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Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites

Yuezhen Bin *, Mariko Mine, Ai Koganemaru, Xiaowen Jiang, Masaru Matsuo **

Department of Textile and Apparel Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8263, Japan

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Abstract

The composites poly(vinyl alcohol) (PVA) and vapor growth carbon fiber (VGCFs) and multi wall carbon nanotubes (MWNTs) were prepared by gelation/crystallization from the mixture of dimethyl sulfoxide (DMSO) and water (H_2O). The composite films were elongated to 5–10-fold uniaxially. The mechanical properties of PVA composites were improved significantly by introduction of VGCFs and MWNTs and also by the orientation of fillers. Compared to VGCFs, MWNTs was more effective to improve the electric conductivity of the composites because of its network structure. The change in the electrical conductivity for the PVA/MWNT composites containing 5 wt% MWNT was independent of the draw ratio up to eight-fold indicating no disruption of the network formation. A certain high level of filler content was proved to be necessary for the promotion of both mechanical and electrical properties in oriented composite.

Keywords: Poly(vinyl alcohol) (PVA); Vapor growth carbon fiber (VGCFs); Multi wall carbon nanotubes (MWNTs)

1. Introduction

Vapor-grown carbon fibers (VGCFs) have been grown by the decomposition of hydrocarbon using transition metal particles as catalyst at the temperature of 1000–1300 °C [1,2]. VGCFs are characterized as with highly preferred orientation of their graphitic basal plane parallel to the fiber axis and with annular ring texture in the cross section. This structure gives rise to excellent mechanical properties, very high electrical and thermal conductivity. Carbon nanotube (CNT) with a similar graphene structure as VGCF but much higher aspect ratio than VGCF has generated a great deal of interest since their discovery in 1991 [3]. Many studies have been focused on the VGCF and CNT as fillers in polymer matrix composite materials with enhanced mechanical, electrical and thermal properties. CNTs can be well dispersed in poly(vinyl alcohol) (PVA) matrix [4]. This paper deals with the fabrication of PVA composite gel films filled with VGCFs and multi wall carbon nanotubes (MWNTs) by using a mixed solvent of dimethyl sulfoxide (DMSO) and water. The focus is mainly concentrated on the improvement of mechanical and electrical properties of composites in terms of the orientation of polymer molecular chains and carbon fillers with different aspect ratios.

PVA is a useful water-soluble polymer. It has been widely studied and applied in fiber and film forms. Normally, PVA fiber with tensile strength of several 100 MPa and Young's modulus of ca. 10 GPa Young's modulus is produced in the traditional solution spinning technology [5]. The gel-spun PVA fiber has much higher tensile strength and modulus than the traditional solution spun fibers [6]. There has been a great deal of work focusing on controlling the phase separation of PVA gels and improving the crystallization and mechanical properties of dry films [6–11]. These studies dealt with the freezing/thawing technique [7,8], hydrogel or films prepared by using mixed solvent dimethyl sulfoxide (DMSO) and water (H_2O) [6,9–11], and uniaxial [9] and biaxial [10] elongation of PVA gel. It was observed that gelation from DMSO/H_2O mixture occurred without phase separation below −20 °C [11]. The volume ratio of DMSO to water (60/40) mixture solvent was conformed to be the highest draw ratio [6]. Thus, DMSO/water mixture was used as a solvent to prepare PVA–VGCFs and PVA–MWNTs gel films by adapting the freezing/thawing technique in this study.

Many studies have been reported for the dispersion of VGCFs [12], MWNTs [13–16] and single-walled carbon nanotubes (SWNTs) [17–19] in PVA matrix. CNTs can be

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* Corresponding authors. Tel./fax: +81 742 20 3462.

E-mail addresses: yuezhen@cc.nara-wu.ac.jp (Y. Bin), m-matsuo@cc.nara-wu.ac.jp (M. Matsuo).

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well dispersed in poly(vinyl alcohol) (PVA) matrix and act as nucleation sites for crystallization of PVA [4]. Cadek et al. [14] proposed that the reinforcement scales with inverse nanotubes diameter for PVA–MWNT composite through comparing PVA composites with six kinds of CNTs.

The orientation of CNTs can be achieved by magnetic field [20], or by mechanical stretching [21–23]. Several studies on CNT-filled PVA composites dealt with the orientation of carbon nanotubes in matrix and its effect on mechanical properties of composites [17,19,21,24] and its anisotropic saturable absorption [18]. The success in fabrication of super-tough PVA–SWNT composites fiber implies a potential of CNT in promotion of mechanical properties of polymer [25].

The main purpose of this paper is the improvement of both of mechanical property and electrical conductivity of PVA by adding VGCFs and MWNTs and making the fillers orientation as well as the polymer chains. Thus, the filler content chosen was a certain high compared with other studies on PVA/MWNTs composites [13–16]. The VGCF and MWNT contents were 5–30 and 1–5 wt%, respectively.

2. Experimental

2.1. Preparation of composites

Two kinds of carbon with typically different shapes and different aspects were used as fillers in the present work. They are (1) MWNTs with the average diameter (D) of ca. 20 nm and with the length (L) of 10–20 μm and (2) VGCFs with average D of ca. 150 nm and L of 10–20 μm. The aspect ratios (L/D) of the MWNTs and VGCFs are about $(1–2)\times10^3$ and 60–130, respectively. As shown in Fig. 1, the VGCFs are rigid, while the MWNTs tend to form bound structure and networks. The VGCFs and MWNTs were used as-prepared state without purification.

PVA (polymerization of 2000 and 98% hydrolyzed) was used as matrix. PVA/MWNTs and PVA/VGCFs composites were prepared by gelation/crystallization from solutions in dimethyl-sulfoxide (DMSO) and water mixtures. The DMSO/-water composition was set to be 60/40 assuring the greatest draw ability of PVA films based on a report by Cha et al. [6] The contents of VGCFs in the composite films were 5, 10, 15, 20 and 30 wt%. The content of MWNT was 1, 3 and 5 wt%. Comparing with other reports on the composites of PVA and MWNT [4,14–16], the content of filler was higher in the present work. This is necessary for keeping a high conductivity while the composites are elongated to high draw ratios.

VGCFs or MWNTs were added into mixed solvent of DMSO/H_2O and treated for 3 h with a sonicator (100 W) at room temperature. VGCFs and MWNTs were well dispersed in solvent. During sonicating the networks of VGCF and MWNT were swollen and a lot of solvent was absorbed and the viscosity of solution became very high. Then, the PVA powders were put into the solution, and the mixture was stirred and heated up to 105 °C under nitrogen and maintained for 40 min at 105 °C. The concentration of PVA against the mixed solvent was fixed to be 10 g/100 mL. The hot homogenized solution was poured it into a petri dish controlled at 120 °C and made the air bulbs left. 15 min later, the solution was removed into a refrigerator controlled at -30 °C, thus generating a gel. The freezing/thawing technique was adapted to take DMSO away for preparing dry films [7–10]. The gels were kept at the quenching temperature for 10 h and then they were immersed in a water bath at room temperature. The freezing/thawing cycles were repeated for five times.

The dry gel films were stretched to desired draw ratios in an oven at 120 °C. The composites with VGCF content <15 wt% or MWNT content <5 wt% could be elongated to more than 10-fold which is almost the same drawability as PVA homo-polymer film. However, the increase in carbon filler content hampered the drawability of the composite. The maximum draw ratios for the PVA composite containing 30 wt% VGCF was five-fold, while that for that containing 5 wt% MWNT was eight-fold.

2.2. Measurements

Dispersion of VGCF and MWNT in the composite films was observed with field emission scanning electron microscopes (FE SEM JSM-6700F of JEOL) at accelerating voltage of 1 kV. X-ray measurements were carried out using a 12 kW rotating-anode X-ray generator (Rigaku RAD-rA) with monochromatic Cu Kα radiation (wavelength of 0.154 nm). Wide angle X-ray diffraction (WAXD) patterns were detected with a flat camera. Differential scanning calorimetry (DSC) was performed using DSC6200 (SII EXSTAR 6000 of Seiko

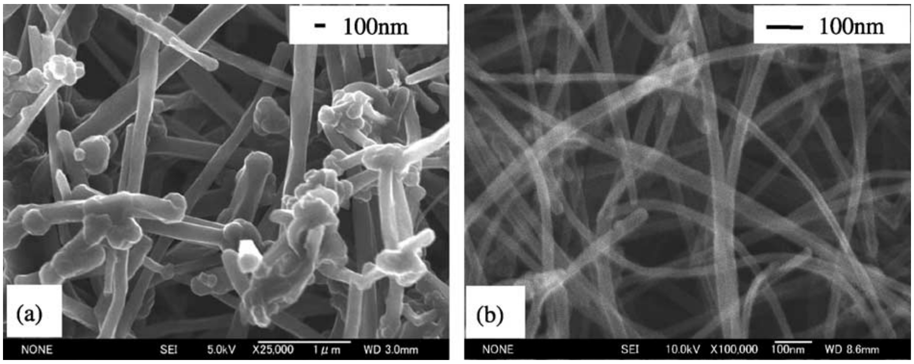

Fig. 1. SEM patterns of VGCFs and MWNTs.

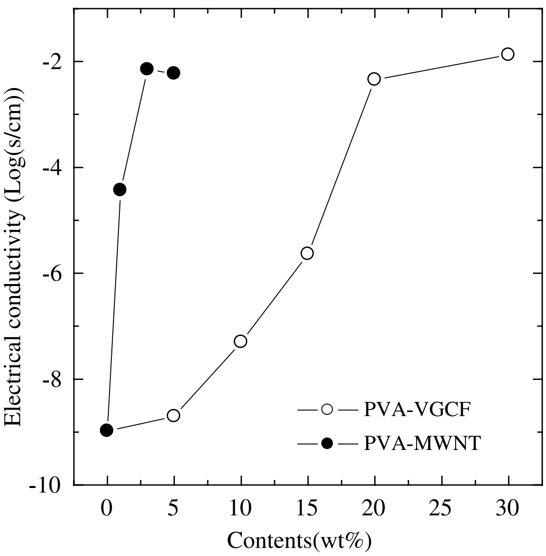

Fig. 2. Electrical conductivity of PVA–VGCFs and PVA–MWNTs composites with different filler contents.

Instrument) with 5 mg samples in aluminum pans. Before measurement, the samples were vacuum dried for 24 h at room temperature. Because the samples were prepared by gelation/crystallization method, the solvent could not be removed perfectly by 24 h vacuum drying. Especially for the composites, the absorption of solvent in the networks of VGCFs and MWNTs during sonication leads to more difficult to take solvent away. The DSC profiles show a big endothermic peak around 70–160 °C and the areas for the PVA/VGCF and PVA/MWNT composite films are bigger than that of PVA film. Thus, the measurement was carried out as heating to 280 °C at a rate of 5 K/min and holding for 5 min, then cooling down to 20 °C and again heating to 280 °C at the same rate under nitrogen. The electrical conductivity of the composites was measured by a two-terminal method. The specimens of electrical resistivity above $10^6\ \Omega$ cm were tested by applying 10 V_{DC} of voltage, while those of low-resistivity ($<10^6\ \Omega$ cm) were measured under the constant current of 0.1–1 mA. Tensile modulus and strength test was performed with Instron TENSILON/STM-H-500BP at a speed of 2 mm/min at room temperature. The size of the test specimens was 20 mm in length and 2 mm in width.

3. Results and discussion

3.1. Characteristic of un-drawn PVA–VGCFs and PVA–MWNTs composites

Fig. 2 depicts the electrical conductivity of PVA composites against the filler content. The electrical conductivity of PVA/VGCFs composites increased steadily but rapidly when the content was below 20 wt%. Beyond 20 wt%, the increase became less pronounced. On the other hand, the electrical conductivity of the PVA/MWNTs composites increased drastically with a very few content of MWNTs and the percolation threshold of PVA/MWNTs was less than 1 wt%. It almost levels off when the MWNTs content was higher than 3 wt%. The electrical conductivity for the PVA/MWNTs with 3 wt% of MWNTs reached almost the same value for PVA–VGCFs with 30 wt% of VGCFs.

To check such different behaviors, the morphology of the both composites was observed by SEM. Fig. 3 compared the SEM images of the cross-section of neat PVA film and the composites. Samples were split under liquid nitrogen to get a natural cross-section. It could be observed that the VGCFs and MWNTs are well dispersed in PVA matrixes. In image (b) for the composite with 10 wt% of VGCFs, VGCFs are dispersed homogeneously in the matrixes, but they seem to be separated each other without making cross-linking points. On the other hand, in image (c) for the composite with 30 wt% of VGCFs, overlapping or connection of VGCFs could be observed. In images (d) and (e) for the PVA/MWNTs composite with 3 and

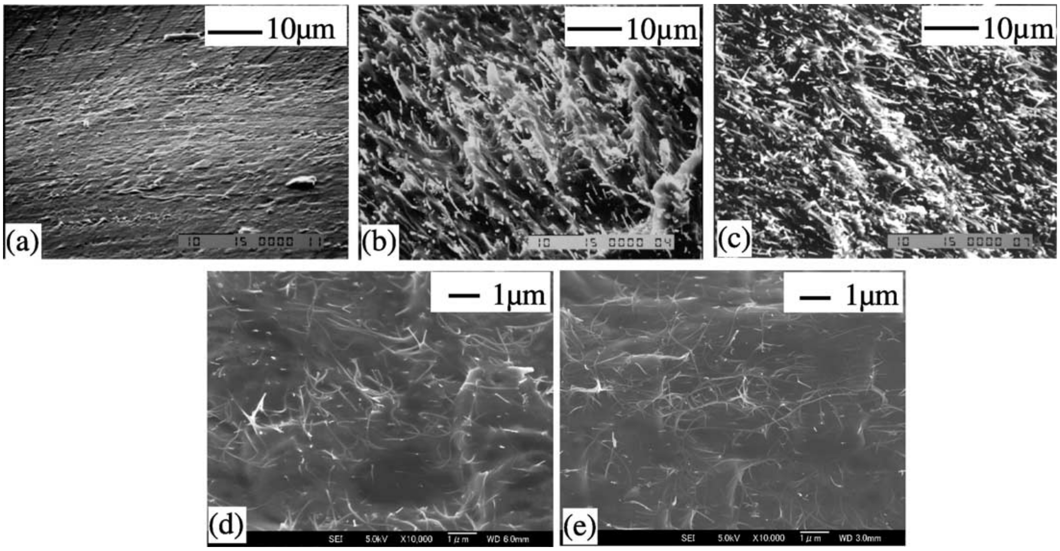

Fig. 3. SEM patterns of the cross-section of (a) pure PVA, (b) PVA–VGCFs (10 wt%) (c) PVA–VGCFs (30 wt%) and (d) PVA–MWNTs (3 wt%) (e) PVA–MWNTs (5 wt%) composite films.

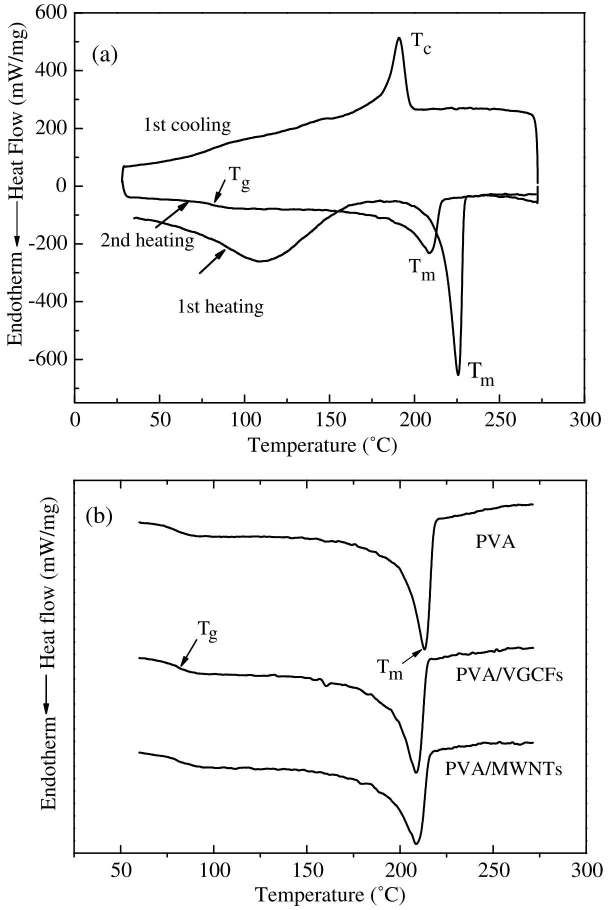

Fig. 4. DSC curves of PVA, PVA–VGCFs (5 wt%) and PVA–MWNTs (5 wt%) dry gel films. (a) Heating and cooling cycles for PVA/MWNT (5 wt%) film; (b) the profiles of three samples obtained from the second heating.

5 wt% of MWNTs, MWNTs formed continuous networks in the matrix. But they also revealed that the loading of MWNT (3 or 5 wt%) seems to be so high that some aggregates are formed. However, the network structure and a suitable high level loading are supposed to be meaningful to keep a high conductivity when the composite being elongated. This will be discussed later.

Fig. 4 shows the DSC profiles measured for the PVA film and its composites where the content of fillers was 5 wt%. Profile in (a) shows a behavior of PVA/MWNT (5 wt%) during the whole thermal cycle including the first heating and cooling and then the second heating. As explained in experimental part, even though all samples were vacuum dried for 24 h at room temperature, the profile for the first heating shows a big endothermic peak around 70–170 °C and the peak disappeared in the second heating process. Fig. 4(b) was the corresponding profiles from the data in the second heating for three kinds of samples, PVA, PVA/VGCF(5 wt%) and PVA/MWNT (5 wt%). To obtain the crystallinity of PVA, the area of endothermic peak was calculated in the temperature range from 188 to 232 °C for the first cycle and in the range of 153–224 °C for the second cycle because of the difficulty in determining the base line of the curves. The weight fraction of PVA was gotten by reducing the filler content of composites. The results for three kinds of samples were submitted in Table 1. The crsytallinity for the composites was a little bit higher than that of the pure PVA film in the first heating, suggesting that VGCFs and MWNTs served as nucleation sites for crystallization of PVA as reported by other researches [4,15], but the effect was not significant. On the other hand, the melting point shifted to lower temperature and the area of endothermic peak became smaller in the second run indicating that the recrystallization made an obvious decrease in crystallinity and crystal size. The melting points and crystallinities for the composites were lower than that of the pure PVA. This phenomenon was suggested that the filler may somewhat obstruct the crystallization of matrix after being melted. The glass transition T_g was not obvious in the first heating. The T_g obtained from the second heating was about 80 °C without significant change for the composites. The results show some different from other reports. For example, the Coleman et al. [15] pointed out the linear increase in crystallinity while the content of MWNTs increased from 0.075 to 0.6 vol%. This is maybe attributed to the different fabrication method and also different molecular weight of PVA. The crystallinity and melting points of PVA in the present research is much higher than their report [4,15]. Another reason is the higher content of filler in the present research. The large amount of filler may obstruct the crystallization of matrix. The opposite effects of nucleation and the obstruction for crystallization make the behavior complicated.

3.2. Morphology of the drawn composites

As mentioned before, many researches have been reported for the dispersion and wetting of VGCFs, MWNTs [12–16] or single wall carbon nanotubes (SWNTs) [17–19] with PVA matrix and their enforcement effect on PVA composites. Apart from those investigations, this work focused on the morphology of elongated PVA composites containing VGCFs and MWNTs, and dealt with their orientation of fillers and matix.

Table 1
Parameters from the DSC curves for the PVA, PVA/VGCFs (5 wt%) and PVA/MWNTs (5 wt%) films

	First heating			First Cooling		Second heating			
	T_m (°C)	ΔH (J/g)	X_c (%)	T_c(°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)	X_c (%)	T_g (°C)
PVA	225.3	72.2	44.7	189.9	46.3	213.1	54.0	33.4	78.6
PVA/VGCFs	224.7	76.9	47.6	189.5	45.7	208.3	53.7	33.2	80.5
PVA/MWNTs	226.0	81.2	50.3	190.9	40.6	208.9	50.0	30.9	82.9

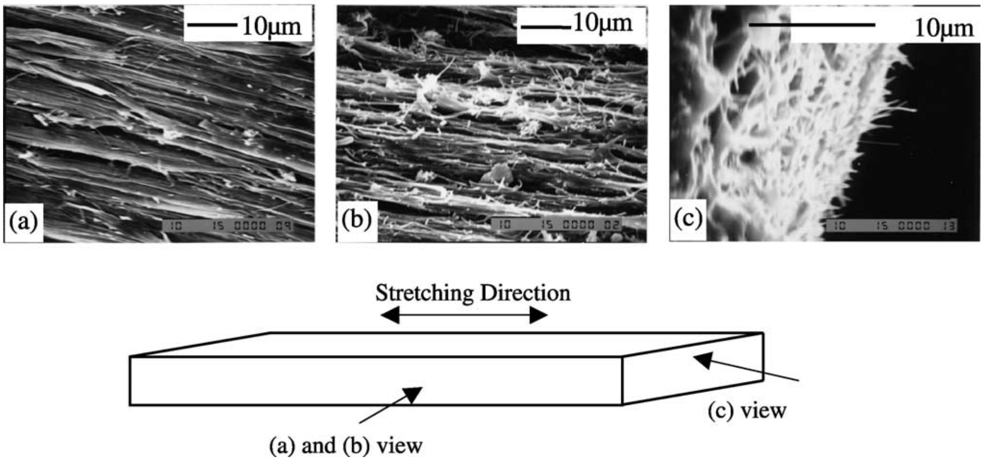

Fig. 5. SEM patterns of elongated PVA–VGCFs films: (a) VGCFs = 10 wt%, $\lambda = 10$ and (b) VGCFs = 30 wt%, $\lambda = 5$ from side view; (c) VGCFs = 10 wt%, $\lambda = 10$ from end view.

Fig. 5 show the SEM images of PVA–VGCFs composites elongated up to the indicated draw ratio. Photos (a) and (b) were observed from the side view after samples were split along stretching direction. Photo (a) was the composite with 10 wt% of VGCFs at a draw ratio of 10 times ($\lambda = 10$) and photo (b) was that with 30 wt% of VGCFs at $\lambda = 5$. In both cases, the PVA fibrils were highly oriented with respect to the stretching direction and fillers were also aligned along the PVA fibrils. Compared with photo (a) in Fig. 5 with the photo (b) in Fig. 3, the amount of VGCFs observed from the side view of split films was very few indicating that the VGCFs were almost coated by PVA fibrils when the filler content was 10 wt%. For the samples with 30 wt% of VGCFs, a large mount of the oriented VGCFs can be observed in photo (b) of Fig. 5. Photo (c) was observed for the same sample as photo (a), but it was from the end view. The stretched fibrils were broken in the direction perpendicular to the stretching direction. The VGCFs coated by PVA fibrils were pulled out at the cross section of the broken fibrils. The coating effect may suggest that VGCFs act as nucleation sites for the crystallization of PVA. But Figs. 3

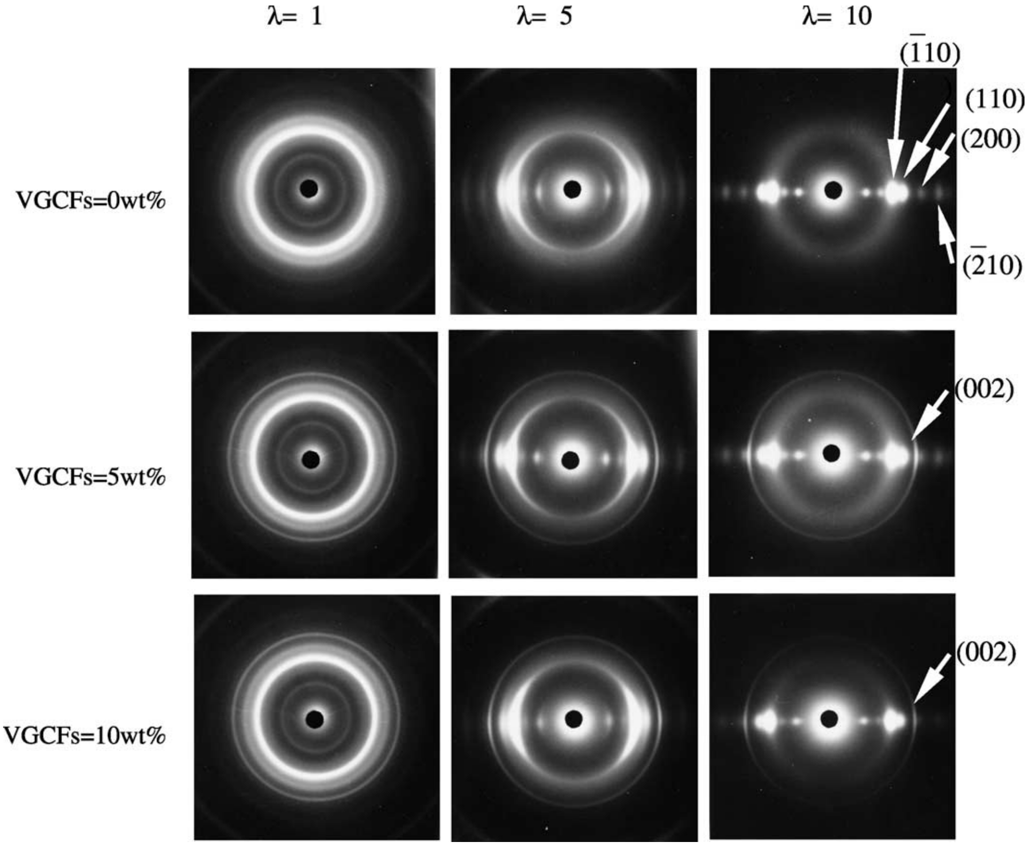

Fig. 6. WAXD patterns for the PVA–VGCFs films.

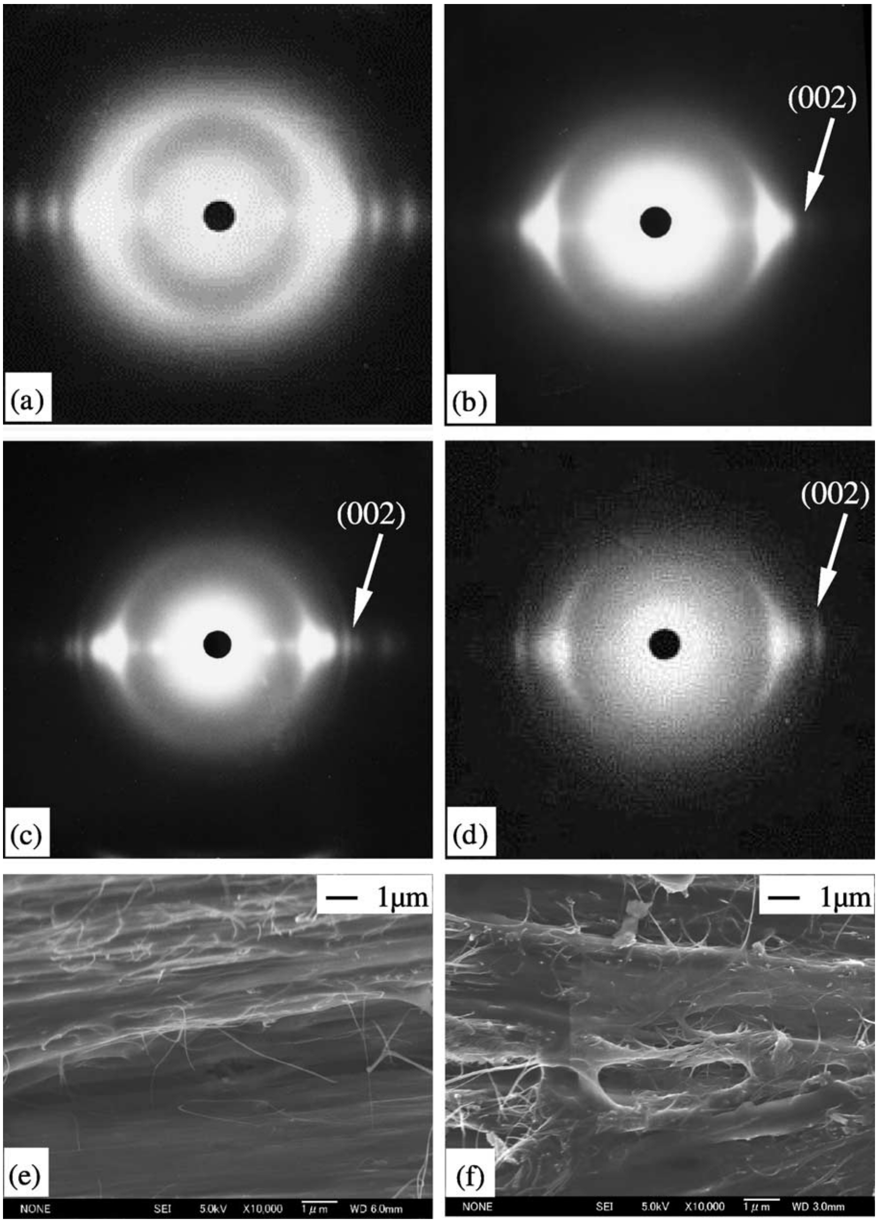

Fig. 7. WAXD and SEM patterns for the elongated PVA–MWNTs films ($\lambda=5$): the contents of MWNTs are (a) 0 wt%, (b) 1 wt%, (c) and (e) 3 wt%, (d) and (f) 5 wt%.

and 5 show obviously the crystal size of PVA became smaller by introduction of fillers. This is coincident with the shift of melting point to lower temperature side shown in DSC curves (Fig. 4).

The orientation of the VGCFs and PVA crystallites was also detected by X-ray diffraction. WAXD patterns for the neat PVA and PVA–VGCFs composite films detected in the through view were shown in Fig. 6. The diffraction arcs from the$(1\bar{1}0)$, (110) and (200) planes of PVA crystallites became smaller and sharper with increasing the draw ratio, which indicates a very highly preferential orientation of PVA crystallites with respect to the stretching direction. The orientation of PVA crystallites was hardly affected by the given VGCFs contents. The change in diffraction from the (002) plane of the VGCFs suggested that the VGCFs are oriented parallel predominantly with respect to the stretching direction together with PVA crystallites, as draw ratio increases.

Similar observation was confirmed for the PVA/MWNTs composite films. Fig. 7 shows WAXD patterns for the drawn composite films ($\lambda=5$) with different MWNTs contents. The diffraction arcs for the (002) planes of the MWNTs indicates that the preferential orientation of MWNTs with respect to the stretching direction. However, it is seen that the diffraction arcs from the $(1\bar{1}0)$, (110) and (200) of PVA crystallites in pattern (d) became wider in comparison with those observed for the composites with lower loading of MWNTs, as shown in patterns (b) and (c). This indicates that the orientation degree of

PVA chains became less pronounced with increasing filler content. The intensity of diffraction from the PVA crystallite decreased significantly for the composites with increasing the content of MWNTs. This indicates that a large mount of filler obstruct the crystallization of matrix. This supported the results of DSC shown in Fig. 4. Photos (e) and (f) are SEM images observed from the side view of the drawn composite films ($\lambda = 5$) with 3 and 5 wt% MWNTs, respectively. It is obvious that the networks of the MWNTs were continuous and mainly aligned along the PVA fibrils. Such a characteristic plays an important role to maintain the high electrical conductivity at high draw ratios, in addition to the improvement of mechanical properties. This will be discussed later.

3.3. Mechanical properties of the composite films

As discussed in Fig. 3, the dispersion of carbon fillers within undrawn composites is dependent upon the aspect ratios. For the PVA/VGCFs systems, the fillers are isolated together without forming network structure because of their toughness. On the other hand, for the PVA–MWNTs systems, the flexible MWNTs formed a number of networks and the network structures were maintained even in the drawn state (Fig. 7). It may be expected that the different dispersion due to the different aspect ratios influence the mechanical and electrical properties in undrawn and drawn states.

Table 2 summarized the Young's modulus and tensile strength of neat PVA film and PVA/VGCFs and PVA/MWNTs films in the undrawn state. The data were the average results measured for five samples. To the best of our knowledge, there is no reports on the characterization of PVA filled VGCFs. However, many studies proposed the improvement of mechanical properties of PVA by filling MWNTs [13–16] and SWNTs [17–19], or functionalized CNTs [26]. They considered the reinforcement of polymer with low loading of CNTs in experiments [14–17] and theory [14–15]. Those results pointed out that the strength and toughness increased from several 10% to 3–4 times when a contents less than 1 vol%. In their reports we can notice that the mechanical properties of the resultant PVA films and its composites were changed due to the characteristic of PVA material such as molecular weight and the degree of hydrolysis and so on, and also due to the preparation of films or fibers. Different from the above researches, this study aims to fabricate the composites not only with improved mechanical properties but also with high electrical conductivity. Thus, we mainly investigated the properties of composites containing a certain high loading of fillers. The Young's modulus increased significantly for both systems of PVA/VGCFs and PVA/MWNTs composites as summarized as in Table 2. The tensile moduli for composites containing 5 wt% VGCFs and 1 wt% MWNTs were three and two times as high as the PVA homo-polymer films, respectively. Further, increase in the content of VGCFs, the Young's modulus of PVA/VGCFs composite was increased linearly to 7.7 GPa when VGCFs content increased to 30 wt%. But the Young's modulus for PVA/MWNTs decreased slightly when MWNT's content was beyond 3 wt%. The same tendency was confirmed for the tensile strength.

Table 2
Young's modulus and tensile strength of neat PVA film, and PVA–VGCFs and PVA–MWNTs composite films

	Sample filler content (wt%)	Young's Modulus (GPa)	Tensile Strength (MPa)
PVA	0	1.4	49.2
PVA/VGCF	5	4.8	71.3
	10	4.9	70.9
	15	5.5	70.9
	20	6.7	68.7
	30	7.7	88.4
PVA/MWNT	1	3.1	50.1
	3	3.6	63.0
	5	3.3	54.0

Judging from the SEM patterns in Fig. 3, it may be suggested that that the MWNT networks seemed to be better wetting with matrix and without pulling out in the cross-section compared with the PVA/VGCFs composites. Thus, the MWNTs may be expected to be more effective to improve the mechanical properties of composites than the VGCFs. However, a contrast result was obtained from the tensile test. Cadek et al. [14] carried out the analysis for PVA composites in relation to characteristics of SWNTs, four kinds of MWNTs and a kind of double wall carbon nanotube (DWNT). They pointed out that the increase of mechanical property depends on the average diameter of the carbon nanotubes and, therefore, on the total surface area per unit volume at the low volume fraction of nanotubes. This is attributed to that the nanotubes act as nucleation sites for the crystallization and promote the crystallinity of PVA. The nucleation of crystal PVA results in an extremely strong interfacial interaction between nanotubes and polymer. So the most important factor for reinforcement of polymer with carbon nanotubes is the interfacial stress transfer between nanotubes and matrix. In this study, the aspect ratio of MWNT was more than 10 times as high as VGCF, thus the average surface area of MWNTs was more than 100 times as large as that of VGCFs at the same content. Thus, the reinforcement of MWNTs should be more powerful than VGCFs. But the Young's modulus of PVA/VGCFs was higher than PVA/MWNTs at the same content of 5 wt% in the present results. This is attributed to the existence of agglomerate of MWNT in the composites because the volume fraction of MWNTs of composites is much higher than the case of VGCFs at the same concentration and 3 and 5 wt% MWNTs contents largely exceed the percolation threshold as shown the Fig. 1. The extra mount of MWNTs made a minus effect on reinforcement of composites in the undeformed state.

Table 3 lists the results of PVA and PVA/MWNTs composites at different draw ratios. The orientation of PVA chains lead to a significant increase in Young's modulus and tensile strength, although the values were not as high as other oriented systems reported in literatures [9,19] since the molecular weight of PVA used here was lower than the reported studies. In addition to the molecular orientation leading to the improvement of the mechanical properties, the filler effect for the drawn composites obviously caused

Table 3
Young's modulus and tensile strength of elongated PVA film and PVA–MWNTs composites at different draw ratios

MWNT content (wt%)	Draw ratio	Young's modulus (GPa)	Tensile strength (MPa)
0	1	1.4	49.2
	5	1.9	162.0
	8	5.2	396.0
1	1	3.1	50.1
	5	7.6	322.0
	8	13.5	437.0
3	1	3.6	60.3
	5	8.6	500.0
	8	18.2	546.0
5	1	3.3	54.0
	5	7.9	374.0
	8	12.6	537

enhancement of the mechanical properties, and this tendency is very significant for the Young's modulus especially. Compared with the neat PVA film, the Young's modulus increased by 160, 250 and 142% for composites containing 1, 3 and 5 wt% MWNTs at $\lambda=8$, respectively. The effect was much more significant than the reported PVA/SWNT composite fibers prepared with gel spinning where Young's modulus of composite fiber (SWNTs = 3 wt%) was 40% higher than the PVA fiber [19]. The increase in tensile strength was not significant by admixture of MWNTs in the undeformed state, but the values increased more by elongation. The values increased more than two and three times for the composites with 1 and 3 wt% MWNT contents at $\lambda=5$ indicating the effect of orientation of MWNTs. This suggests that elongation is one of the best methods to improve mechanical properties of the composite materials. Actually, super-tough PVA–SWNTs composite fibers containing ca. 60 wt% SWNTs were reported to have a tensile strength of 1.8 GPa [25].

Here it may be noted that the Young's modulus and tensile strength at 5 wt% MWNT content become lower than those at 3 wt% content at $\lambda=5$ and 8. This is maybe due to existence of a number of aggregates and entanglements of MWNTs within the composites. This means that admixture of excess amounts of MWNTs is unfavorable for promotion of mechanical properties of the composites.

3.4. The draw ratio dependence of electrical conductivity of the composites

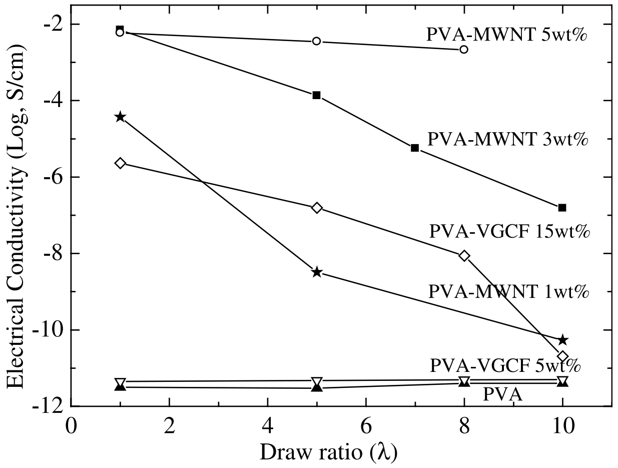

Fig. 8. Draw ratio dependence of the electrical conductivity of PVA, PVA–VGCFs and PVA–MWNTs films.

Fig. 8 depicts the electrical conductivity against the draw ratio for PVA and its composite films with different filler contents. The conductivity was measured along the stretching direction with two-terminal method. The values for the PVA/VGCFs composite, the VGCFs content being 5 wt%, were almost equal to those of the neat PVA films before and after elongation. The conductivity of undrawn composites ($\lambda=1$) containing 15 wt% of VGCFs was improved drastically in comparison with the pure PVA film, but the conductivity decreased gradually with increasing draw ratio. A similar phenomenon was observed for the PVA/MWNTs composites containing 1 and 3 wt% of MWNT. However, the PVA/MWNT composite with 5 wt% of MWNTs assures a stability of electrical conductivity superior to others. The value was almost independent of the draw ratio up to $\lambda=8$ and maintained almost the same level as obtained for the undrawn film. Such behavior indicates that network structure assured enough electric channels when the samples were elongated, since MWNTs with large aspect ratio are flexible in comparison with VGCFs. As shown in Figs. 3 and 5, the rigid VGCFs are easy to be separated in the matrix when the loading was few, and the overlapped VGCFs did not form network structures even when the VGCFs content was very high. In contrast, the MWNTs form the continuous network structures within the composite and the networks were well wetting with PVA matrix. A certain amount of network structures was thought to be important to maintain a high level conductivity when the composites were elongated to improve their mechanical properties. Even though a high level loading of MWNTs seems to be not so effective on improvement of the crystallite structures and mechanical properties as described before, the promotion of both mechanical and electrical properties in oriented composite requires a certain high level content. Besides the electrical properties, this concept should be suitable for the thermal properties such as thermal conductivity and also other properties for the polymer–carbon nanotubes composite. It suggests that selecting suitable nanotubes with a specified morphology is very important when designing a kind of composite.

With further investigation, anisotropic characteristics of the elongated films were estimated using the PVA/MWNTs composite with 3 wt% MWNTs. When the draw ratio was four-fold, the electrical conductivities measured by two-terminal method were 7.94×10^{-4}, 1.58×10^{-5} and 1.26×10^{-7} S/cm in the stretching, transverse and thickness directions, respectively. Especially, the difference was very large along the stretching and thickness directions, which

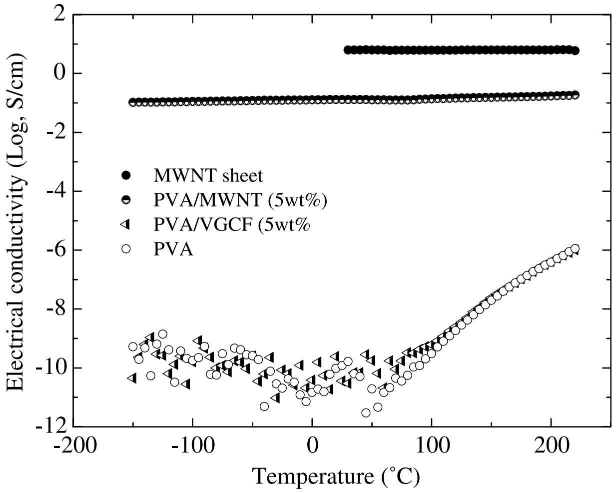

Fig. 9. Temperature dependence of electrical conductivity measured for the elongated PVA, PVA–VGCF, PVA–MWNT films with filler contents 5 wt% ($\lambda=5$), and MWNT sheet.

demonstrate that the oriented MWNTs assure continuous network along the stretching direction.

Temperature dependence of electrical conductivity of the PVA and its composites was measured in the temperature range of −150 to 220 °C. The measurements were done for undrawn materials ($\lambda=1$). The content of VGCFs and MWNTs was 5 wt%. The electrical conductivity of MWNTs was tested on a loosen MWNTs sheet which was prepared by mixing them in methyl alcohol and then filtering. It was measured in the temperature range of 20–220 °C. The results were shown in Fig. 9. It is seen that the values measured for neat PVA film and PVA/VGCFs composite containing 5 wt% VGCFs are almost the same but the both values increased with increasing temperature beyond 80 °C corresponding to the glass transition temperature T_g of PVA [19]. In the temperature range lower than T_g, the conductivities were uneven but did not change a lot and then increased gradually above T_g. Other the other hand, the values for the PVA/MWNTs with 5 wt% MWNTs content was hardly affected by the change of temperature as that of pure MWNT sheet indicating a superior thermal stability. Here it should be noted that the values for the composites are much lower than the intrinsic conductivity of the MWNT sheets. This indicates that the further improvement of electric conductivity of this PVA/MWNTs composite film should be realized. Incidentally we could not success in making a VGCF sheet for measuring the temperature dependence suitable to our equipment like MWNTs. We prepared pellets of VGCFs and MWNTs and detected the conductivities at room temperature. Due to the limit of facility and also considering that the same method should be taken as in the case of composites, we measured it using the two terminal methods. The corresponding values of VGCFs and MWNTs were 17.4 and 14.1 S/cm, respectively. They are very close even they are not the intrinsic electrical conductivity.

4. Conclusions

The PVA/VGCF and PVA/MWNT composites were prepared by gelation/crystallization from a mixed solvent of DMSO and water with 60/40 composition. The composite gels were fabricated to dry gel films by repeated freezing/thawing under the drying process. The percolation threshold of electrical conductivity for the PVA/MWNTs was less than 1 wt% MWNT loading which was much lower than that of PVA/VGCFs composites. The mechanical properties of the PVA composite films were improved significantly by adding VGCFs and MWNTs.

The composite films were elongated to 5–10-fold uniaxially. The orientation of fillers and polymer chains and its influence on mechanical and electrical properties of composites were investigated. The diffraction of X-ray and SEM observation revealed that VGCFs and MWNTs were highly oriented in the stretching direction in accordance with the orientation of PVA chains. The orientation of the fillers by elongation provided further improvement of the mechanical properties of the composites.

Comparing with the VGCF, MWNT was confirmed to be more effective to improve the electrical conductivity because of the network structure of MWNTs. The electrical conductivity for the PVA/MWNTs composites containing 5 wt% of MWNTs was independent of the draw ratio up to eight-fold, implying a possibility of improvement of mechanical property and electrical conductivity at the same time. The thermal stability of PVA composite was promoted greatly by adding MWNTs.

Even though a high level loading of MWNTs seems to be not so effective on improvement of the mechanical properties, a certain high level of filler content was proved to be necessary for the promotion of both mechanical and electrical properties in oriented composite.

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