 times larger than that at 200 ºC. This is the origin of the difference in the dispersion state of CNTs.

3.2 CNT Imprinting

The CNT imprinting is performed by annealing the piled sheets comprising of a pure PC sheet and a PP/CNT (80/20) sheet. The surface resistivity of the PP/CNT (80/20) is approximately 10^3 Ω/sq., which is a similar level of the PC/CNT (80/20). It is generally recognized that PP is immiscible with PC. Further, the interfacial thickness of the polymer pair in a molten state is considerably thin because of the high interfacial tension (8-18 mN/m) [29]. Therefore, it is no difficulty to separate the piled sheets after quenching, irrespective of the annealing conditions.

It should be noted that the surface resistivity of the PC sheet, which has an annealing history in the piled sheets at 300 °C for 2 min, is 10^5 Ω/sq. The result indicates that CNTs move from PP to PC during the applied annealing procedure. Further, the surface resistivity of the PP/CNT sheet is unchanged, i.e., 10^3 Ω/sq.

In order to characterize the CNT distribution in the separated PC sheet, SEM observation is carried out as shown in Figure 4. As seen in the edge-view picture (Figure 4(a)), CNTs are locally distributed in the thin surface layer of the PC sheet. Moreover, the surface picture (Figure 4(b)) demonstrates that a CNT network is clearly formed, which is responsible for the conductivity.

[Figure 4]

The diffusion distance of CNTs into the PC sheet is dependent on the applied annealing conditions. Figure 5 shows the surface SEM picture of the separated PC sheet annealed at 200 °C for 2 min. As seen in the figure, the density of CNT is significantly lower than that shown in Figure 4 (b). Correspondingly, the surface resistivity of the PC sheet is 10^{13} Ω/sq., which is considerably higher than that annealed at 300 °C. This is reasonable because exposure to high temperature enhances the Brownian motion of CNTs, i.e., driving force of the interphase diffusion [27], as discussed in the previous section.

[Figure 5]

The present experimental results demonstrate that CNT imprinting technique performed at high temperature enables to reduce the amount of CNTs greatly for the conductive material. Further, it should be noted that the CNT imprinting occurs even employing the PP/CNT (80/20) sheet that was used five times for the same experiments.

Figure 6 shows SEM images of the cross-section of PC sheets separated from the PP/CNT (80/20) sheet after annealing at 300 °C for various residence times (2, 5, 10, and 20 min). It was found that the thickness of the layer containing CNTs increases gradually with the annealing time.

[Figure 6]

The diffusion distance of CNTs is plotted against the square root of the annealing time in Figure 7. As seen in the figure, the thickness of the CNT-rich layer is proportional to $t^{1/2}$ with the diffusion constant of approximately 6.5 x 10^{-9} [m^2/s]. Moreover, the figure indicates that the diffusion distance in the range $t < 1$ [s] is zero, which would be attributed to the temperature increase of the sample and the CNT transfer from PP to PC. The surface resistivity of PC sheets at room temperature is also plotted in Figure 7. The electrical resistivity decreases rapidly with the annealing time and then keeps the constant value which is the same as that of PC/CNT (80/20). The resistivity would correspond with the amount of CNTs on the surface of PC. Therefore, it is deduced that approximately 2 wt% of CNTs are distributed in the surface layer of the PC sheet annealed for 2 min. Furthermore, it also suggests that the CNT content in the surface layer becomes a constant after a certain residence time.

[Figure 7]

The CNT imprinting test is also performed for the piled sheets comprising of pure PP and PC/CNT (80/20) following the procedure illustrated in Figure 1. It is found that CNT transfer does not occur in this system even annealed at 300 °C for 30 min, although both polymers show a similar zero-shear viscosity at 300 °C. The surface resistivity of the separated PP sheet after the annealing is more than 10^{15} Ω/sq., i.e., the same level as that for the pure PP sheet.

The compatibility between the polymers and the CNTs would be attributed to the difference in the surface tension. Dujardin et al. [30,31] reported that the surface tension of CNT is around 150 mN/m. Further, the surface tension of PC is 32 mN/m at 200 °C [32] and that of PP is 19 mN at 200 °C [32]. The information suggests that the surface tension of CNT employed would be larger than those of the polymers. Therefore, the present results indicate that the interdiffusion of CNTs occurs from the polymer with high interfacial tension to that with low interfacial tension. However, it is well known that the surface tension of CNT is affected by various conditions such as surface defects, purification process, and the production method. Although detailed characterization was reported for the CNTs used in the study [21,22], the surface tension was unfortunately undetermined. For the quantitative understanding of compatibility between the polymers and the CNTs, the real value of the surface tension of the current CNTs should be measured.

We are currently studying the detailed mechanism employing various polymer species and CNTs. Since the driving force is Brownian motion, this technique will be also applicable to single walled CNT.

4. Conclusion

A new technique to localize CNTs at the surface of a polymer sheet is proposed using the CNT transfer between immiscible polymers. In this study, a pure PC sheet is placed on the top of a PP/CNT composite sheet and annealed either at 200 or 300 °C. It is found that the CNTs move from the PP/CNT to the PC during the applied annealing, which is obvious especially at 300 °C. On the contrary, the interphase diffusion from the PC/CNT to the PP does not take place. The CNT transfer to the PC would be attributed to low interfacial tension between PC and CNT as compared with that between PP and CNT.

Since Brownian motion is required for the interphase diffusion, a long residence time at high temperature enhances the CNT transfer. Further, this technique provides a polymer sheet with low level of the surface resistivity with a considerably small amount of CNTs because of the conductive CNT network formed only in the surface layer.

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Figure 1 Experimental procedure for CNT imprinting; A pure PC sheet and a PP/CNT (80/20) sheet are piled each other and heated, i.e., annealed for various conditions. The sheets are separated after quenching. Then the surface resistivity of the separated PC sheet is measured.

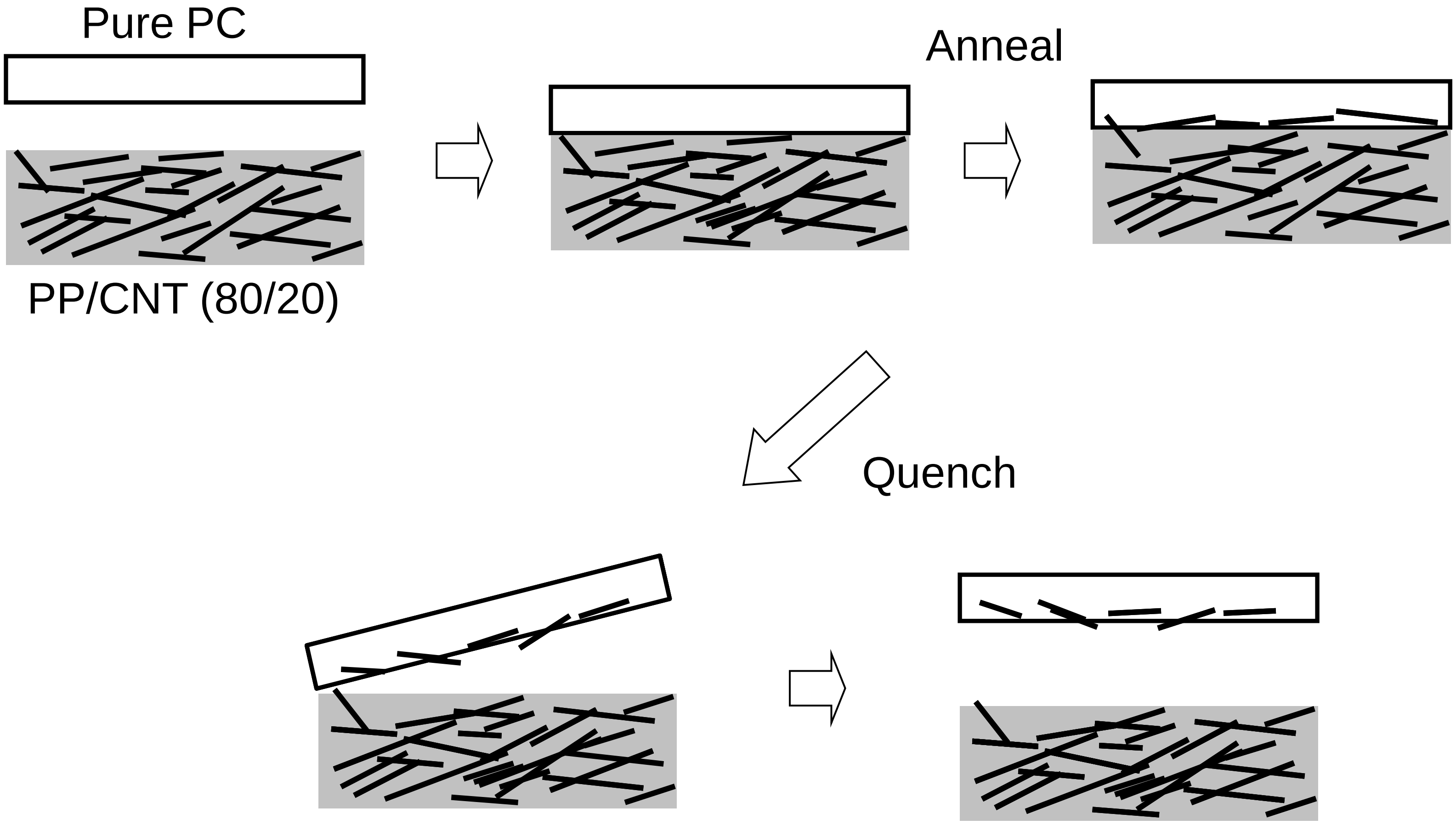


Figure 2 Surface resistivity of PC/CNT composites as a function of the CNT content for the samples compressed at (a) 200 °C and (b) 300 °C.

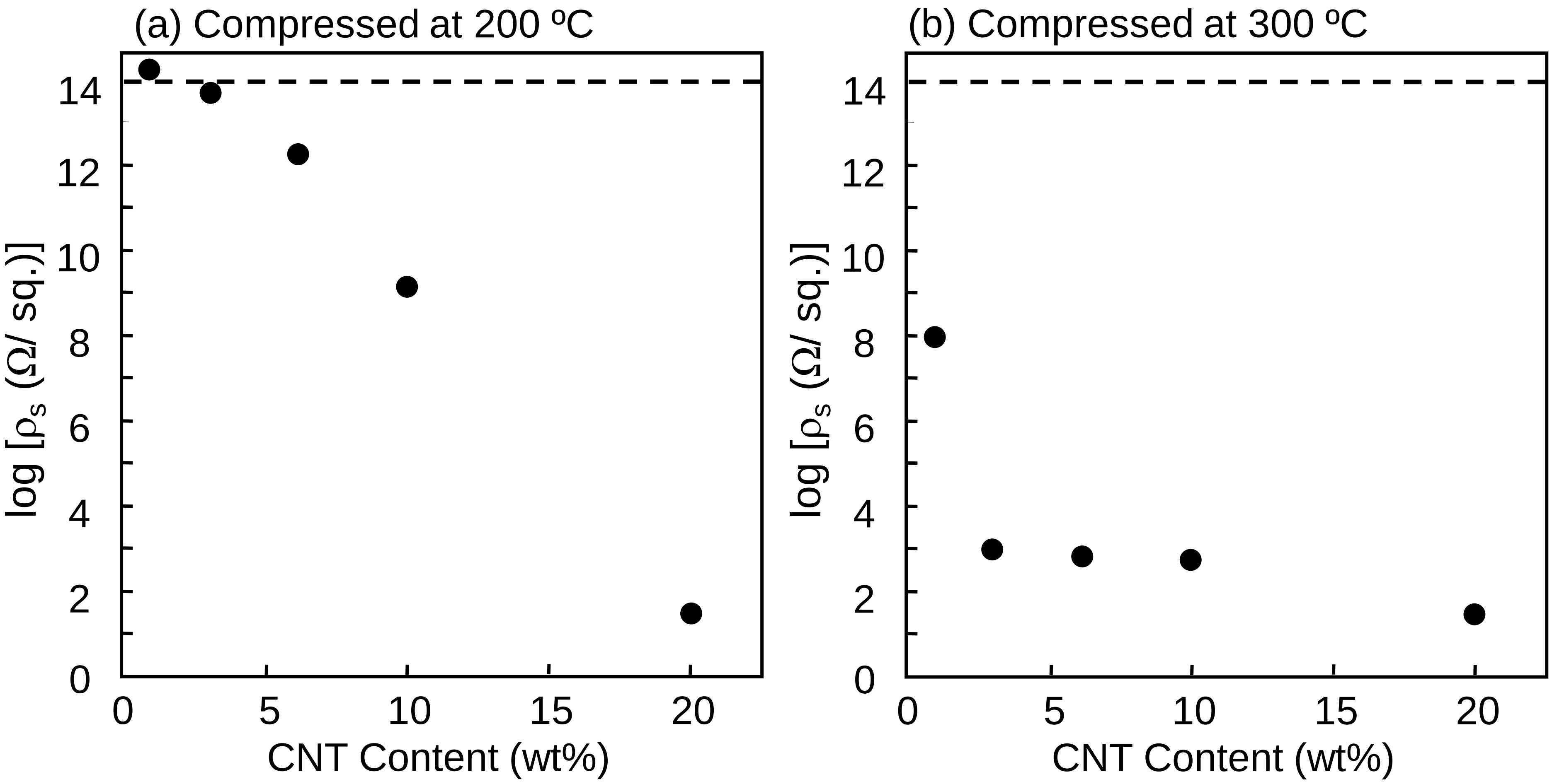
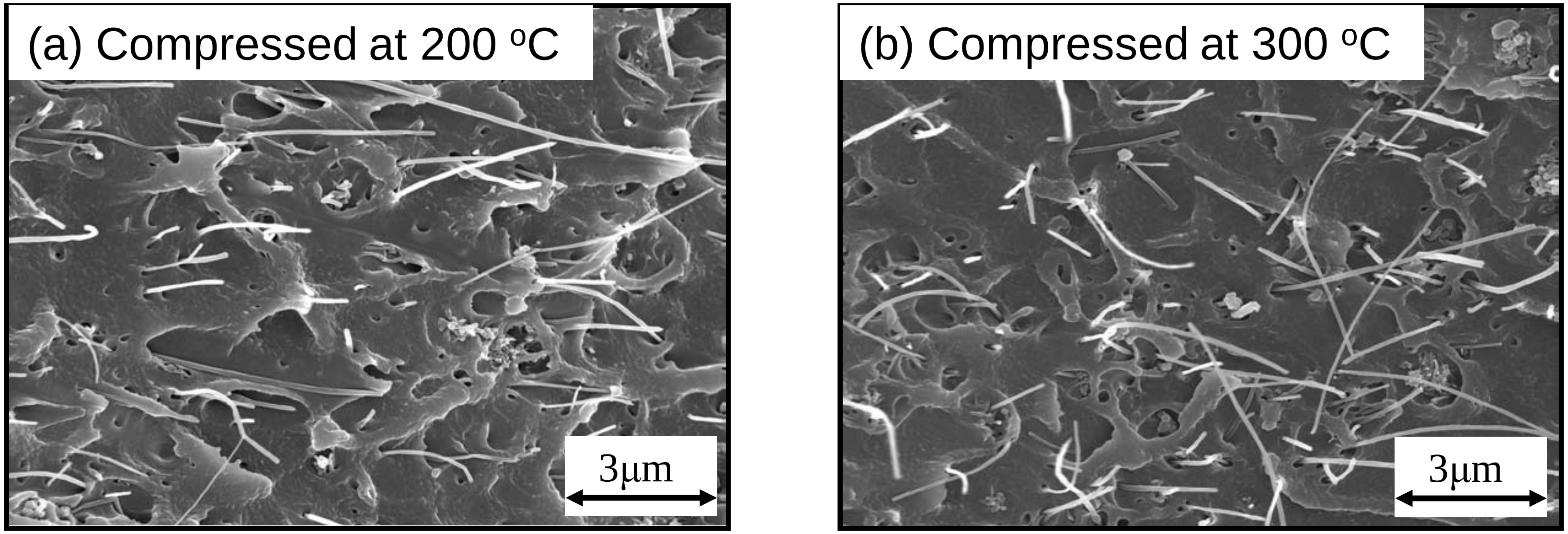


Figure 3 Distribution of CNTs at the cut surface of the compressed sheets at (a) 200 °C and (b) 300 °C. The compressive deformation is applied in the normal direction.


(a) Compressed at 200 ^{o}C

(b) Compressed at 300 ^{o}C

Figure 4 SEM images of (left) cross-section and (right) surface of a PC sheet separated from PP/CNT (80/20) after annealing at 300 °C for 2 min.

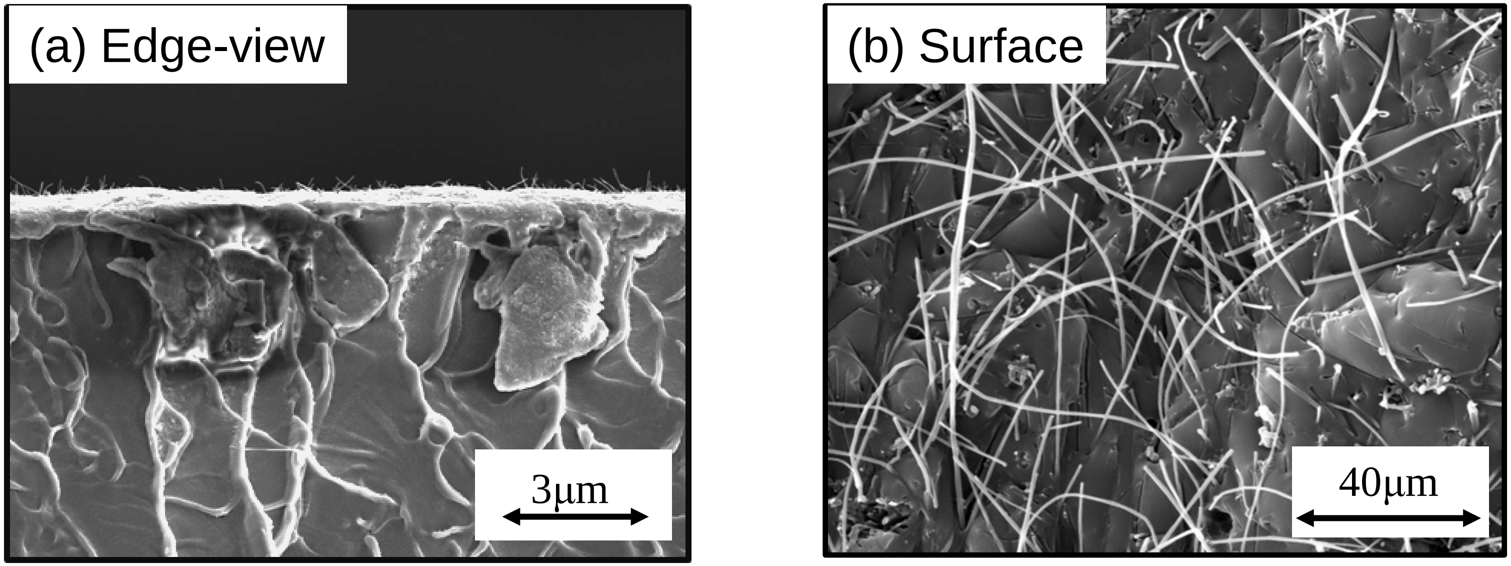


Figure 5 SEM image of surface of a PC sheet separated from PP/CNT (80/20) after annealing at 200 °C for 2 min.

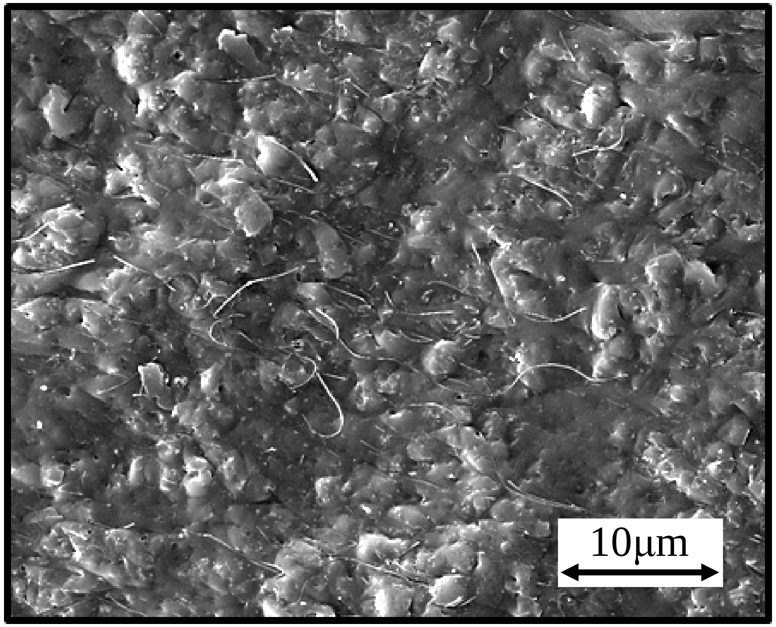


Figure 6 SEM images of cross-section of a PC sheet separated from PP/CNT (80/20) after annealing at 300 °C for various time; (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min.

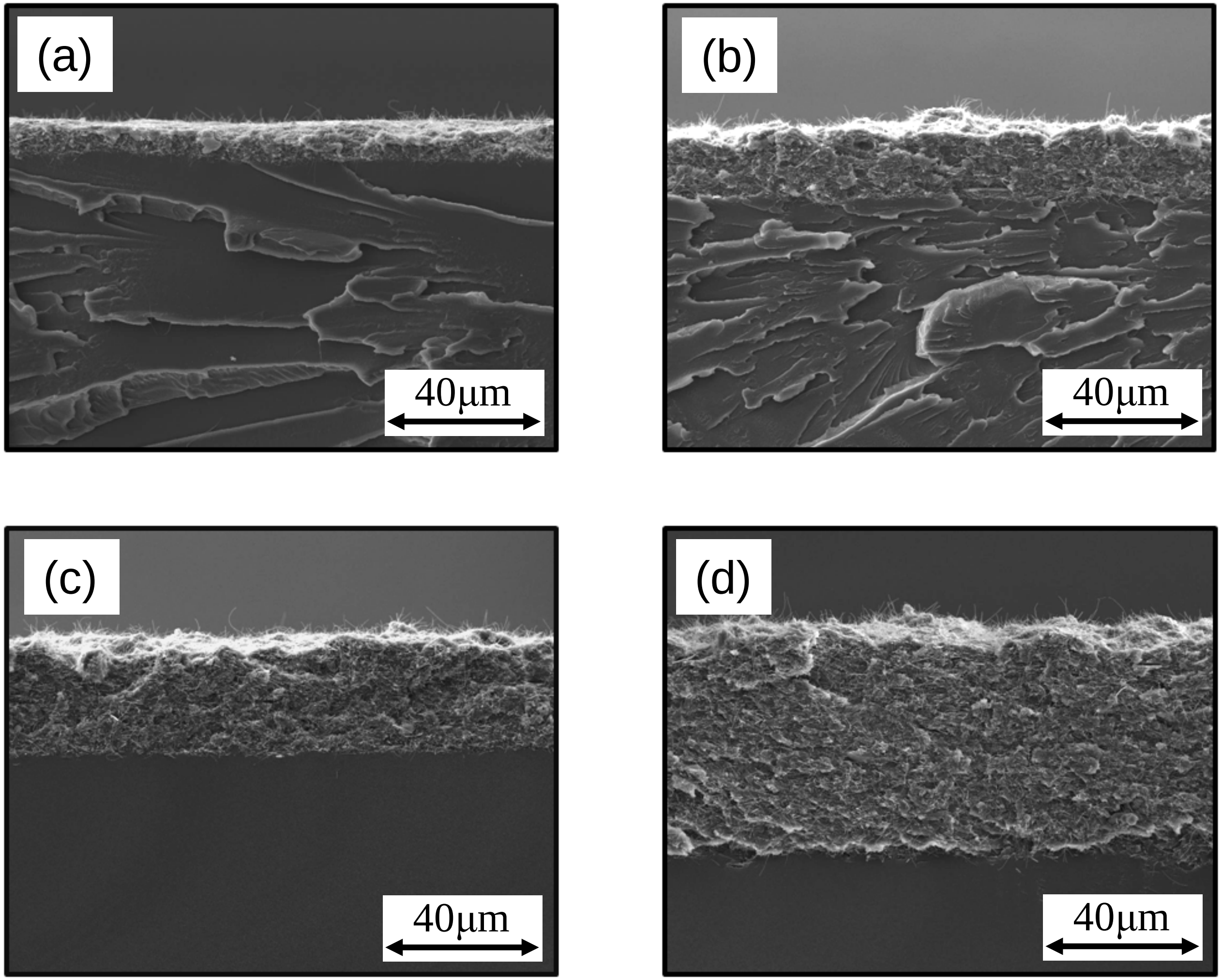


Figure 7 Thickness of CNTs-rich layer (mm) and the surface resistivity (ρ_s, (Ω/sq.)) of the separated PC sheet plotted against the square root of annealing time at 300 °C.