



Effect of matrix polymer viscosity on nanofiller exfoliation during compounding

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Abstract

The functionality of carbon nanotube (CNT) composite materials relies on good CNT dispersion within the polymer matrix. Current CNT dispersion enhancement methods involve the use of organic solvents. However, the mass production of polymer-CNT composites requires more cost effective and environmentally friendly methods. Specifically, the defibrillation and dispersion of CNTs via the dry kneading process is a promising alternative approach. This study investigated the effect of the viscosity of the matrix polymer (polycarbonate, PC) on CNT defibrillation and dispersion during the dry processing of a polycarbonate-CNT composite. The importance of shear force and wettability as factors affecting CNT dispersion in the polycarbonate-CNT composite were evaluated. The results suggested high conductivity in PCs with low molecular weight and low viscosity, and the defibrillation of CNTs proceeded predominantly. Consequently, the wettability was more important for the defibrillation of CNT than the high shear force, and the CNT defects increase on account of the high shearing force in PCs with high viscosity. Further, this study established the pretreatment of the PCs and CNTs using supercritical CO₂ as a promising alternative to organic solvent-based pretreatments. The results provide a guideline for the selection of the CNT matrix and increase the number of CNT matrix options.

Keywords Carbon nanotube · Dispersion · Polycarbonate · Shear force · Wettability

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Introduction

Inorganic and organic nanomaterials, such as carbon nanotubes (CNTs) and cellulose-nano fibers (CNFs) [1–3], have homogeneous chemical structures and consequently exhibit excellent properties. The use of these nanomaterials as nanofillers in composite materials relies on their effective incorporation into the matrix material. Nanofillers generally have a large specific surface area and exhibit a strong aggregation tendency. Therefore, the compounding of nanofillers in another material relies heavily on the efficient dispersion or defibrillation of the nanofiller.

CNTs are particularly attractive fillers in polymer composites due to their excellent mechanical strength, electrical conductivity, and thermal conductivity. CNTs typically exist as fibers instead of particles, unlike other nanomaterials such as carbon black and titanium dioxide. Therefore, efficient defibrillation and dispersion are required to enable the functionalization of polymer-CNT composites[4]. This dispersion of CNTs is typically performed using organic solvents[5–7]. These organic solvents are well understood and are selected to attain the desired dispersibility[8, 9]. However, this approach requires the use of organic solvents at ratios of 100 to 1000 times the weight of the CNTs, which not suitable for industrial processing. Thus, methods for preparing large quantities of polymer-CNT composites without the excessive use of organic solvents to defibrillate and disperse the CNTs must be developed.

The direct kneading of CNTs and polymers in a twin-screw kneader shows promise in achieving high-throughput polymer-CNT composite production. The organic solvent used as a dispersion medium should be selected according to the solubility of the nanofiller. When a nanofiller is dispersed in a kneader, its dissolution is uniquely determined by the target polymer. Although the solubility of the CNTs can be adjusted, the associated increases in cost and impurities are disadvantageous. Alternatively, the viscosity of the resin can be adjusted, where a high viscosity can effectively improve the defibrillation of CNT bundles during kneading due to the generation of higher shear stress. A study by Kobashi et al. demonstrated that CNTs were well-dispersed in a highly viscous solvent, but not in a low viscosity solvent[10].

This study aimed to investigate the effect of resin viscosity on nanofiller dispersion by directly dispersing CNTs in three polycarbonate (PC) resins with different viscosities. These insights can be extended to the effect of resin viscosity on the dispersion of other nanofillers. As resin viscosity is dependent to some extent on the temperature, this approach has wide application potential.

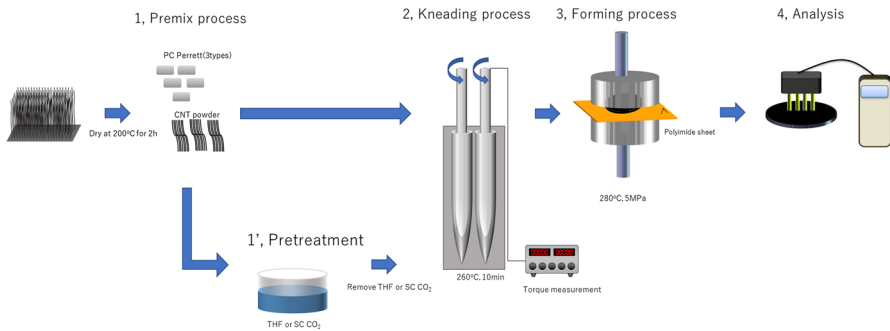


Fig. 1 Schematic outline of the experimental procedure

Experimental

PC-CNT composite preparation

The experimental procedure is schematically illustrated in Fig. 1. Two commercially available CNTs were used as fillers, namely single-walled CNTs (SWCNTs; Zeonano, ZEON Corporation, Japan) prepared via the super-growth method [11] and multi-walled CNTs (MWCNTs; Knanos100T, Kumho Petrochemical, Korea). The diameters of the SWCNTs and MWCNTs were 3.7 and 9.1 nm, respectively [12]. Three bisphenol-A type PC resins with different melt viscosities were used as the polymer matrix. These included Panlite L-1225LL (PC_{low}), L-1225Y (PC_{middle}), and K-1300Y (PC_{high}) (Teijin Limited, Japan) with melt volume rates (MVRs) of 18, 8.0, and 2.8 $cm^3/10$ min (300 °C/1.2 kg), respectively [13]. The CNTs were dried at 200 °C for 2 h and kneaded with press-formed PC pellets in a twin-screw kneader at 50 rpm and 260 °C (Explore MC15, DSM, Netherlands). A kneading time of 15 min was used, unless otherwise noted. The weight fraction of the CNTs in the composite was adjusted to 1 wt%. The kneaded samples were press-molded and subsequently annealed at 280 °C for 10 min to increase the electroconductivity. The surface resistance of the as-molded and annealed samples was determined under constant voltage application/leakage current using the four probe method (Hiresta UP MCP-HT450/URS and Loresta UP MCP-T610/LSP, Mitsubishi Chemical Analytech, Japan) [14]. Damage of the CNTs during kneading was evaluated based on the intensity ratio of the G and D band (G/D ratio) using Raman scattering (inVia Reflex RE04, Renishaw). The cross sections formed by freezing fracture of PC-CNT composites were observed by scanning microscopy (SEM, S-4800, Hitachi, Japan). Platinum-palladium was vapor-deposited for observation. Observation with an optical microscope was performed with a digital microscope (VHX-1000, KEYENCE, Japan).

The molecular weight of the PC before and after kneading was performed by a high-speed GPC (EcoSEC Elite HLC-8420GPC, Tosoh, Japan). The kneaded PC/CNT was dissolved in THF, filtered through filter paper (No. 4/retained particle size 1 μ m, Advantech), and GPC measured.

Pretreatment of PC-CNT masterbatches before kneading

The CNTs and PCs were pretreated with either anhydrous tetrahydrofuran (THF; Tokyo Chemical Industry Co., Ltd., Japan) or supercritical CO₂ (RyuSyco SCRD4, Rexam, Japan). This pretreatment corresponds to Process 1' in Fig. 1. For THF pretreatment, THF (10 wt%) was added to a Petri dish containing press-formed PC pellets and CNTs, and left to dry for 24 h at 80 °C. For supercritical CO₂ pretreatment, PC pellets and CNTs were impregnated with supercritical CO₂, as PC is known to dissolve supercritical CO₂ well. Neither pretreatment involved physical processes that led to defibrillation or dispersion of the CNTs.

Results and discussion

PC-CNT composites based on PC_{low}, PC_{middle}, or PC_{high} with 1 wt% SWCNTs or MWCNTs were prepared using a twin-screw kneader. The conductivity of each composite was measured after 10 min kneading (Fig. 2), which revealed that PC_{low} led to a higher conductivity, regardless of CNT type. This trend in the effect of PC resin viscosity on CNT dispersion was opposite to that previously reported for organic solvents. Conduction paths were continuously formed in the CNT composite material as the defibrillation of CNTs progressed, thus conductivity tended to increase over kneading time. The higher conductivity achieved during the compounding of PC_{low} and CNTs suggested that a lower viscosity matrix polymer enhanced CNT defibrillation.

In order to clarify the effect of the resin viscosity for de-fibrillation of SWNT and MWNT, the conductivity values normalized by the conductivity of the composite material of PC_{high} were plotted with MVR of matrix PC in Fig. 2b. The trend in

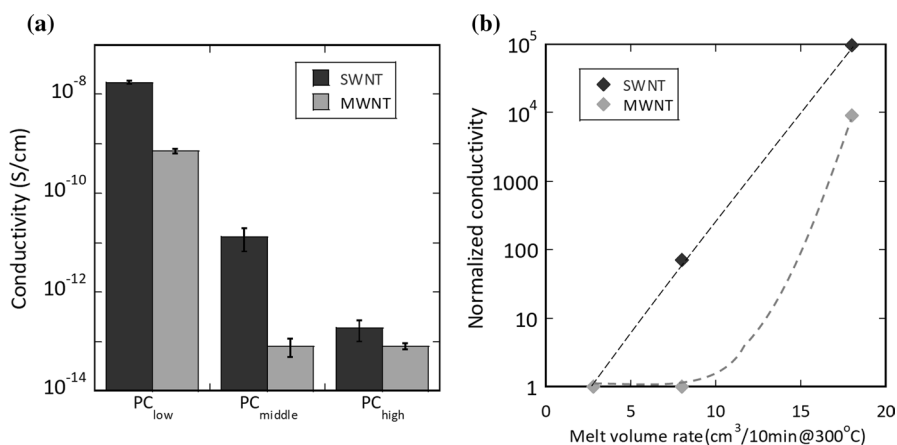


Fig. 2 **a** Conductivity of PCs-SWNT and PCs-MWNT composites with kneading time at 10 min. **b** Normalized conductivity by conductivity of PC_{high}-SWNT and -MWNT. Each point corresponds to PC_{high}, PC_{middle}, and PC_{low} from the left

conductivity according to PC viscosity differed between the SWCNTs and MWCNTs, which was attributed to the difference in their dimensions. Specifically, in SWNT, the conductivity increased at power low as the viscosity of the PC decreases, and in PC_{low}, the conductivity reaches 10⁵ times that of PC_{high}. On the other hand, in MWNT, there was no big difference in conductivity between PC_{high} and PC_{middle}, and in PC_{low}, the conductivity has finally increased to about 10⁴ times. In general, SWNTs with a small number of layers tend to be superior in forming conductivity path at the same filling amount, but this result also shows that SWNTs with a small diameter were more strongly affected by resin viscosity than MWNTs. The MWCNTs had a smaller aspect ratio than the SWNTs, as well as a higher weight fraction at percolation threshold in the composite. Evaluate the structure of CNTs in resin. The frozen fracture surface of the sample was observed by SEM (Fig. 3). CNTs and bundles were observed at PC_{high}, but no CNTs were observed at PC_{low} or PC_{middle}. This was also confirmed by low-magnification observation with only in PC_{low}, as evidence of plastic deformation of the PC. This also suggests that the defibrillation of CNTs is proceeding at PC_{low}. We also observed CNTs with an optical microscope. It was impossible to observe PC/CNT with an optical microscope. Therefore, the sample was dissolved in THF, cast into a glass substrate, and the morphology of CNTs was observed (Fig. 3). As a result, a large bundle of undefibrillated fibers was observed in SWNT, but the other parts were colored gray, suggesting that CNTs were being

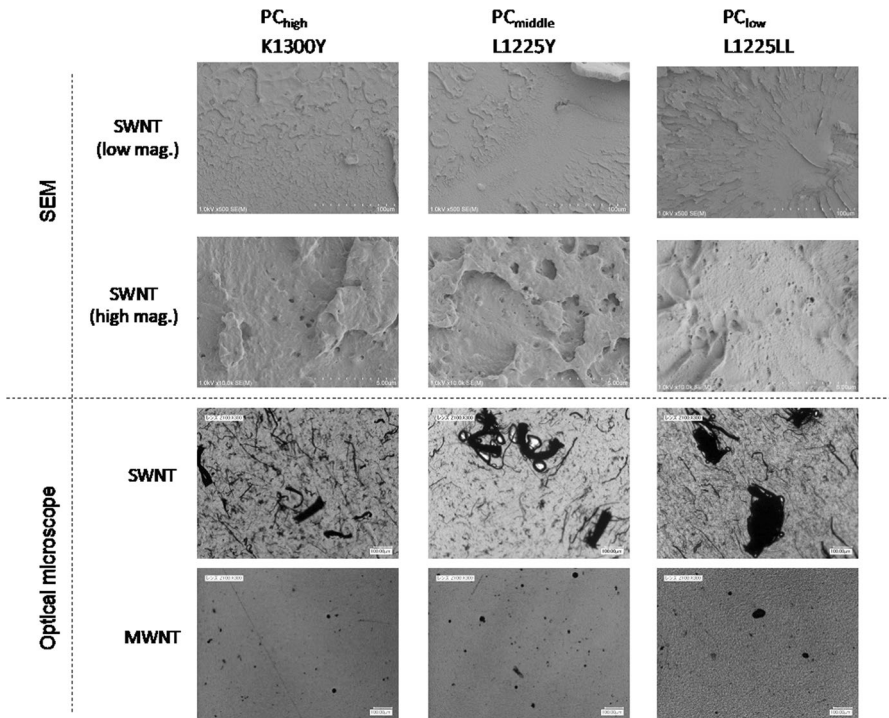


Fig. 3 SEM images of frozen-fractured cross section and optical image of casted CNTs

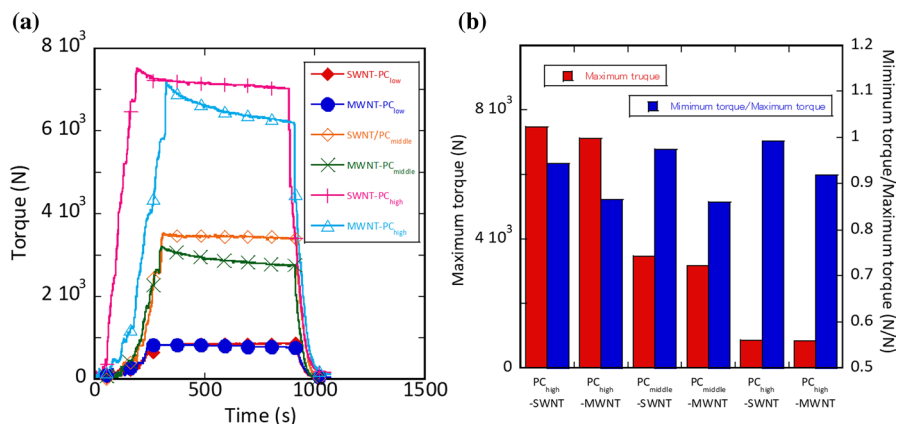


Fig. 4 **a** Torques during the kneading process. **b** Maximum torque and ratio of minimum torque/minimum torque for each sample

defibrated. In addition, no clear difference was observed in MWNT depending on the viscosity of the resin.

Torque was monitored during kneading of the PC-SWCNT and PC-MWCNT composites (Fig. 4a), where torque increased with increasing PC viscosity. Thus, the ratio of shear force applied to the CNTs in PC_{low}, PC_{middle}, and PC_{high} was approximately 1:2:4. Shear energy is necessary for the defibrillation and dispersion of CNT bundles bonded via a certain aggregate energy, where a greater shear force is generated at a higher PC viscosity. Therefore, better defibrillation and dispersion of CNTs were expected at a higher PC viscosity. As disaggregation occurred, the number of CNTs or CNT bundles increased, and more conductive paths were formed. In past studies, it has been reported that when CNTs are kneaded under the same conditions, the higher the molecular weight, the more the defibrillation of the CNT bundle progresses[15]. In this study, it was suggested that the lower the resin viscosity, the more the defibrillation of CNTs progresses.

The maximum torque during kneading and the ratio of the maximum to minimum torque was determined (Fig. 4b). A higher maximum torque was achieved in PC-SWCNT compared to PC-MWCNT, regardless of PC viscosity. This was attributed to the higher aspect ratio of the SWCNTs, which increased the viscosity to a larger degree. Further, the ratio of maximum to minimum torque increased with increasing PC viscosity. This trend was investigated further based on the factors determining the viscosity during kneading (Fig. 5).

The applied shear force was dependent on PC viscosity, which led to a change in conductivity behavior according to kneading time. Therefore, the conductivity of the PC-SWCNT composites was evaluated as a function of kneading time (Fig. 6). PC_{high} behaved completely differently from PC_{low} and PC_{middle} in terms of conductivity during kneading and exhibited a lower maximum conductivity and less effective CNT dispersion. Specifically, the conductivity of the PC_{low}- and PC_{middle}-SWCNT composites increased between 5 and 15 min and reached maximum values of 10^{-3} – 10^{-1} S/cm. Further, the conductivity improved in two steps, where the second

Fig. 5 Conductivity of the PC-SWNT composites as a function of mixing time for PCs with different viscosities

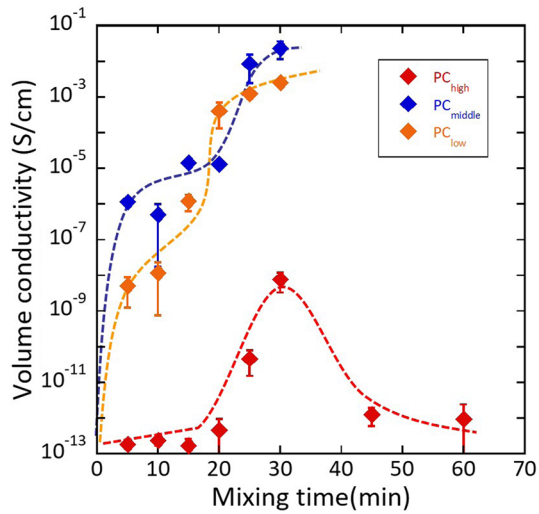
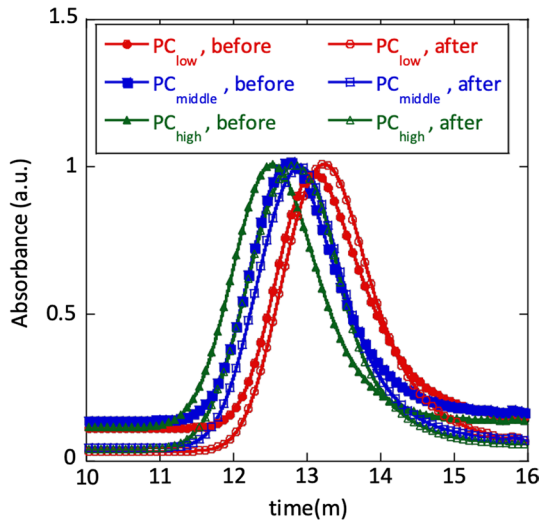


Fig. 6 Results of GPC measurement of PCs before and after kneading



step was attributed to uniform CNT dispersion within the composite. However, the PC_{high}-SWCNT composite only exhibited an increase in conductivity between 20 and 30 min to reach a maximum value of 6.8×10^{-9} S/cm, after which it began to decrease.

In order to clarify the influence of the molecular weight during kneading, the molecular weight before and after the kneading process was measured. The results of GPC measurement are shown in Fig. 5. In addition, M_n , M_w and M_w/M_n are shown in Table 1. It was confirmed that the molecular weight of PC was slightly reduced in the kneading process. This means that the molecular weight of the PC is reduced, and the viscosity is also reduced by kneading. That is, the decrease in the molecular

weight due to kneading means that the shearing force is reduced, and the wettability is improved in the latter stage of kneading. In other words, it is suggested that the conductivity of PC_{low} and PC_{middle} is a limit value that does not improve any more.

High-viscosity polymer matrices generally have a significant effect on the dispersibility of CNTs and tend to cause CNT breakage and damage [15, 16]. This was evaluated based on G/D ratio during Raman scattering analysis of the SWCNTs in the PC-SWCNT composites. The G/D ratio is a well-known factor of CNT crystallinity [17] and remained between 4.3 and 5 for the SWCNTs in all PCs after 15 min kneading (Fig. 7a). The G/D ratios of PC_{low} - and PC_{middle} -SWCNT dropped to 3.8 after 30 min, while that of PC_{high} -SWCNT decreased further to 2.2 (Fig. 7b). Finally, the G/D ratios of all three composites reached 1 after 60 min. This decrease in G/D ratio from 5 to 1 was indicative of considerable damage to the SWCNTs.

The shear force (σ) applied to the CNTs in PC during kneading can be described as follows:

$$\sigma = \eta Dn \quad (1)$$

where η is viscosity, D is shear velocity, and n is correction coefficient. The viscosities of PC_{low} , PC_{middle} , and PC_{high} were 18, 8.0, and 2.8 $cm^3/10$ min, respectively. Thus, the CNTs in PC_{high} were subjected to about 6.5 times as much shear stress as the CNTs in PC_{low} . Consequently, the CNTs in PC_{high} became more damaged during kneading, and the CNT conductivity, CNT aspect ratio, and number of contact points between the CNTs all decreased, thereby compromising the conductivity of the composite material.

A highly viscous PC matrix is unable to penetrate the interstices of the CNT bundles, which are ~ 50 – 500 nm [18]. This lack of penetration hinders disintegration. The Lucas-Washburn equation [19, 20] is a fundamental equation for characterizing

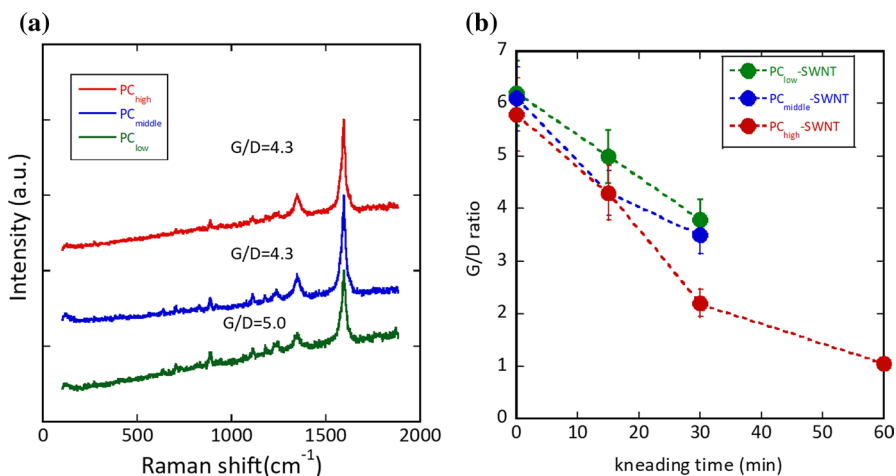


Fig. 7 **a** Raman spectra of PCs-SWCNT composites and the G/D ratios of SWCNTs. **b** G/D ratio of PCs-SWCNT change with time

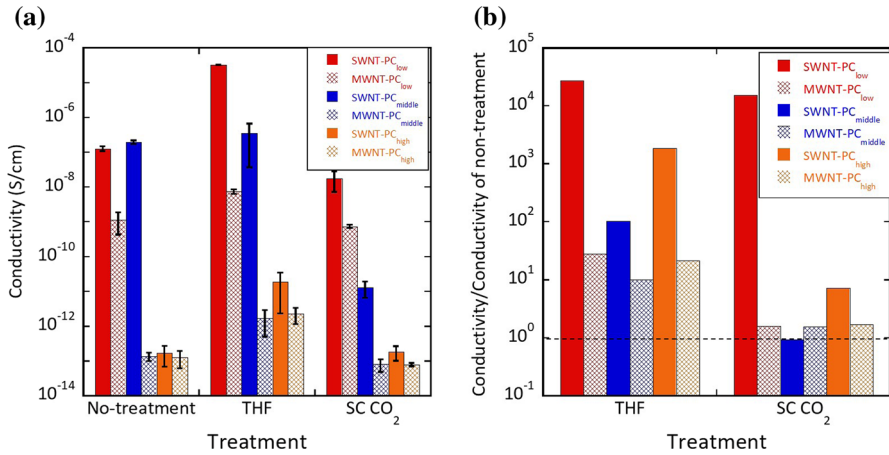


Fig. 8 **a** Conductivity of PC-CNT composites from the normal kneading process and with pretreatment using THF or supercritical CO₂ (SC CO₂). **b** Ratio of the conductivity of the pretreated samples to the untreated samples

Table 1 Molecular weight and polymer dispersity index of PCs before and after kneading measured by GPC

Sample		M_n	M_w	M_w/M_n
PC _{low}	Before	15.62	30.85	1.98
	After	15.30	28.72	1.87
PC _{middle}	Before	22.95	47.63	2.08
	After	22.64	43.52	1.92
PC _{high}	Before	35.42	65.64	1.85
	after	25.87	50.51	1.95

the penetration of a non-Newtonian fluid, can be rewritten according to the PC-CNT systems as follows:

$$I = \sqrt{\frac{r\gamma t \cos \theta}{2\eta}} \tag{2}$$

where I is the penetration depth, r is the capillary radius, γ is the surface tension of the liquid, θ is the contact angle, η is the viscosity, and t is time. This equation demonstrates that it is difficult to wet the surface of a material with small capillaries, such as the as-grown CNTs. When a low molecular weight liquid (e.g., organic solvents) is used as a matrix, the penetration depth is considerable due to the low viscosity. However, PC is much more viscose than an organic solvent, which results in insufficient penetration depth and an inability to completely wet the CNTs. Thus, shear stress increases and wettability decreases with increasing viscosity. Wettability and shear stress are both essential for filler defibration. The dispersion of nanoparticles or a relatively large filler in a solution is majorly affected by shear stress, as

all particles are easily wetted and, in turn, the effect of viscosity on wettability is minimal. However, wettability plays a major role in the case of CNTs, especially SWCNTs with a small diameter and small voids. Therefore, PC with a low viscosity and superior wetting ability allowed for higher CNT densification and conductivity.

When dispersing CNTs using a high-viscosity resin, one possible method is raising the temperature to lower the resin viscosity. However, in recent years, the heat resistance of resins has improved, such as engineering plastics, and the decomposition temperature (T_d) value of the process temperature is close. Therefore, it is assumed that a simple increase in process temperature may not be sufficient. The simplest approach to overcome this issue is reducing the viscosity of the resin at the raw material stage, followed by wetting the CNT surface. The effect of viscosity was investigated by lowering the PC viscosity before kneading via either THF (i.e., organic solvent) addition or saturation with supercritical CO_2 [21]. The conductivity of the PC-CNT samples pretreated using the two methods were measured and compared to those prepared without pretreatment (Fig. 8). Pretreatment with both THF and supercritical CO_2 led to increased conductivity of the PC-CNTs after kneading, especially in the PC-SWCNT composites. This was attributed to the smaller diameter and, in turn, smaller pores of the SWNTs, where the improved surface wettability upon viscosity reduction had a more pronounced effect. Pretreatment was more effective using THF. This was likely due to the lower solubility of supercritical CO_2 compared to THF, which resulted in a less effective less reduction in viscosity. However, the use of organic solvents such as THF in large-scale production poses serious concerns regarding safety and environmental pollution. Instead, supercritical CO_2 is a promising alternative, as it can be mass produced and removed easily. Continued optimization of the pretreatment time and temperature could further improve the conductivity enhancing effect of the supercritical CO_2 method.

CNTs and nanocellulose have various similarities, as both are agglomerated fibrous substances that require defibrillation. However, nanocellulose is very tightly packed and does not contain the same voids as the as-grown CNTs. Therefore, the application of a high shearing force is more important than wettability. Regardless, techniques that enhance the wettability of the cellulose nanofiber surface would offer advantages cellulose nanofiber compounding. For example, the proposed use of supercritical CO_2 could be extended to cellulose nanofibers. As wetting properties are important in CNTs than cellulose nanofibers, their cohesive force is small. Thus, it is important to select appropriate viscosity conditions based on the characteristics of the aggregated structures.

Conclusions

The effect of PC viscosity on the defibrillation and dispersion of CNT bundles in PC-CNT composites was evaluated based on shear stress and wettability. The results demonstrated that wettability has a larger effect on CNT defibrillation and dispersion than shear stress. This means that the defibrillation of CNTs tends to proceed when the viscosity of the matrix is low. That is, CNTs are often defibrated when the molecular weight is relatively low or when the process temperature is high. Moreover, the raw

materials of the PC-CNT composite were pretreated using either THF or supercritical CO₂. Both pretreatments improved the conductivity of the PC-CNT composite, and further demonstrated that wettability was a more critical factor than shearing force due to the presence of voids in the CNTs, particularly when the pore diameters were several μm. Although THF pretreatment was more effective, the use of supercritical CO₂ is more suited to industrial processing. Overall, this study provides guidelines for the kneading of PC-CNT composites, where the effective dispersion of CNTs by increasing the kneading temperature to lower the polymer viscosity was more favorable than increasing the shear force by lowering the kneading temperature.

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