CHAPTER VI
DYNAMIC MECHANICAL PROPERTIES OF α-CHITIN WHISKER-REINFORCED POLY(VINYL ALCOHOL) NANOCOMPOSITE NANOFIBERS

6.1 ABSTRACT

α-chitin/poly(vinyl alcohol) films and fibers were prepared by solution casting from water and electrospinning from water. The influence of the chitin whiskers on dynamic mechanical properties and crystallization behavior of the composites were investigated by dynamic mechanical analysis (DMA), wide angle X-ray diffraction (WAXD), and differential scanning calorimeter (DSC). The storage modulus of the composites increased with increasing filler loading. Chitin whiskers also inhibit the crystallization of the PVA presumably due to an increase in viscosity. Accordingly with the presence of the chitin whiskers, the dynamic mechanical and thermal properties are increased due to the strong hydrogen bonding interaction between chitin whiskers and PVA-matrix. In addition water content plays important roles in the PVA/chitin whiskers composites. The percent crystallinity of PVA in the composites was increased when the water is present in the composites. This is because the water allows the movement of the PVA chains to rearrange and crystallization. However, it was found that water molecules can incorporate into the crystalline phase of the PVA leading to a reduced melting temperature for the crystalline region.

6.2 INTRODUCTION

Nanocomposites are a class of composites that at least exhibit one ultrafine phase in the dimensions of 1-1000 nm. Because of the nano-size effect, these composites have some unique properties with respect to their conventional microcomposites. Fillers used for preparing nanocomposites generally are synthetic materials; their biocompatibility and biodegradability are much more limited than those of natural origin. In nature a large number of animals and plants synthesize

extra cellular high-performance skeletal biocomposites consisting of a matrix reinforced by fibrous biopolymers [1]. Cellulose is a classical example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner [2].

Favier et al. [3] was the first to prepare cellulose whiskers from tunic of tunicate *Microcosmus fulcatus* by acid hydrolysis (i.e. tunicin whiskers) and use them as reinforcing nanofillers in a terpolymer latex consisting primarily of styrene and butyl acrylate. Since then, tunicin whiskers have been used as reinforcing nanofillers in poly(β-hydroxyoctanoate; PHO) [4], poly(hydroxyalkanoate; PHA) [5], plasticized maize starch [6], and poly(oxyethylene) [7]. Whiskers from other polysaccharides, such as starch [8] and chitin [9], can also be prepared. Unlike tunicin whiskers which can only be prepared by hydrolysis in a strong sulfuric acid (H_2SO_4) solution [3-7, 9], both starch and chitin whiskers can be prepared by hydrolysis in hydrochloric acid (HCl) solution [8, 9].

Chitin is a high molecular weight biopolymer constituting of the structure of exoskeleton shells of arthropods as well as the internal flexible backbone of cephalopods and is one of the major components of the fibrous material of cellular walls in mushrooms and algae. Usually the waste from shellfish canning industry (shrimp or crab shells) consists of 8-33% chitin, which is the main source of this polymer. Chemically, chitin molecules consist of *N*-acetyl-*D*-glucosamine units. The outstanding properties of chitin are non-toxic, odorless, highly crystalline, biocompatible with living tissues, and biodegradable. Chitin whiskers have been successfully prepared from crab shells [9, 11, 12], squid pens [13], and tubes of *Riftia pachyptila* tube worms [14]. Regardless of the source, the commonly-used hydrolytic condition to produce chitin whiskers is suspending the chitin in boiling 3 N HCl for 90 min under vigorous stirring [9, 10, 14]. We recently reported successful preparation and characterization of nanocomposite films of poly(vinyl alcohol) (PVA)/α-chitin whiskers and chitosan/α-chitin whiskers with or without heat treatment [15]. The whisker content ranged between 0 and 29.6 wt.%.

Electrostatic spinning or electrospinning is a technique for the continuous production of fibers with diameters in the nanometer to sub-micrometer range. This

method has attracted significant interest because of its versatility in spinning a wide variety of polymeric fibers and the potential applications of such in membranes, electronic devices, and nanocomposites [16, 17]. The kernel of the technique is the use of a high electrostatic potential applied to a spinning liquid across a charged nozzle and a grounded screen collector. Under certain conditions, a charged stream of the spinning liquid is ejected and a mat of non-woven fibers is collected on the collector [18]. Various materials have successfully been electrospun into ultrafine fibers. There have been increasing reports about the preparation of nanocomposite electrospun fibers as novel functional materials. Some nanomaterials that have been incorporated into electrospun polymeric matrices are layered nanosilicate, calcium carbonate, hydroxyapatite, or silver nanoparticles, cadmium sulfide nanorods, graphite nanoplatelets, and multi-wall carbon nanotubes [19-22]. Recently, we reported successful fabrication of α-chitin whisker-reinforced poly(vinyl alcohol) nanocomposite nanofibers by electrospinning and their mechanical properties [23] The whisker content ranged between 0 and 11.38 wt.%.

6.3 EXPERIMENTAL

6.3.1 Preparation of α-chitin whiskers

α-Chitin whiskers were prepared from chitin flakes derived from shells of *Penaeus merguiensis* shrimps [Seafresh Co., Ltd. (Thailand)]. Chitin flakes were first hydrolyzed with 3 N hydrochloric acid (HCl) under vigorous stirring with refluxing at 120°C for 6 hrs. The ratio of HCl to chitin flakes was 30 $cm^3 \cdot g^{-1}$. After acid hydrolysis treatment, the chitin whisker suspension was diluted with distilled water, followed by centrifugation at 10,000 rpm for 10 min. The suspension was then transferred to a dialysis bag and dialyzed in distilled water for 2 days. The solid content of the as-prepared chitin whisker suspension was measured gravimetrically to be about 5.10 wt.% [23].

6.3.2 Preparation of nanocomposite fiber mats and films

Poly(vinyl alcohol) (PVA) powder (M_w = 75,000 Da and degree of hydrolysis (DH) = 98%; Fluka, USA) was first dissolved in warm distilled water (85°C) under slight stirring for 3 hrs to obtained a PVA solution at a fixed concentration of 10 wt.%. A varying amount of the as-prepared chitin whisker suspension (between 1 and 5 g) was well mixed with 20 g of the as-prepared PVA solution. Distilled water was sometimes added into the mixture so that the total weight of the mixture was about 30 g. Table 6.1 summarizes the composition of each of the as-prepared mixtures. The final concentrations of both PVA and chitin whiskers in the mixtures were calculated and are also summarized in Table 6.1. The weight content of chitin whiskers with respect to the total weight (i.e. the CW/total weight ratio) ranged between 0 and 11.38%. The PVA/chitin whiskers mixtures were continuously stirred overnight prior to further fabrication.

To prepare nanocomposite fiber mats, each of the as-prepared PVA/chitin whiskers mixtures was placed in a 50-ml plastic syringe. A blunt-end stainless-steel gauge 20 needle (i.e. outside diameter = 0.91 mm) was used as the nozzle. The tilt angle of the syringe and the needle was 45° from a horizontal baseline to ascertain a constant presence of a liquid droplet at the tip of the nozzle. A sheet of aluminum foil on a plastic backing was used as the screen collector. A Gamma High Voltage Research DES30PN/M692 power supply was used to generate a high DC potential across the needle (connected to the positive emitting electrode) and the screen collector (connected to the grounding electrode). The applied potential was fixed at 15 kV over a fixed collection distance between the tip of the nozzle and the screen collector of 15 cm. The feed rate of the solutions for most experiments was controlled by means of a Kd Scientific syringe pump at 3 ml/hr. The collection time was also fixed at 12 hrs. The as-spun fiber mats were kept in room condition for one day prior to further characterization.

To prepare nanocomposite films, each of the as-prepared PVA/chitin whiskers mixtures was poured onto a glass petridish. The sample was dried at room temperature and pressure for 3 days prior to further characterization.

6.3.3 Characterization

Morphological appearance of the as-spun fiber mats was observed using a JEOL JSM-5200 scanning electron microscope (SEM). The electrospun fibers were sputtered with a thin layer of gold prior to SEM observation. Both the as-prepared neat PVA and PVA/chitin whiskers nanocomposite fiber mats and films were characterized for thermal and dynamic mechanical integrity.

Wide-angle x-ray diffraction patterns were collected were collected on an Osmic Micro Max® System for Small Angle X-ray Scattering which also contained an image plate detector located approximately 5 cm from the sample. Patterns were collected in vacuum so no water would be present in the patterns. The 2-dimension (2D) image was collected and neither the fiber mats nor the films showed any preferential orientation. The patterns were circularly averaged and are presented as intensity vs. scattering angle (2θ). The collection time for film samples was 2 hours, while collection time for electrospun fibers was 4 hours due to the smaller intensity of the latter for the sample thicknesses used in our experiments. Small-angle patterns were collected but are not presented since the chitin-PVOH contrast dominated the scattering.

Dynamic mechanical analysis (DMA) was collected at 1 Hz using a Rheometric Scientific Analysis II in tension mode. The storage and loss moduli of samples which corresponds to energy store (response of elastic component) and energy lost (response of viscous component) by the materials, respectively, were measured. Note that since fiber mats were used, the DMA spectra are not measuring the material properties of the composite per se, they are measuring the properties of the mats.

A DSC was used to investigate the glass transition temperature, crystallization temperature, melting temperature and percent crystallinity of both the composites films and electrospun fibers. The measurements were carried out at heating rate 20°C/min and cover the temperature range from 30 to 220 °C.

6.4 RESULT AND DISCUSSION

6.4.1 Morphological appearance

Electrospinning of the as-prepared PVA/chitin whiskers mixtures was straightforward. Figure 6.1 shows selected SEM images of the as-spun fibers from neat PVA solution and PVA/chitin whiskers mixtures (see Table 6.1 for detailed information about the composition of the spinning dopes). All of the as-spun fibers were cross-sectionally round; however; a slight difference between the fibers obtained from neat PVA solution and PVA/chitin whiskers mixtures is evident. Clearly, the as-spun fibers from neat PVA solution were smooth, while those from PVA/chitin whiskers mixtures exhibited a combination of smooth and bead-on-string morphology. Statistical analysis of the fiber diameters was presented in the previous studied [23]. Moreover all the SEM images of the as-spun fibers also show completely random orientation.

6.4.2 WAXD results

Figure 6.2 and 6.3 shows X-ray diagrams for the specimens of chitin whisker/PVA composite films and fibers with different composition. In Figure 6.2, 2-dimensional (2D) images of the specimens were shown; the results show that when the chitin whisker is present, additional three rings appear which correspond to the characteristic of the chitin crystalline phases and intensity of the three rings trend to increased with amounts of the chitin whiskers. Moreover, intensity of the 2D images of the films is relatively high as compared to that of the electrospun fibers because bulk densities of films are much higher than that of electrospun fibers [23]. In the Figure 6.3 the 1-dimensional (1D) images or X-ray pattern were shown (adjusted the intensity of the peak based on intensity of PVA). With the presence of chitin whiskers additional three peaks appear at $9.3°$, $12.7°$, and $26.2°$ and intensity of these three peaks is increased with the amounts of added chitin whiskers.

Neat-PVA shows the broad peak which usually consist of four characteristic peaks at the position of $2\theta = 11.6°$, $17.0°$, $19.1°$, and $21.3°$ (Figure 6.4) which correspond to 100, 001, 101, and 101 reflections, respectively. This is consistent with observation by J.D. Cho *et al.* in 1999 ($11.5°$, $16.2°$, $19.4°$ and $20.2°$)

[24]. When chitin whiskers are introduced in the specimens, three other peaks clearly appear at 2θ = 9.3°, 12.7°, and 26.2°. An additional peak at 19.13° is found underneath the 19.2° of the PVA. This is in agreement with the observation made by Seong Soo Kim *et al.* [25] that α-Chitin exhibited crystalline peaks at around 2θ = 9.8° and 19.3° due to the presence of (020) and the mixture of (110) and (040), respectively. In addition, three small crystalline peaks between 2θ = 20° and 27°, due to the presence of (101), (130) and (013) also appeared in α-chitin. Therefore not only PVA crystalline part appear at $2\theta \approx$ 19° but also those of chitin whiskers, meaning that the deconvolution has to use pure PVA to set the relative intensity of this peak based on the intensity of other crystalline peaks and the leftovers go to chitin.

The percent crystallinity of PVA in both composite films and electrospun fibers were calculated using the area under the peak of the four crystalline phases of PVA divided by the total area, excluding the areas under chitin whisker peaks. Table 6.2 shows the relative percent crystallinity of PVA in the films and electrospun fibers. These results reveal that the composite films have relatively higher percent crystallinity of PVA as compared to that of electrospun fibers. Lower crystallinity likely occurs because the solvent evaporation rate in the electrospinning process is relatively fast, providing less opportunity for PVA chains to rearrange, nucleate, and crystallize. When chitin whiskers are presented in the composites, the percent crystallinity of PVA is decreased which could be explained by two main reasons 1) the viscosity of the solution, increased which increasing in the amount of chitin whiskers, leading to more restriction of chain movement. 2) chitin whiskers inhibit the crystal formation of the PVA chains by form hydrogen bond with PVA (typically, the crystallization of PVA occur through the hydrogen bonding) which in turn should inhibit the movement of PVA chains and hence the crystallization of PVA matrix is hindered. As the concentration of the chitin whiskers increases, the degree of crystallinity of the PVA is decreased.

6.4.3 Dynamic Mechanical Properties results

Figure 6 shows temperature dependence storage modulus (E') of both films and electrospun fibers (-70 to 200 °C). The storage moduli of the films (in the

range of 2×10^{10} MPa) are relatively higher than electrospun fibers (in the range of 5×10^9 MPa) due to the different in bulk density of the mats vs. a continuous film [23]. At temperature lower than the glass transition temperature, the storage modulus of samples increases with the amounts of added chitin whiskers

The decreasing in storage modulus of the electrospun fibers corresponding to the glass transition was observed at higher temperature as compared to that of the films (Figure 6.7). It is difficult to know whether this effect represents an artifact of mats vs. films, or does this mean that the softening temperature of the polymer in the fibers is significantly higher, as would be expected for a highly oriented polymer. No orientation was of course seen in WAXD spectra because individual fibers are randomly oriented; however certainly it is expected that within an individual fiber the polymer is highly oriented. Interestingly, the decrease in modulus corresponding to the melt transition of PVA occurs at significantly higher temperature for the film samples, i.e. there is a significant plateau in the latter. Given the rather small differences in crystallinity shown in WAXD, it is likely that this result is a direct consequence of the fact that a mat is used.

The temperature dependence of tan δ for both films and electrospun fibers is shown in Figure 6.8. The transition occurs at temperature around 50°C which assigned to glass transition temperature of the composite films and electrospun fibers. Figure 6.9 shows the glass transition temperature of the composite films and electrospun fibers. As the chitin whiskers content increase from 0 to 11.38 wt.%, the glass transition temperature of nanocomposite films and electrospun fibers are shifted from 42 to 51°C and 84 to 93°C, respectively. These results suggest that chitin whiskers restrict the PVA chains movement upon heating, possibly via hydrogen bond formation.

6.4.4 DSC results

Crystallization behavior of composites were investigated by DSC, from 30 to 220°C with a heating rate is 20°C per minute. The DSC thermograms of the first heating of both films and electrospun fibers are shown in Figure 6.10. PVA film exhibits the endotherm at 145.2°C corresponding to its crystalline melting temperature. The fact that a melting point of PVA observed in this experiment is lower than that generally reported in literature [27], is due to the presence of water in

the samples (10 wt.%) [23]. This is because the water can facilitates the movement of PVA chains in the crystalline part. Nevertheless, the melting temperature of the electrospun fibers is relatively higher as compared to that of films. This is because, in electrospinning process, polymer solutions experienced very high electrostatic force. This induces a better orientation of the polymer chains in the single fibers which leading to the increasing in the lamella thickness which correspond to the crystal size of the PVA. It is possible to suggest that a relatively denser lamellar may well be formed in crystalline phase of the electrospun fibers in a manner similar to that observed with the highly drawn PVA fibers [27]. Accordingly higher melting temperature of electrospun fibers is revealed.

It can also be seen that the melting temperature of the composites increase with increasing in the amounts of chitin whiskers and reach the maximum value at 161.2°C with the chitin whiskers content is 9.25 wt.%. This is because chitin whiskers have very strong hydrogen bonding interaction with PVA chains providing higher rigidity of the composites. As a result, the restriction in the chains mobility can readily inhibit the movement of the PVA chains in the crystalline part. However when the amounts of chitin whiskers is increase to 11.38 wt.%, the melting temperature of composites decease to 155.4°C. This can be explained by the agglomeration of the chitin whiskers, which reduce the degree of hydrogen bonding between the incorporate chitin whiskers and PVA matrix.

The degree crystallinity of composites, which were calculated using the enthalpy of 155 J/g for a theoretical 100% crystalline PVA [26], are shown in the Figure 6.11. It can be seen that the degree crystallinity of PVA films is relatively higher than that of electrospun fibers. This is because in the electrospinning process the solvent evaporation rate is relatively fast. Therefore it is somewhat difficult for the PVA chains to completely rearrange into a large region of well define crystalline phase. Accordingly higher percent crystallinity of films was observed.

When chitin whiskers were present, the percent crystallinity of composites is slightly decreased with the amounts of chitin whiskers added. This trend imitates the relative percent crystallinity observed by X-ray diffraction. This can again be explained by the interaction of chitin whiskers and PVA chains as discussed earlier.

Figure 6.12 shows the cooling and second heating thermograms in which the thermo-mechanical processing history was erased and the water in all samples was eliminated. It is expect that the crystallization behavior of PVA matrix should be the same. However, it is not the case. It can be seen that the crystallization temperature (T_c) of the films is slightly increase with the amounts of the chitin whiskers added. In contrast the crystallization temperature of electrospun fibers is somewhat deceased with the amounts of chitin whiskers and then slightly increased when the amounts of chitin whiskers is added up to 9.25 wt.%. This can be explained that chitin whiskers in the films might have the high opportunity to agglomerate as compared to that of in the electrospun fibers. This is because, during the film preparation, large amounts of water would allow chitin whiskers to move and agglomerate in films. The agglomerated chitin whiskers would be rigid and inhibit the movement of the PVA chains during cooling down. Hence only a rapid crystallization of melted PVA can take place within a small region, leading to a relatively higher crystallization temperature but lower percent crystallinity as observed in Table 6.3. On the other hand, the dispersed chitin whiskers were expected in the electrospun fibers. This is because electrostatic force applied during spinning process would help dispersion of the rigid chitin whiskers in the electrospun fibers, as discussed previously. Therefore, after melting in the first heating, the dispersed chitin whiskers in the polymer melt would interact with the PVA chains and hence inhibit its crystallization. Accordingly the lower crystallization temperature would be observed in the electrospun fibers. However, this is applied only for electrospun fibers with chitin whiskers content lower than 9.25 wt.% since a higher chitin whiskers incorporate can lead to its agglomeration.

It can be worthy noted that melting temperature of neat-PVA films in the second heating is increased from 145.2°C to 167.8°C. This result designate that the crystalline PVA phase from the solution casting is weaker than that of the molten films. This is because in the solution casting water molecules might incorporate in the crystalline region of PVA leading to a loosely bounded lamellar. As a result, melting temperature from the solution casting (observed by the first heating) is lower than that of melting films (observed by the second heating). The effect of water in the crystallization of PVA is not only illustrated by the different in melting

temperature, but also the percent crystallinity of the PVA. It can be seen that percent crystallinity of the PVA film (ca. 7.5%) observed in the second heating is tremendously reduced, as compared to the percent crystallinity of the PVA film (ca. 29.5%) observed in the first heating. This can be explained that water allows polymer chains to move, relax energy, and rearrange which lead to more crystallization. Accordingly the percent crystallinity of PVA in the molten film is less than the solution casting.

The glass transition temperatures which cannot be observed by the first heating scan appear in cooling and second heating scan. This can be explained that the reduced in the percent crystallinity after first heating scan lead to increasing in the amorphous region. Hence glass transition temperature is pronounced as shown in Table 6.3. The glass transition temperature (T_g) of the composites are not significantly changed. This is because thermo-mechanical processing history was erased and water was eliminated. Therefore the chitin whiskers will have less opportunity to interact with PVA chains in amorphous phase and enhance the rigidity of the PVA chains. Therefore the glass transition temperatures of the composites were not significantly changed.

6.5 CONCLUSION

In previous work [23] chitin whiskers, prepared by acid hydrolysis of chitin, were successfully used as the reinforcing agent due to the rigidity and strong interaction of the chitin. In order to extend the cause of the improved mechanical properties, this work has demonstrated the influence of the chitin whiskers on the crystallization behavior, dynamic mechanical and thermal properties using the WAXD, DMA, and DSC. It was suggested that chitin whiskers can readily form strong hydrogen bonding interaction with the PVA chains in the amorphous region. This inhibits the crystallization of PVA in the composites leading to the decrease in the relative percent crystallinity when the amounts of added chitin whiskers are increased. The strong interaction by chitin whiskers also increases storage modulus and glass transition temperature of the composites. Moreover the electrostatic force applied in the electrospinning process induces the stronger crystalline structure, as

compared to that prepare from the solution casting process. This increased in the melting temperature of the electrospun fibers despite it contain relatively less percent crystallinity. In addition the water molecules in the composites allow PVA chains and chitin whiskers to move, rearrange, and crystallization as a result of increasing in the percent crystallinity. The crystal size (lamella thickness) of the PVA from the solution state is smaller than the bulk state. (T_m from the 1st heating scan and 2nd heating scan).

6.6 ACKNOWLEDGEMENTS

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Table 6.1 The composition of the PVA solution, PVA/chitin whiskers mixtures and solid phase

Sample	Weight (g)			Concentration (wt.%)		Wt.% in the solid phase (wt.%)	
	PVA solution	Chitin whisker suspension	Distilled water	PVA	Chitin whiskers	PVA	Chitin Whisker
PVA	20.12	0.00	10.13	6.65	0.00	100.00	0.00
1g CW	20.01	1.01	9.01	6.66	0.17	97.49	2.51
2g CW	20.02	2.01	8.04	6.66	0.34	95.13	4.87
3g CW	19.97	3.00	7.01	6.66	0.51	92.88	7.12
4g CW	20.03	4.00	6.17	6.63	0.67	90.75	9.25
5g CW	20.01	5.04	5.01	6.66	0.85	88.62	11.38

Table 6.2 The percent crystallinity and glass transition temperature of composites from DSC

	Percent crystallinity of PVA (%)			Glass transition Temperature (°C)	
	1st Heating Scan	Cooling Scan	2nd Heating Scan	Cooling Scan	2nd Heating Scan
PVA F	29.5	7.5	6.6	68.2	70.6
1g F	29.2	6.9	7.2	66.3	70.1
2g F	29.3	9.0	6.3	66.6	69.4
3g F	23.8	9.6	6.8	66.7	68.8
4g F	27.3	9.0	7.7	65.5	67.2
5g F	23.6	5.1	7.4	66.7	68.7
PVA ES	20.4	8.9	7.5	61.5	66.5
1g ES	23.7	6.0	6.1	66.6	70.9
2g ES	25.5	6.1	5.4	66.0	70.3
3g ES	20.6	8.4	5.5	65.7	71.2
4g ES	19.7	8.5	7.0	61.9	67.5
5g ES	19.9	6.2	9.1	56.3	60.6
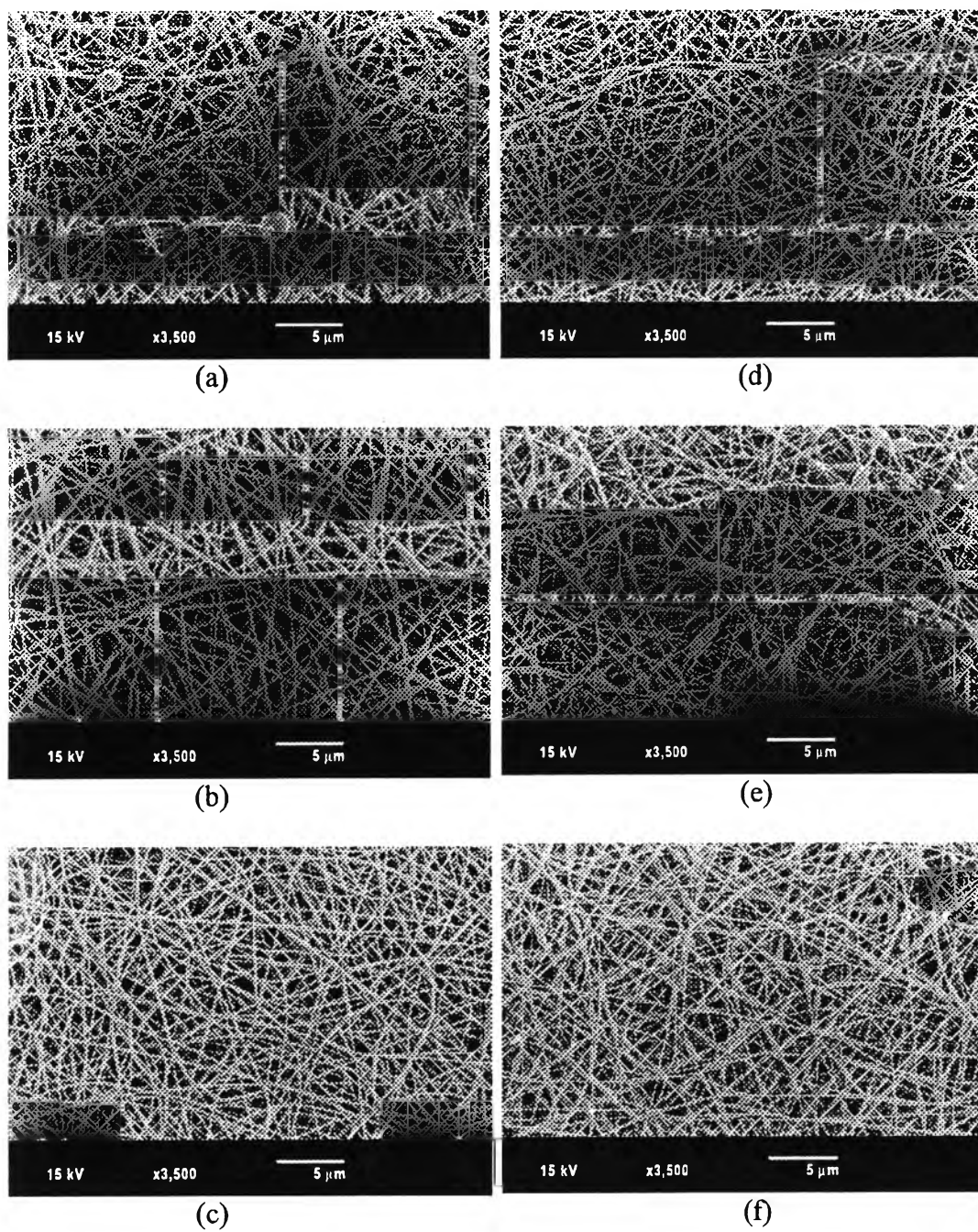
Figure 6.1 SEM micrograph of the nanocomposite nanofibers of (a) neat PVA, (b) 2.51 wt%, (c) 4.87 wt%, (d) 7.12 wt%, (e) 9.25 wt%, and (f) 11.38 wt% of chitin whisker.

a) PVA Film   b) 2.51 wt% of CW Film   c) 4.87 wt% of CW Film

d) 7.12 wt% of CW Film   e) 9.25 wt% of CW Film   f) 11.38 wt% of CW Film

g) PVA ES   h) 2.51 wt% of CW ES   i) 4.87 wt% of CW ES

j) 7.12 wt% of CW ES   k) 9.25 wt% of CW ES   l) 11.38 wt% of CW ES
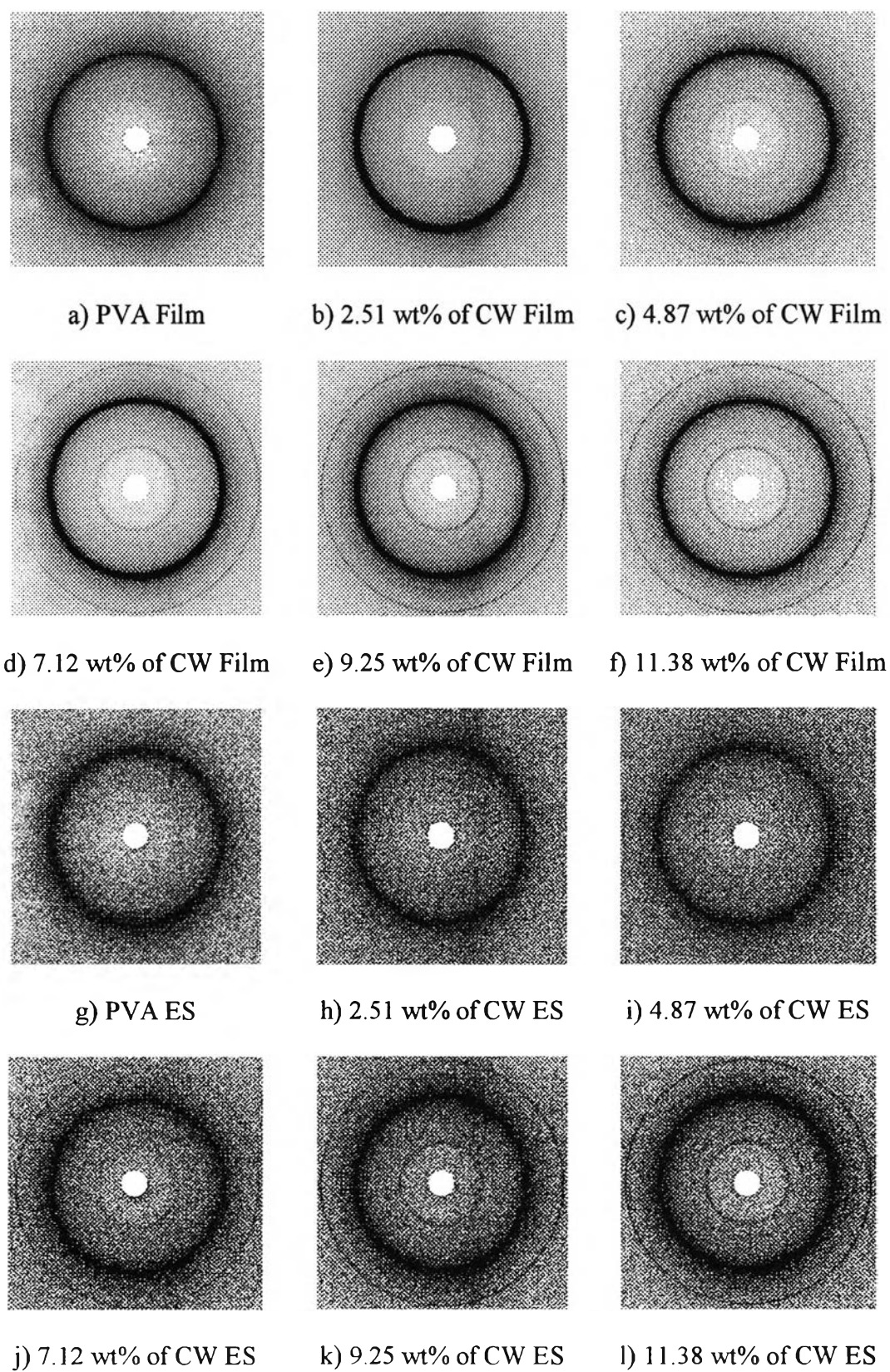
Figure 6.2 Picture Image (2D-WAXD) of all samples from the X-Ray Diffraction.
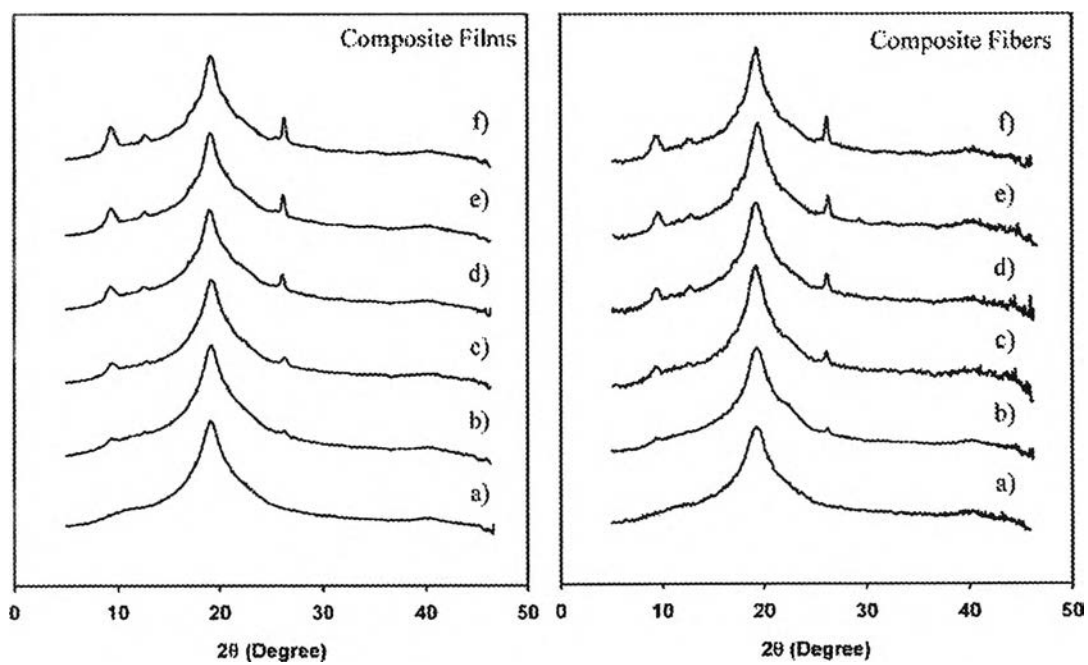
Figure 6.3 WAXD patterns of the nanocomposite films and nanofibers of (a) neat PVA, (b) 2.51 wt%, (c) 4.87 wt%, (d) 7.12 wt%, (e) 9.25 wt%, and (f) 11.38 wt% of chitin.
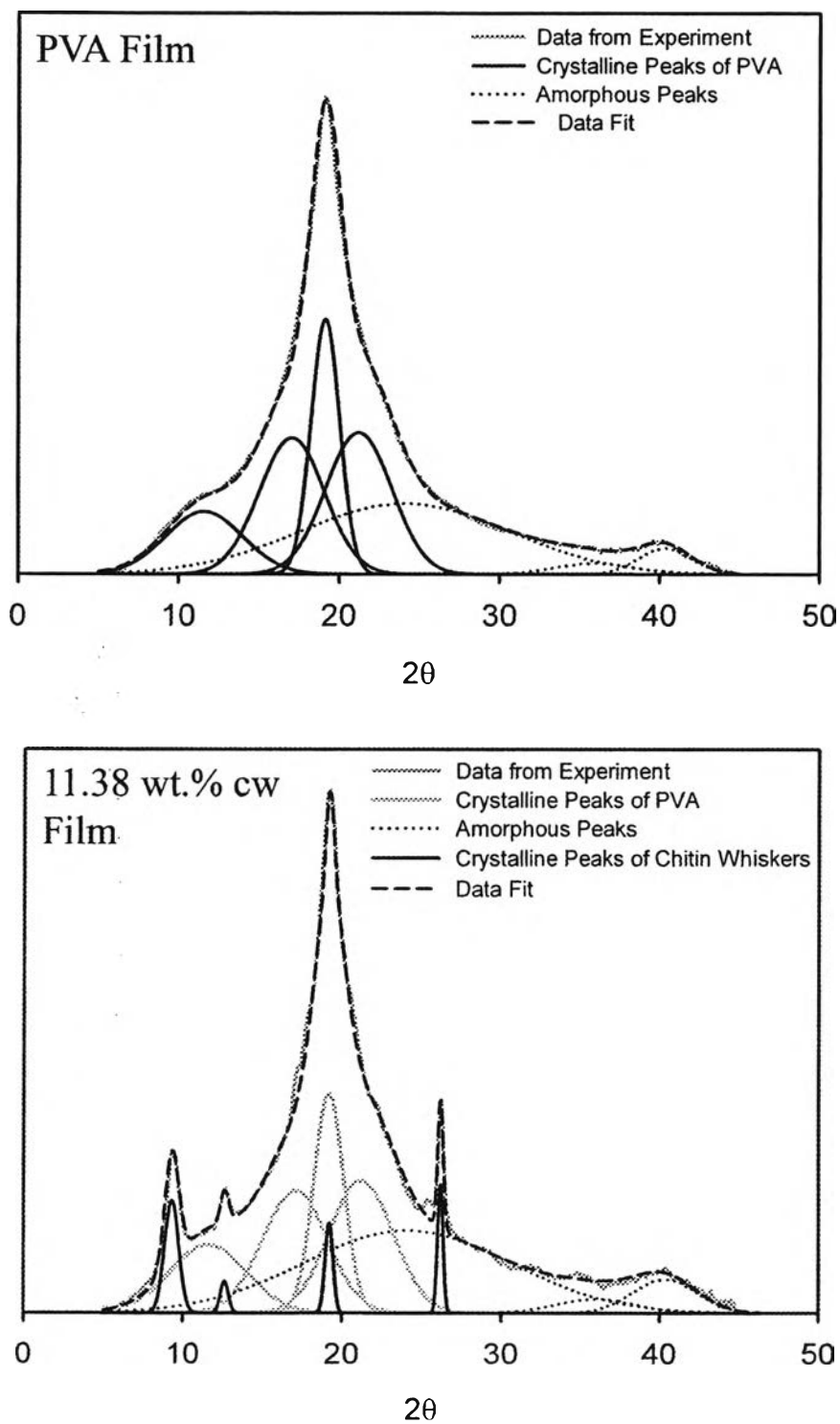
Figure 6.4 The deconvolution of XRD pattern of neat-PVA film and 11.38 wt.% chitin whiskers film.
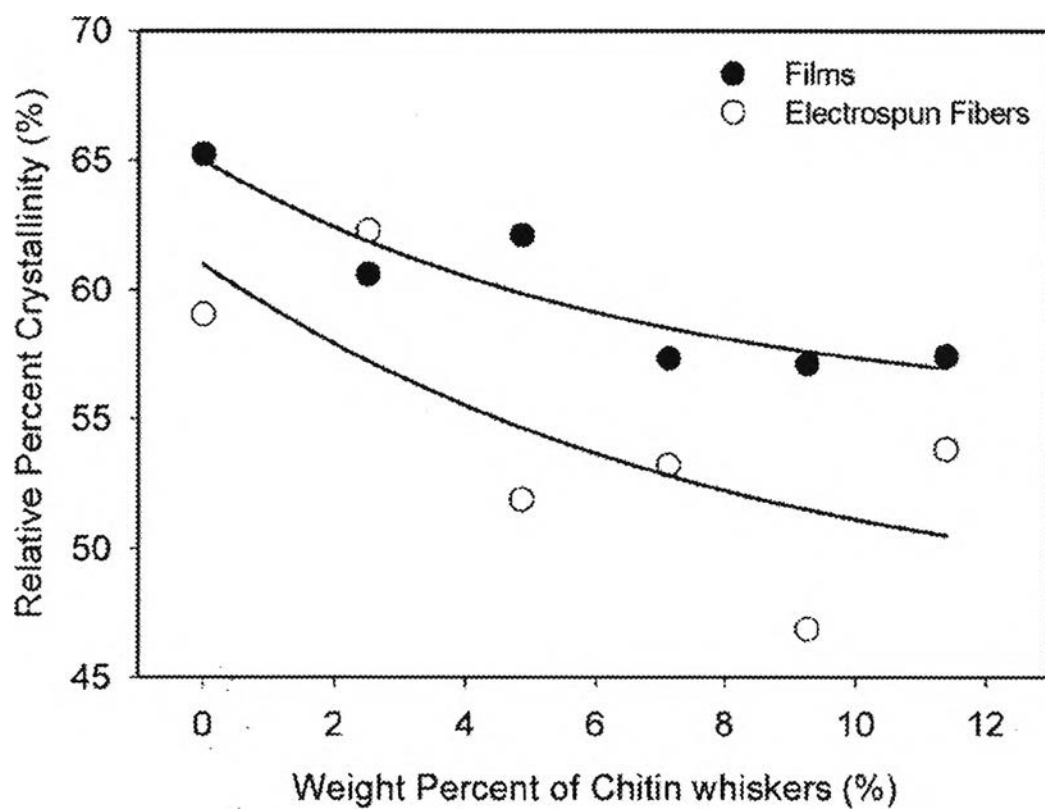
Figure 6.5 The relative percent crystallinity of the PVA in films and fibers from the WAXD results.
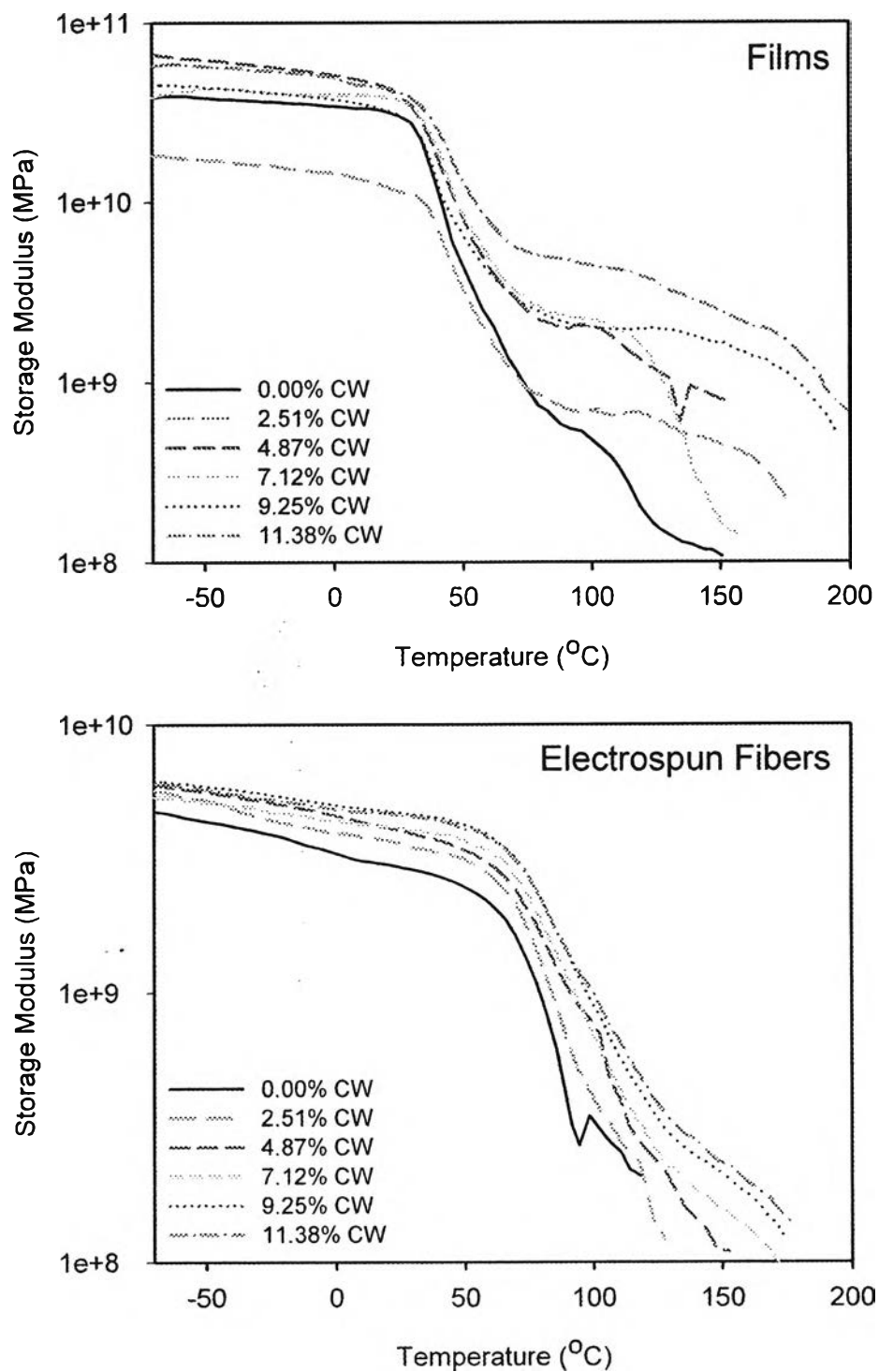
Figure 6.6 The relationship between storage modulus and temperature of films and fibers.
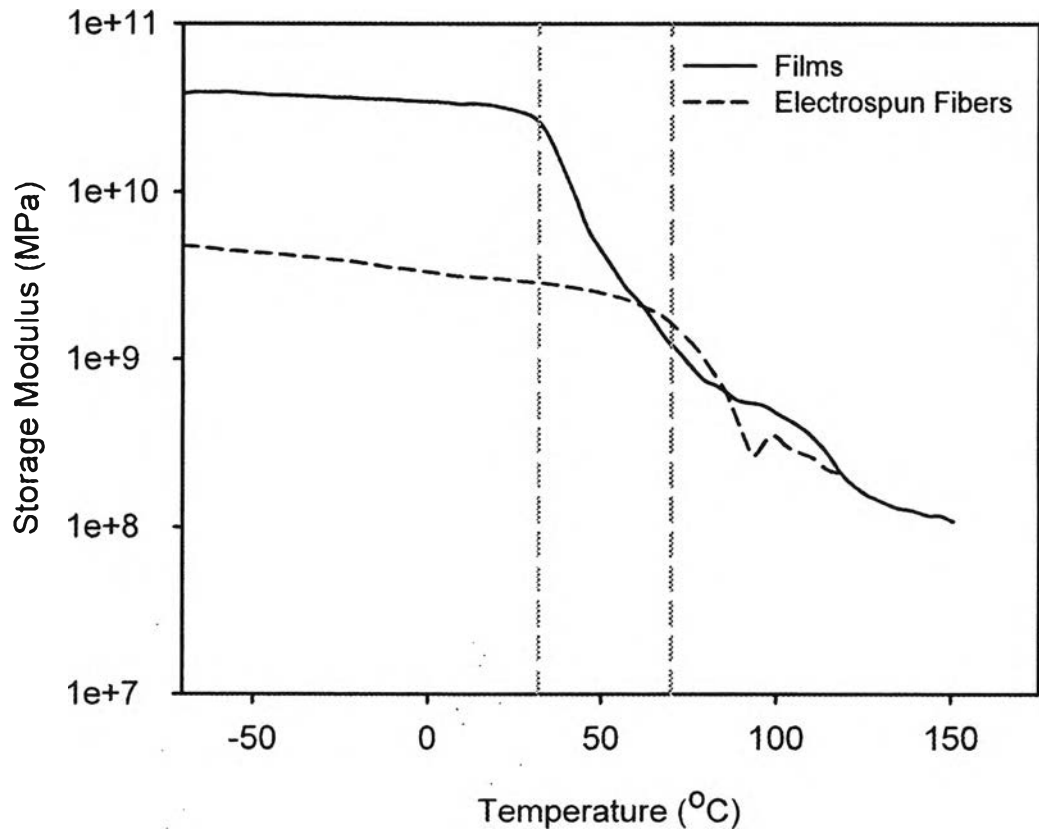
Figure 6.7 Compare storage modulus (E') between neat-PVA film and electrospun fibers.
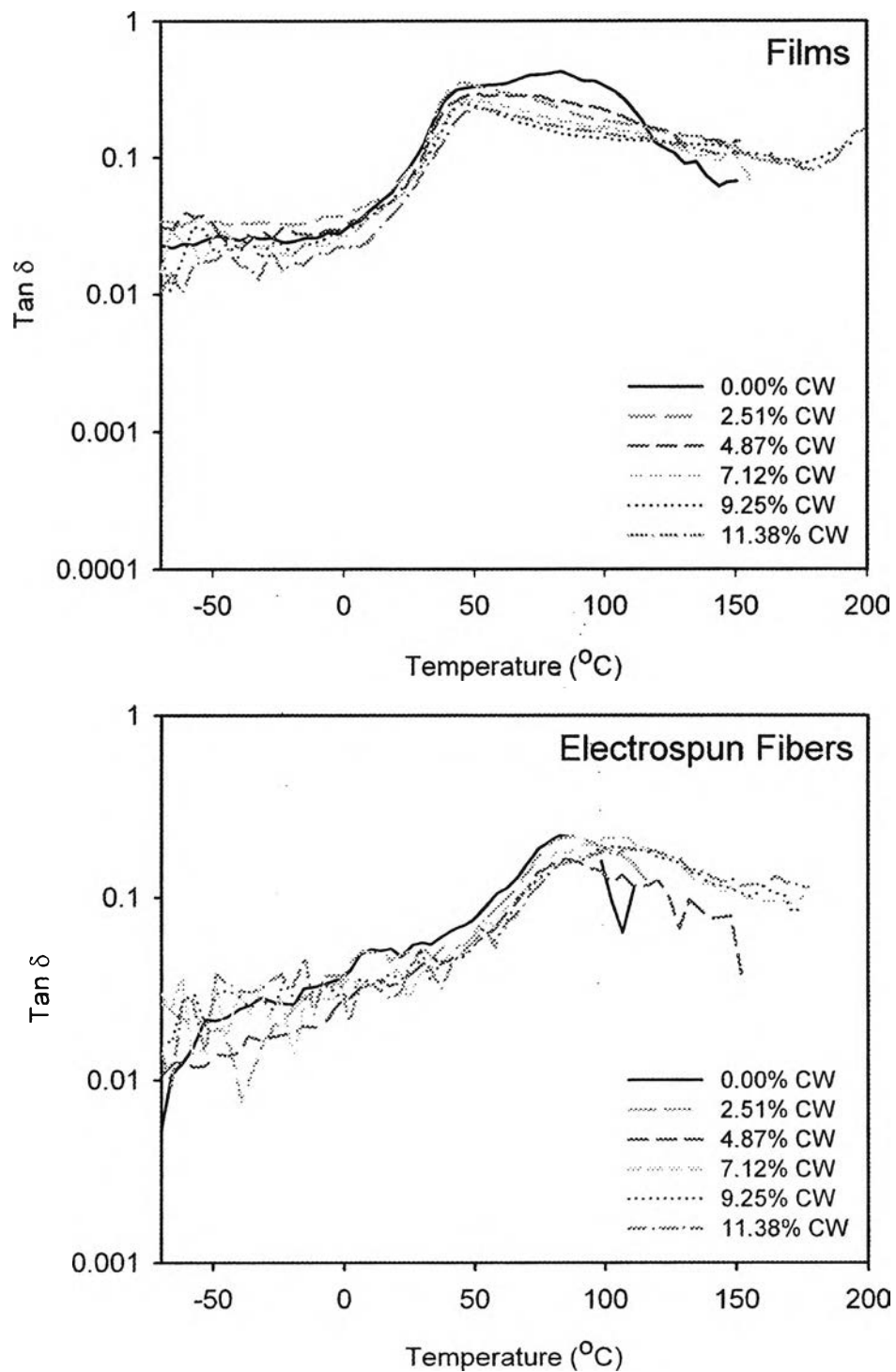
Figure 6.8 Tan δ versus temperature.
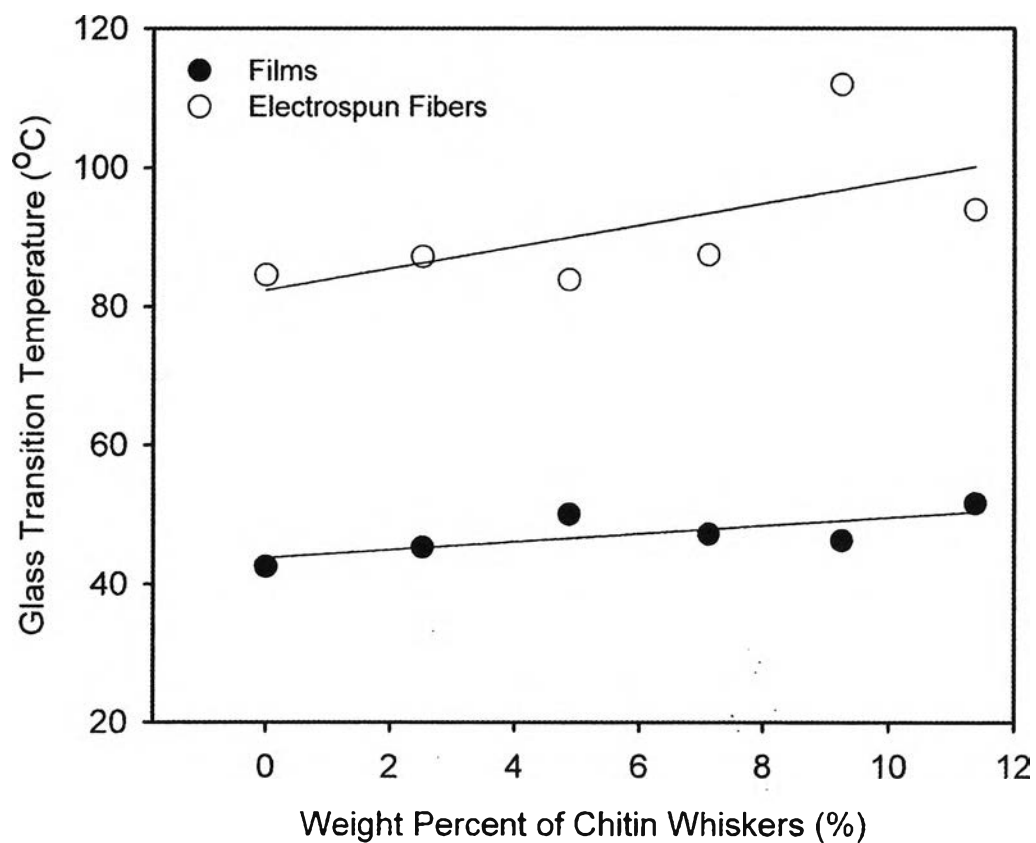
Figure 6.9 The relationship between glass transition temperature and amount of added chitin whiskers as determined by the maximum in tan δ for both films and electrospun fibers. Lines drawn to guide the eye.
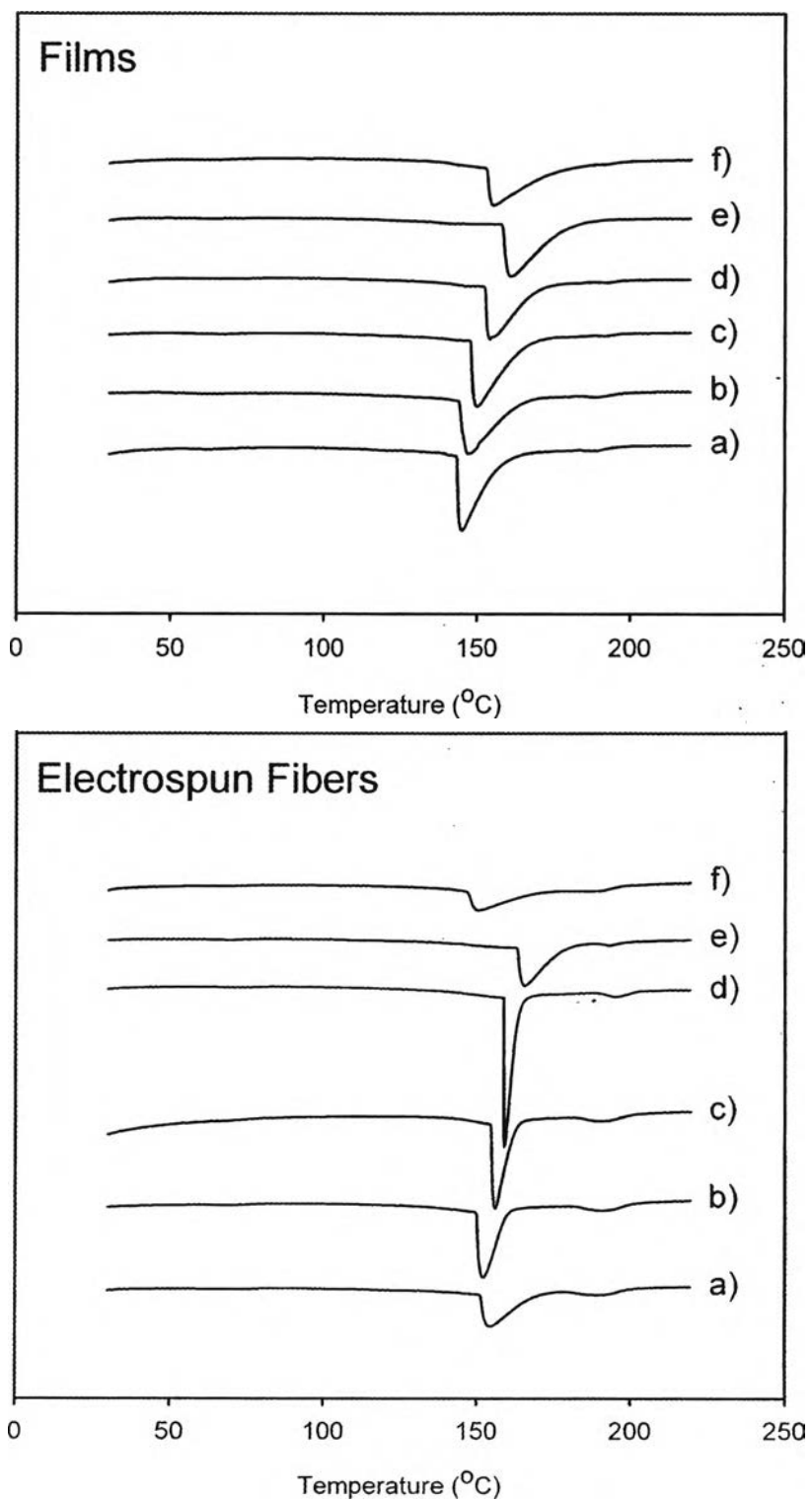
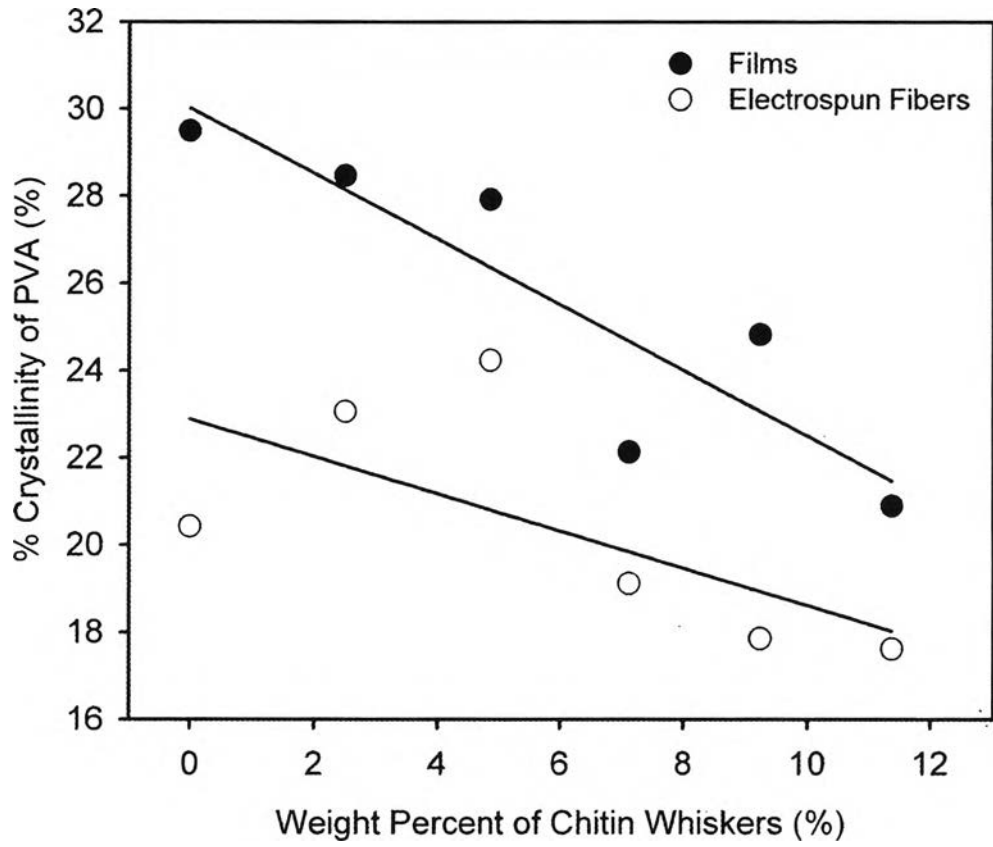**Figure 6.10** The first heating DSC of films and electrospun fibers.

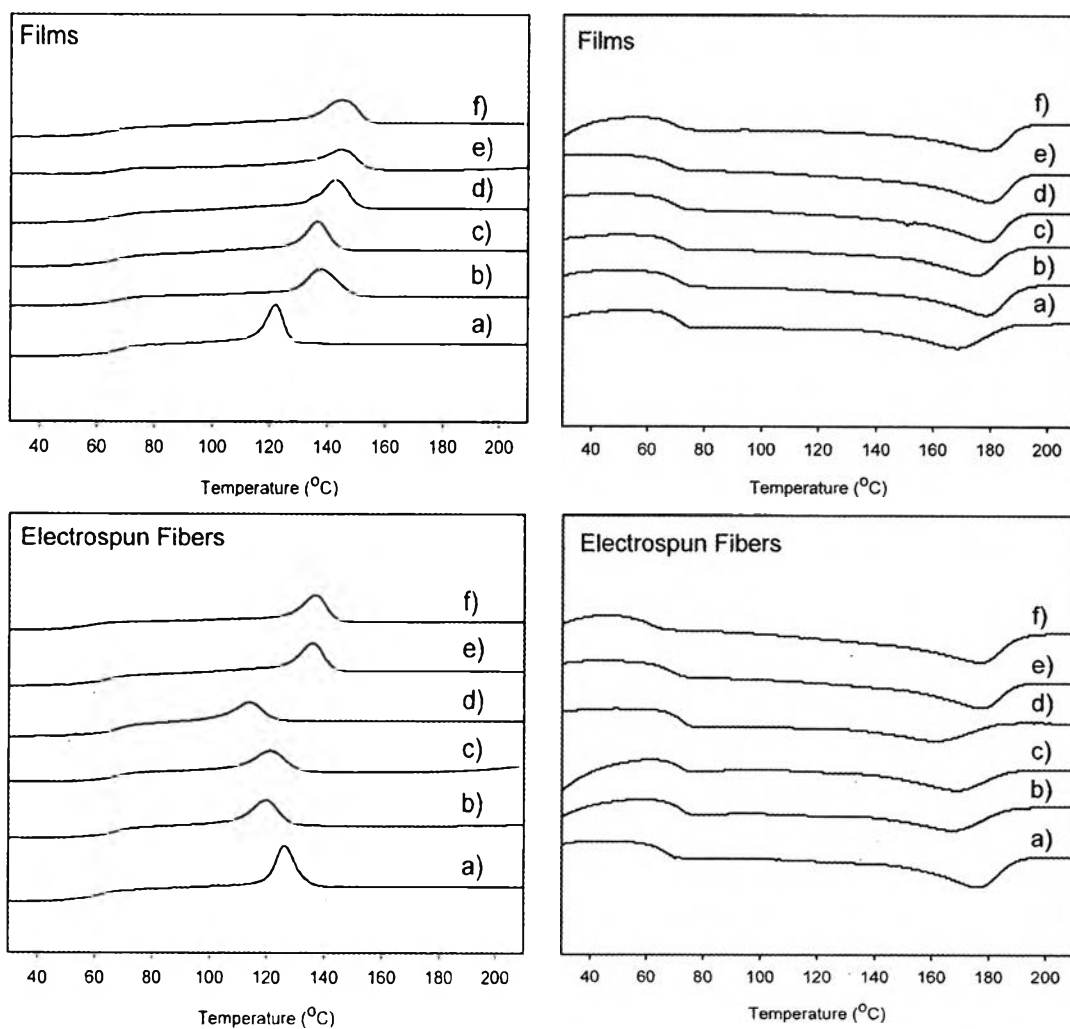**Figure 6.11** Percent Crystallinity of PVA from the first heating scan of DSC.

Figure 6.12 The cooling and second heating scan of both films and electrospun fibers.