PHYSICAL PROPERTIES OF CARBON NANOTUBE/POLYPROPYLENE COMPOUNDS

Naoyuki Oya[1], Kazuaki Nishiyabu[1], Takashi Yanagisawa[2], Shunji Higaki[2] and Shigeo Tanaka[3]

[1] Department of Mechanical Engineering, Osaka Prefectural College of Technology, 26-12 Saiwai, Neyagawa-shi, Osaka 572-8572, Japan
[2] GSI Creos Corporation, 2-3-1 Kudan-minami, Chiyoda-Ku, Tokyo 101-0052, Japan
[3] Taisei Kogyo Corporation Limited, 26-1 Ikeda Kitamachi, Neyagawa-shi, Osaka 572-0073, Japan

ABSTRACT

Physical properties of the cup-stacked carbon nanotube/polypropylene compounds are experimentally investigated by thermal and mechanical tests carried out using several kinds of specimen geometries. The thermal expansion and dynamic viscoelasticity tests show that thermal durability of the compounds improves with increased CNT quantity. Static tensile tests also reveal improvements of tensile properties when CNT quantity increases. Particularly, tensile properties significantly increase for injection moulding products in which sufficient fibre orientations along the loading direction can be observed by means of SEM fractography.

1. INTRODUCTION

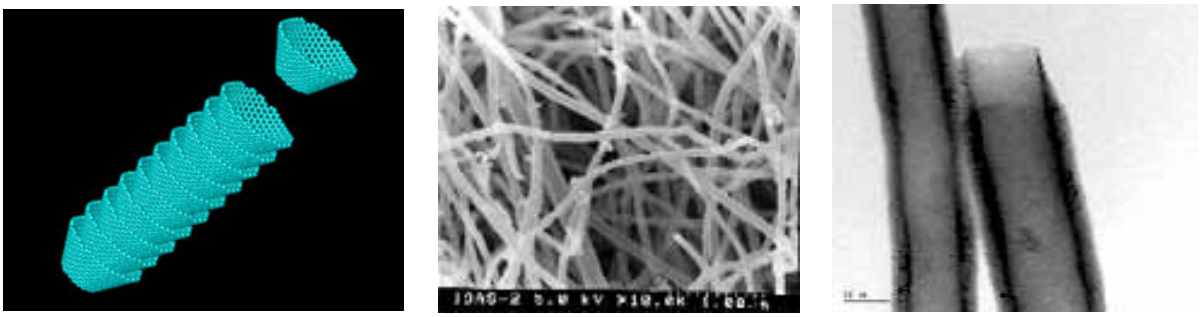
A carbon nanotube (CNT) has been gathering growing attentions as it is predicted to possess interesting and excellent physical properties based on its unique structure incorporating a honeycomb graphene lattice rolled into a cylinder. The size of a CNT is as small as nanometer size in the diameter and micrometer size in the length, which indicates that a CNT has a fibrous structure. Since the C=C bond in graphite is the strongest bond in nature, a CNT should have ultimate strength along the longitudinal axis whereas it should have flexible characteristics in the perpendicular axis. Further, a CNT has excellent thermal properties such as restricted thermal expansion and electrical properties such as a unique electrical conductivity that depends on the variety of possible helical geometries known as chirality [1].

These theoretical findings in characteristics of a CNT have stimulated global interests to perform a variety of experimental developments of purified and continuous CNTs with desired helical geometries [2,3]. The efforts have provided fair possibilities in the future to realize actual industrial applications of CNTs including innovatively small semiconductor devices and outstandingly strong structural materials. For the structural use, it will be a good step starting with compound mixtures consisted of CNTs and various matrices such as polymers, metals and ceramics. Since a CNT has extremely small size compared with conventional carbon fibres, it might be capable of contributing to the field of micro-machines by providing special characteristics to small structural components at micrometer size. A number of technical efforts have been reported from which the reinforcing effects of CNTs on matrices actually demonstrated [4-6]. It is thought that surface and sidewall structure of CNTs are crucial for physical performances of CNT compounds. Possibilities of producing industrial products using such materials by means of various moulding techniques such as hot-press, extruding, and injection moulding should also be examined. This paper describes experimental findings obtained from thermal and mechanical tests performed on CNT/polypropylene compounds, for which CNTs with unique sidewall structure were used as reinforcements and various moulding methods were adopted for specimen preparations.

2. MATERIALS USED

In this study, CNTs with ‘cup-stacked’ sidewall structure depicted in Fig.1 were used as reinforcements. The cup-stacked CNT was grown from a metallic catalyst supplying hydrocarbon gas by means of a CVD technique. The cup-stacked CNT has graphene cups

consecutively stacked forming hollows inside and relatively rough sidewalls, which should be effective to enhance interfacial adhesion compared with the ideal single-wall CNT. It should also have a fair amount of flexibility to form a curvature by allowing some amount of slipping between each graphene cup. This property is significantly important when the cup-stacked CNTs are filled in structural components with complicated shapes. Typical physical properties expected in the cup-stacked CNT were listed in Table 1. The cup-stacked CNTs and polypropylene (Novatec MA3, Japan Polychem Inc.) were pulverized and mixed in the melt state, and subsequently extruded and pelletised as CNT compounds. The compound pellets with different CNT quantities (0wt%, 1wt%, 5wt% and 10wt%) were used to prepare several kinds of test specimens as described later.



(a) (b) (c)

"**Fig. 1.** Structure of cup-stacked CNT; (a) molecular model, (b) SEM micrograph, and (c) TEM micrograph."

"**Table 1.** Physical properties of cup-stacked CNT."

Physical properties	Value
Fibre diameter	80nm
Strain to failure	0.5%
Tensile strength	7.0GPa
Density	2.1g/cm^3
Electric resistance	55μΩcm

3. EXPERIMENTAL METHODS

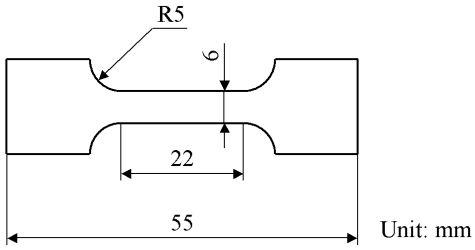
3-1 Specimen preparations

3-1-1 Film specimens

Compound pellets were firstly hot-pressed in order to obtain films with 0.4mm uniform thickness. Several pellets were placed on a specially designed brass-mould, which was subsequently heated up to 493K in the hot-press moulding machine (NF-37, Shinto Metal Industries, Inc). Melt pellets were then compressed between the moulds applying 3MPa pressure for the duration of 5mins, and finally cooled down to the room temperature keeping the moulding pressure. Films were trimmed by means of a hot-knife to obtain the rectangular geometry with 3mm width and 10mm length, and used for the thermal and mechanical tests described later.

3-1-2 Dumbbell specimens

Compound pellets were moulded into dumbbell specimens (Fig.2) by means of the hydraulic-type injection moulding machine (PN-40, Nissei Plastic Industrial Co., Ltd) that was operated under the moulding parameters listed in Table 2. The injection gate was positioned at the end of the cavity so that it can be expected to have CNT's orientations along the longitudinal direction of the tested portion. A uniaxial strain gauge (KFG-5-120-C1-11, Kyowa Electronic Instruments Co., Ltd.) was put on the dumbbell specimen to measure stress and strain relationship in static tensile test carried out in the universal testing machine as described later.



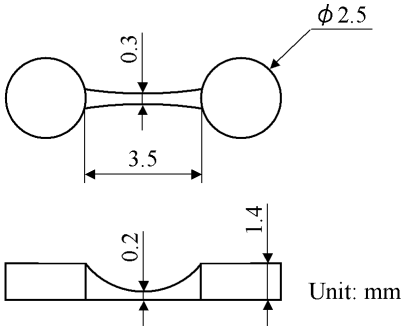
"**Fig. 2.** Specimen geometry of dumbbell specimen (thickness = 4mm)."

"**Table 2.** Moulding conditions for dumbbell specimen."

Moulding conditions	Value
Injection time	35 sec
Cooling time	5 sec
Injection rate	50 mm/sec
Injection pressure	120 MPa
Holding pressure	150 MPa
Resin temperature	483 K
Mould temperature	363 K

3-1-3 Micro-dumbbell specimens

Micro-dumbbell specimens schematically shown in Fig.3 were also fabricated by means of the injection moulding machine in order to perform static tensile tests at different thermal conditions and facilitate SEM observation of fracture aspects. The injection gate was positioned at the end of the cavity to obtain CNT's orientations in the tested portion as well as the dumbbell specimens. The moulding parameters used were listed in Table 3.



"**Fig. 3.** Specimen geometry of micro-dumbbell specimen."

"**Table 3.** Moulding conditions for micro-dumbbell specimen."

Moulding conditions	Value
Injection time	2.5 sec
Cooling time	20 sec
Injection rate	500 mm/sec
Injection pressure	250 MPa
Keeping pressure	120 MPa
Resin temperature	483 K
Mould temperature	353 K

3-2 Thermal expansion test

The thermal expansion tests for film specimens were carried out using the thermal mechanical analysis machine (TMA/SS-120, SII Inc), which is capable of applying and measuring force and displacement up to 5N and 40mm respectively, while increasing the furnace temperature

up to 1273K. The film specimen was preliminarily stretched applying 0.2N force at 300K until no further elongation observed, and then heated up to 473K at a rate of 60K/min. Coefficients of thermal expansion (CTE) were evaluated from the thermal elongation vs. temperature curves with different CNT quantities.

3-3 Dynamic viscoelasticity test

Cyclic tensile tests were also carried out for the film specimens using the same testing setup as the thermal expansion test in order to evaluate the viscoelasticitic properties. The film specimen was preliminary stretched applying 0.2N force until no further elongation observed, and then repeatedly stretched in a sine-waveform loading with 0.3N amplitude and 0.01Hz loading frequency. Mechanical loss factor associated with the specimen's viscosity can be known by measuring the phase difference between stress and strain, which is normally expressed as a ratio of the real and imaginary parts in the complex modulus, tan δ. In this study, tan δ was measured for each CNT quantity when heating from 300K up to 473K.

3-4 Static tensile test

Static tensile tests were performed for the film and micro-dumbbell specimens using the same testing setup as the dynamic viscoelasticity test. The specimen was clamped and uniaxially stretched at a uniform rate of 0.6N/min in order to evaluate the tensile properties. The furnace temperature was kept at 300K during the tests for the film specimens, whereas the furnace temperature of 373K was also used for micro-dumbbell specimens in order to examine the tensile behaviour in the heated environment. Furthermore, after the tensile tests, micro-dumbbell specimens were coated with platinum layer by the ion-sputter (E-1010, Hitachi Ltd.) and observed by SEM (S-2460N, Hitachi Ltd).

Static tensile tests for dumbbell specimens with uniaxial strain gauges attached were also carried out by means of the universal testing machine (AG-10TD, Shimadzu Co) in order to perform more precise stress-strain measurements at room temperature (300K). Signals of load and strain data were digitally collected via A/D converter (NR-2000, Keyence Co.) with the sampling frequency of 5Hz.

4. RESULTS & DISCUSSION

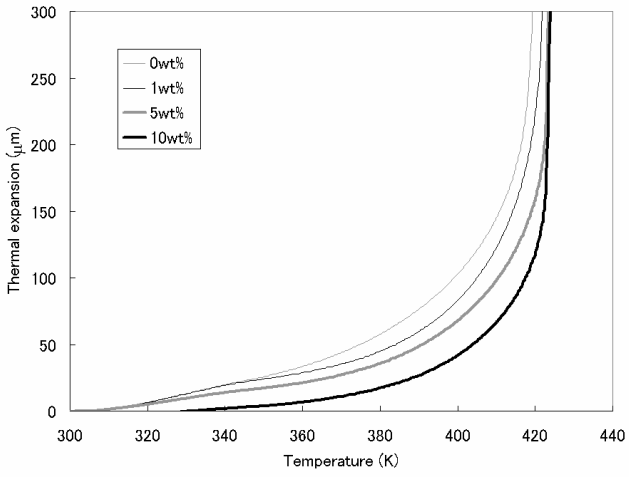
4-1 Thermal expansion test

Fig.4 shows typical thermal expansion vs. temperature curves obtained from thermal expansion tests for film specimens with different CNT quantities. It is apparent that thermal expansion was generally suppressed by increasing CNT quantities. Table 4 lists the coefficients of thermal expansion (CTE) and the melting temperatures. CTE was evaluated from the slope of the curve between 343 and 353K. It was revealed that CTE decreased by approximately 50% when adding more than 5wt% CNT compared with that of polypropylene. The melting temperature also increased with increasing the CNT quantity.

4-2 Dynamic viscoelasticity test

Fig.5 shows typical tan δ vs. temperature curves obtained from the dynamic viscoelasticity tests for the film specimens. Each curve exhibited that tan δ generally increased with increasing the temperature. A small peak appeared at around 340K in each curve indicating the relaxation of molecular chains of the polypropylene matrix. However, there was no

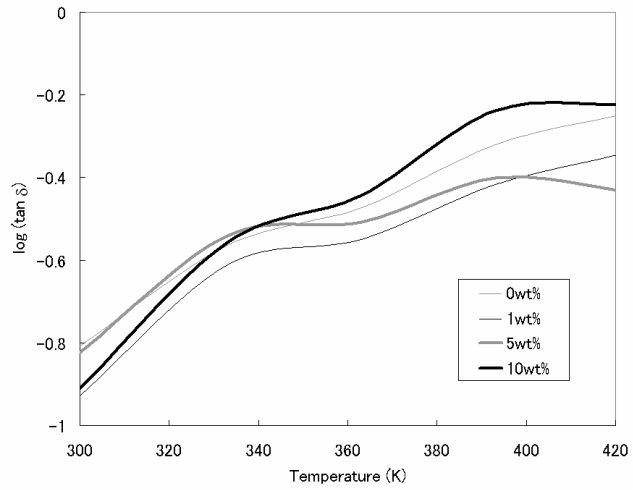
increase of tan δ with temperatures higher than 390K in the cases of 5wt% and 10wt% specimens, whereas it continuously increased for 0wt% (polypropylene) and 1wt% specimens. The viscosity of polypropylene matrix should have increased with higher temperatures. However, it is deduced that elastic responses of the films were maintained with higher CNT quantities.



"**Fig. 4.** Thermal expansion vs. temperature curves obtained from film specimens."

"**Table 4.** Coefficients of thermal expansion and melting temperatures obtained from film specimens."

CNT quantity (wt%)	CTE ($1x10^{-4}$/K)	T_m (K)
0	8.29	421.8
1	6.14	427.6
5	4.34	428.2
10	4.46	431.5

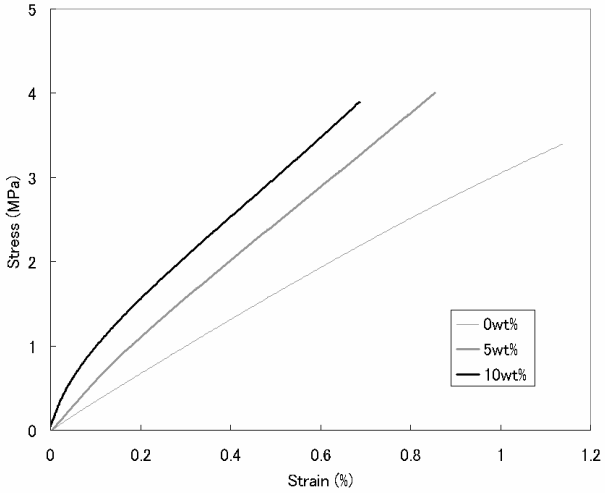


"**Fig. 5.** tan δ vs. temperature curves obtained from film specimens."

4-3 Static tensile test

Fig.6 shows typical stress vs. strain curves obtained from static tensile tests for the film specimens. Each test finished with very low tensile stress due to the limited load capacity in the apparatus. Non-linearity in the initial portion of the curve was significant for 5wt% and 10wt% specimens compared with that of 0wt% (polypropylene) specimen. Elastic modulus evaluated from the range between 0.1 and 0.2% strains in each curve was listed in Table 5. As strain was measured from extension divided by the specimen length and considerable stress

concentrations occurred in the clamp, elastic modulus was very low for each CNT quantity. Nevertheless, it was revealed that the elastic modulus increased with increase of the CNT.

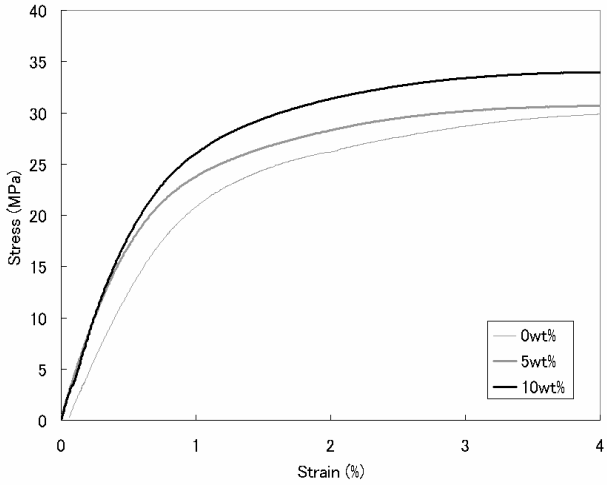


"**Fig. 6.** Stress vs. strain curves obtained from film specimens."

"**Table 5.** Elastic modulus obtained from film specimens."

CNT quantity (wt%)	Elastic modulus (MPa)
0	428
5	509
10	568

Fig.7 shows typical stress vs. strain curves obtained from static tensile tests for the dumbbell specimens. Each curve exhibited non-linearity and large plastic deformation. Elastic modulus evaluated from the range between 0.1 and 0.2% strains in each curve based on the strain gauge output was listed in Table 6. It was revealed that the elastic modulus increased with increase of the CNT quantity.

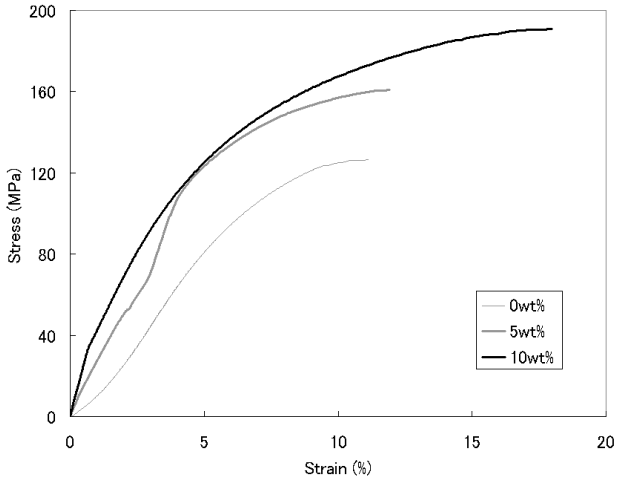


"**Fig. 7.** Stress vs. strain curves obtained from dumbbell specimens."

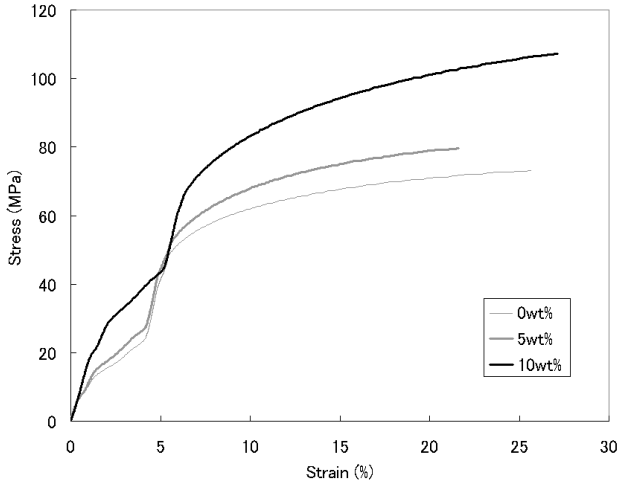
"**Table 6.** Elastic modulus obtained from dumbbell specimens."

CNT quantity (wt%)	Elastic modulus (MPa)
0	2627
5	3376
10	4468

Fig.8 and Fig.9 show typical stress vs. strain curves obtained from static tensile tests for the micro-dumbbell specimens performed at 300K (room temperature) and 373K, respectively. Due to difficulties in clamping of the specimens, some results showed irregular increases of strain when applying stress of 10 to 40MPa. However, linear increases of stress and strain could be observed in the initial portion of the curves, and elastic modulus was evaluated from such a range (strain between 0.1 and 0.2%) for each case. As shown in Table 7, it was revealed that the elastic modulus increased with increase of the CNT quantity even with the high temperature environment.



"**Fig. 8.** Stress vs. strain curves obtained from micro-dumbbell specimens at 300K."



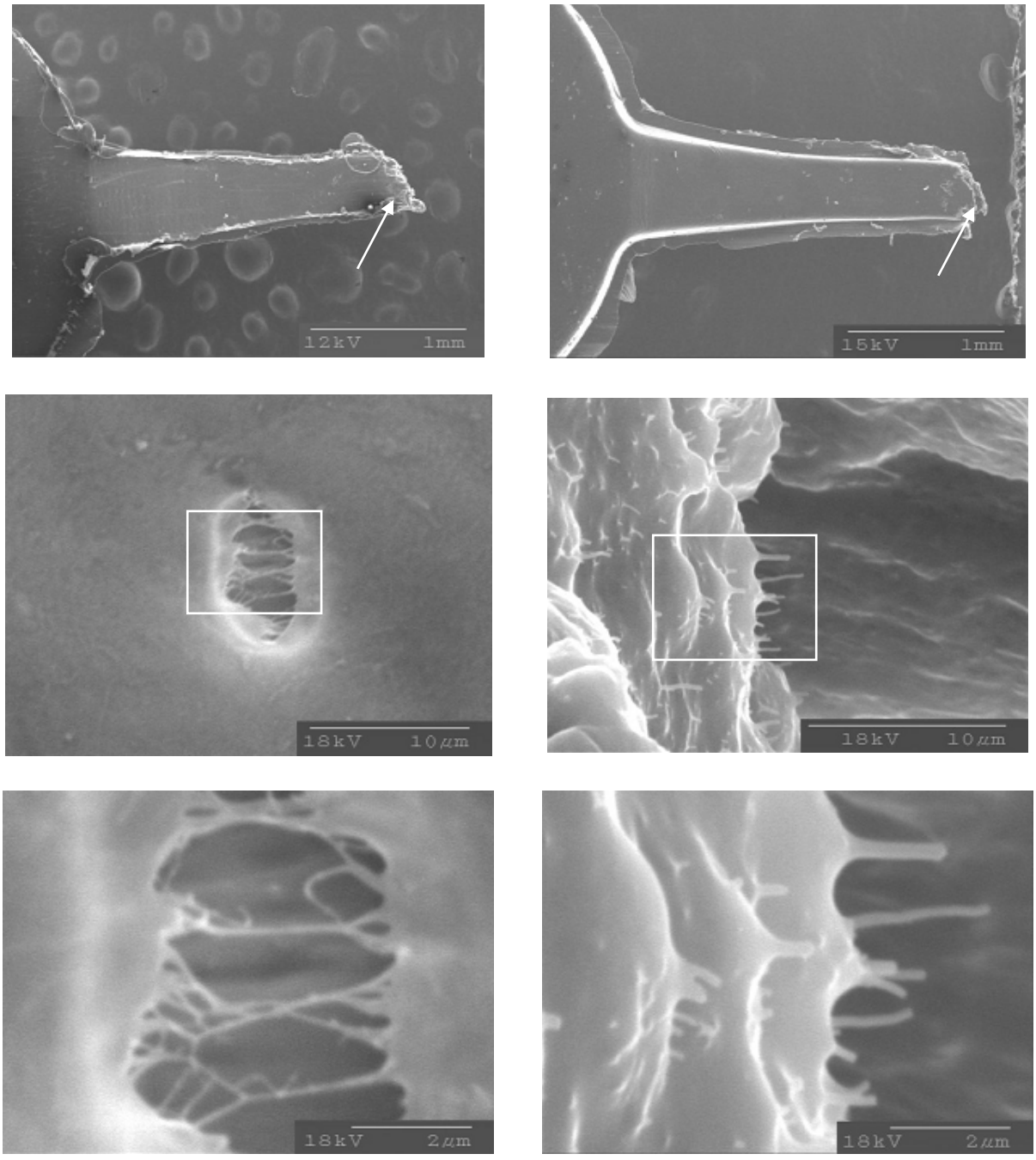
"**Fig. 9.** Stress vs. strain curves obtained from micro-dumbbell specimens at 373K."

"**Table 7.** Elastic modulus obtained from micro-dumbbell specimens."

CNT quantity (wt%)	Elastic modulus at 300K (MPa)	Elastic modulus at 373K (MPa)
0	2746	1478
5	3357	2117
10	4491	2457

Results of SEM fractography for micro-dumbbell specimens were presented in Fig.10. It was found that the CNT network had prevented failure propagations, and the CNTs had been pulled out aligning along the loading direction. It suggests that fibre orientations had been achieved by the melt-flow during the injection moulding leading to considerable effects on the tensile properties. Certainly, the increase of elastic modulus between 0wt% and 10wt% specimens was more significant in the injection moulding products than in the films, which

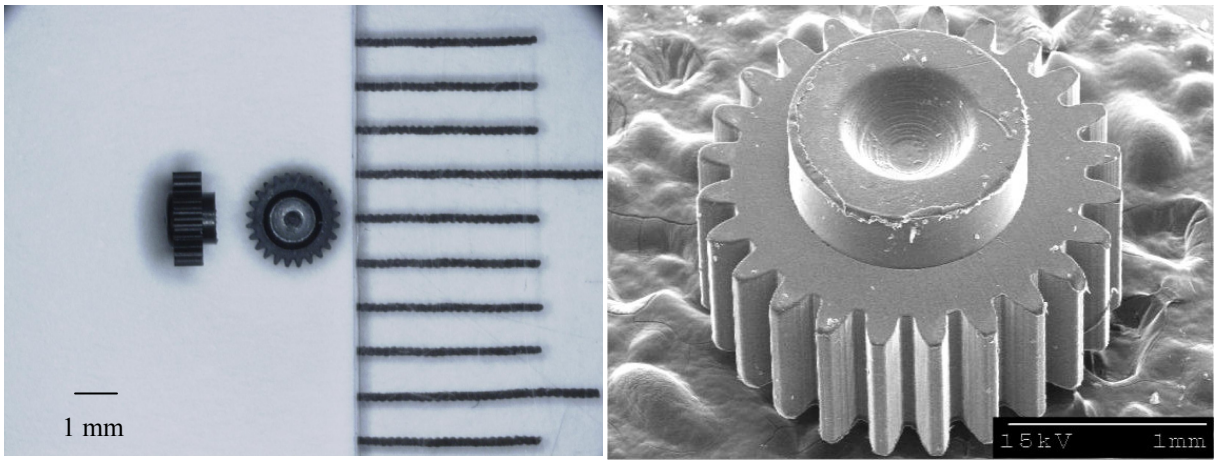
should have relatively random fibre orientations. The results suggest that the CNT used provide enough adhesions with matrix improving the physical properties, which can be further enhanced with appropriate controls of the fibre alignments in final products.



(a) (b)

"**Fig. 10.** SEM micrographs of fractured micro-dumbbell specimens; (a) 5wt% and (b) 10wt% specimens."

In addition to the improved thermal and mechanical properties, the cup-stacked CNT should have a great advantage over conventional carbon fibres when used as reinforcements in small mechanical parts like micro-gears presented in Fig.11. As indicated, small and complicated shapes can be produced with evenly dispersed CNTs functioning as reinforcements. It is expected that the cup-stacked CNT used in this study can provide improved physical properties and flexibility to produce required geometries that are difficult to manufacture with conventional materials.



"**Fig. 11.** Micro-gears produced from cup-stacked CNT/PP compounds."

5. CONCLUSIONS

Physical properties of the cup-stacked CNT/PP compounds were investigated from various viewpoints such as thermal and mechanical studies; those include thermal expansion test, dynamic viscoelasticity test, static tensile test and subsequent SEM fractography carried out for film, dumbbell, and micro-dumbbell specimens. It was demonstrated that thermal and mechanical properties considerably improved with increasing the CNT quantity. SEM microscopy carried out for fractured micro-dumbbell specimens revealed that the CNT network had prevented failure propagations and most of the CNTs had been aligned along the melt-flow during the injection moulding. It is thought that such fibre orientations can contribute to enhanced mechanical properties of the compounds. The cup-stacked CNT/PP compounds have a potential to be used as high performance materials in micro-scale mechanical components that are difficult to be produced with conventional carbon fibres.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. Kenji Okubo in Taisei Kogyo Co. Ltd. and Mr. Nobuhiro Nukuyu in Osaka Prefectural College of Technology for their experimental supports throughout this study.

References

1. **Saito, R., Dresselhaus, G.** and **Dresselhaus, M.S.**, "Physical properties of carbon nanotubes", London: Imperial College Press, 1998.
2. **Ren, Z.F. et al.**, "Synthesis of large arrays of well-aligned carbon nanotubes on glass", *Science*, **282** (1998), 1105.
3. **Zhu, H.W., Xu, C.L., Wu, D.H., Wei, B.Q., Vajtai, R.** and **Ajayan, P.M.**, "Direct synthesis of long single-walled carbon nanotube strands", *Science*, **296** (2002), 884.
4. **Schadler, L.S.**, **Giannaris, S.C.** and **Ajayan, P.M.**, "Load transfer in carbon nanotube epoxy composites", *Applied Physics Letters*, **73**/26 (1998), 3842.
5. **Xu, X.**, **Thwe, M.**, **Shearwood, C.** and **Liao, K.**, "Mechanical properties and interfacial characteristics of carbon-nanotube-reinforced epoxy thin films", *Applied Physics Letters*, **81**/15 (2002), 2833.
6. **Barber, A.H.**, **Cohen, S.R.** and **Wagner, H.D.**, "Measurement of carbon nanotube-polymer interfacial strength", *Applied Physics Letters*, **82**/23 (2003), 4140.