

CHAPTER VII
MECHANICAL PROPERTIES OF NYLON 4,6 NANOFIBERS -
REINFORCED POLY(VINYL ALCOHOL)

7.1 ABSTRACT

Nylon 4,6 nanofibers was prepared by using electrospinning process with the average diameter about 116 nm. The nylon 4,6 as-spun fibers/PVA composite films were prepared by the solution casting. Successful incorporation of the nylon 4,6 nanofibers was verify by scanning electron microscope. With the incorporation of the nylon 4,6 nanofibers, the tensile strength and Young's modulus were increased as compare to that of PVA films. The experimental data was compared to the prediction from the Halpin-Tsai model.

7.2 INTRODUCTION

In the recent years nylon 4,6 (poly(tetramethylene adipamide)) was studied as well as nylon 6,6 (poly(hexamethylene adipamide)). However, nylon 4,6 has not been well developed in contrast to the success of nylon 6,6 as a commercial product due to the difficulty of obtaining a high molecular weight. This difficulty has been overcome markedly by a recent progress of polymerization technology [1]. Nylon 4,6 is available for commercial which is believed to be the most successfully in mechanical performance and dimension stability. The main reason is the high number of amide units in the main chain of molecule, which leading to high percent crystallinity and enhances the formation of hydrogen bonding [2]. A tensile strength of nylon 4,6 was reported at about 80 MPa by J.Kroschwitz in 1985 [3]. And typically the modulus was depended on the degree of orientation and the morphology of nylon.

Electrospinning process is widely used processes which can fabricate very fine fibers. The electrospun fibers have been used in many applications such as filters, membrane, electronic, and biomaterials applications [4,5]. The basic concept

of electrospinning process is, applied high voltage power into the polymer solution or polymer melt. When electrical force overcomes the surface tension of the polymer solution or polymer melt, the electrical charged jet is ejected through the air while the solvent evaporation or solidification occurs. The as-spun fibers are collected by using the grounded metal plate. It is well known that the morphology of the as-spun fibers is depending on the solution parameters (i.e. viscosity, conductivity, surface tension, and concentration) and processing parameters (i.e. voltage, collector distance, and ambient parameters). The interesting features of as-spun fibers are their high surface which can achieve the ultimate performance of materials. Thus, as-spun fibers with diameters in the range of 100 nm or less (nanofibers) are very interesting in both technological and scientific points of view.

In this study, nylon 4,6 were dissolved in 98% of formic acid with the concentration was 17.5 %wt/v, respectively. The solutions were electrospun at the voltage of 17.5 kV and as-spun fibers were collected on the grounded aluminum plate which was placed horizontally at the distance of 12 cm underneath the syringe. The syringe was placed in the angle of 20° from horizontal line. The weight percent of as-spun fibers in composites was varied by the amount of PVA solution which cast on the as-spun fibers. Therefore the weight percent of these as-spun fibers embedded in the composites might not precisely control.

7.3 EXPERIMENTAL

7.3.1 Preparation of Nylon 4,6 electrospun fiber mats

Nylon 4,6 (density=1.18, Sigma Aldrich, USA) nanofibers were prepared by electrospinning process. Nylon 4,6 was first dissolved in the 98 wt% formic acid (Analytical grade 98/100%, Fisher Scientific, UK) under slight stirring for 7 hrs to obtained a nylon 4,6 solution. The concentration of nylon 4,6 in the solution was fixed at 17.5 wt% by volume. Nylon 4,6 solution was placed in a 10-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 20° from a horizontal baseline to ascertain a constant presence of a liquid droplet at the tip of the nozzle. An aluminum drum on a plastic backing was used as the

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 collector drum (connected to the grounding electrode). The applied potential was fixed at 17.5 kV over a fixed collection distance between the tip of the nozzle and the collector drum of 12 cm. The thickness of nylon 4,6 as-spun fibers was controlled by fixed the amount of the nylon 4,6 solution 4,6 at 30 ml. The as-spun fiber mats were kept in room condition for one day prior to further characterization.

7.3.2 Preparation of nylon 4,6/PVA composites

Poly(vinyl alcohol) (PVA) powder ($M_w = 72,000$ Da and degree of hydrolysis (DH) $\geq 98\%$; Merck, USA) was dissolved in warm distilled water (85°C) under stirring for 3 hrs to obtained a PVA solution at a fixed concentration of 7.5 wt.%. PVA solution was cooled at room temperature before further use.

The composites films were prepared by PVA solution casting on the Nylon 4,6 as-spun fiber mats. The weight fraction of nylon 4,6 as-spun fiber mats in the composites was controlled by the amount of PVA solution which was varied from 3, 4, 5, 6, and 7 ml. The composite films were dried at room temperature 3 days and keep it at room temperature a day before further characterized.

7.3.3 Characterization

Morphological appearance of the as-spun fiber mats of nylon 4,6 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. Sizes of the as-spun fibers were measured by using SemAfore software.

The thermal stability and amount of nylon 4,6 in the composites were measured using thermogravimetric analyzer (TGA). Samples of about 3-10 mg were placed in the platinum pan. The temperature scanning range was 40- 650°C using heating rate of 10°C/min in the nitrogen atmospheric.

The Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a $\text{CuK}\alpha$ 1 radiation was used to study the crystallization behavior of as-spun fibers, PVA films, and all composites. The X-rays of 1.54 Å wave length was generated by a $\text{CuK } \alpha$ source.

The angle of diffraction was varied from 5 to 45° with the rate of scan is 5°/min and the step of scan is 0.01°.

The tensile properties of all composite were measure using Lloyd LRX universal tester, according to the ASTM D882 standard test method. The dimension of the samples was 5x80 mm², with the thickness ranging between 45 and 150 μm. The gauge length and the crosshead speed were 30 mm and 10 mm·min⁻¹, respectively. The reported values were averages from ten measurements.

The surface area and porosity of nanofibers were investigated using N₂ adsorption/desorption isotherms which were obtained by Quatachrome Autosorb I using a BET model at -196°C. Samples were first degassed in a vacuum furnace at 100°C, 12 hours. Surface areas were calculated using the BET equation. Pore volumes were determined by the t-plot method of De Boer and pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

7.4 RESULT AND DISCUSSION

7.4.1 Nanofibers Characterizations

The selected SEM image of as-spun fibers from nylon 4,6 are shown in Figure 7.1. It was shown that the as-spun fibers were smooth and has round shape cross section. The Figure 7.2 show the statistical analysis result of the fibers diameters of nylon 4,6 from more than 3000 fibers using 10 SEM micrographs. It was revealed that the average size of the nylon 4,6 and nylon 6,6 as-spun fibers is about 116 ± 29.7 nm. In 1999, Vancso and his co-workers [6] made nylon-4,6 nanofibers with diameters of 30–150 nm using 10% concentration by weight. And the influence of concentration of the nylon 4,6 solution on the diameter of electrospun nanofibers was fully investigate by Chaobo Huang and co-workers in 2006 [7]. It was found that 20% by weight of nylon-4,6 in formic acid produced a ribbon-like electrospun fiber with a width of about 850 nm. A semi-dilute concentration of 2% by weight produced the thinnest nanofibers with diameters of 1.6 nm or less. The surface area and porosity of the as-spun fibers from nylon 4,6

nanofibers were investigated and shown in Table 7.1. It was shown that nylon 4,6 nanofibers has very high surface area.

7.4.2 Composites Characterizations

The fiber formation of nylon 4,6 as-spun fiber mat in the composite films was verified using SEM image as shown in Figure 7.3. Thermogravimetric analysis for the as-spun fiber mats and the composites films was used for verifying the amount of nylon 4,6 as-spun fibers in the composites. Figure 7.4 shows the derivative curves of the TGA thermograms for the as-spun fiber mats and composite films. According to Figure 7.4, neat PVA film exhibited three steps in the loss of their mass at about 90, 310, and 480°C, respectively while the neat as-spun nylon 4,6 exhibited only one step in the loss of their mass at about 430°C. The last two steps degradation of PVA corresponds to the dehydration reaction and chain scission, respectively [8]. And the low-temperature mass loss (ca. 90°C) should correspond to the loss of the moisture. Additionally, all of the composite films exhibited four steps in the loss of their mass at about 90, 285, 380, and 480°C which confirm the presence of the nylon 4,6 within the composites. The mass loss associate with the thermal degradation of the nylon 4,6 increased with decreasing amount of the PVA solution that was cast on the nylon 4,6 fiber mats. Specifically, the moisture content for neat as-spun nylon 4,6 fiber mats and PVA film was about 1.46 and 12.70%, respectively, while that for all composite films was in the range of 9.31–10.84% which increased with the amount of the PVA. This can be concluded that the water is incorporate in the PVA phase. Table 7.2 shows weight percentage of PVA, nylon, moisture, and ash for both nylon 4,6 and the bulk density of all specimens which was used to convert the mechanical properties to the specific mechanical properties was calculated by measuring the weight and volume of specimens.

The bulk density of both nylon 4,6 as-spun fibers and composite films was calculated from both the mass and the volume of the samples which was shown in the Table 7.3. The bulk density of the nylon 4,6 as-spun fiber mats was about $0.208 \pm 0.014 \text{ g}\cdot\text{cm}^{-3}$, while that of neat PVA film was about $1.097 \pm 0.046 \text{ g}\cdot\text{cm}^{-3}$. Furthermore, the bulk density of all composite films ranged between 1.165 and 1.242 $\text{g}\cdot\text{cm}^{-3}$. Weight fractions of nylon 4,6 as-spun fiber mats in the composites were calculated from the actual weight of both nylon 4,6 as-spun fibers and PVA which

also were shown in Table 7.3. It was founded that weight fractions of the nylon 4,6 as-spun fiber mats were varied from 0.0613 to 0.1343 which can be converted to the volume fraction by the relationship:

$$V_{\text{nylon}} = \frac{W_{\text{nylon}} \times \text{Density}_{\text{PVA}}}{\text{Density}_{\text{PVA}} - W_{\text{nylon}}(\text{Density}_{\text{PVA}} + \text{Density}_{\text{nylon}})}$$

Where V_{nylon} and W_{nylon} are the volume and weight fraction of nylon 4,6 as-spun fiber mats in the composite, respectively.

Figure 7.5 shows the mechanical properties of nylon 4,6 as-spun fiber mats, PVA film, and all composite films. As shown in Table 7.3, the weight content of nylon 4,6 as-spun fiber mats with respect to the total weight were ranged between 0.00 to 13.43 wt.%. The thickness of the composite films increased from 57 μm (nylon 4,6 as-spun fiber mats) to 159 μm with increasing in the amount of PVA solution. The tensile strength of films increased from that of the neat PVA film (i.e., 28.29 \pm 4.06 MPa) with incorporation of the nylon 4,6 fiber mats to reach a maximum value (i.e., 32.05 \pm 5.09 MPa) at the percent weight of nylon 4,6 fiber mats of about 10.40 wt.% and decreased with further increase in the nylon 4,6 fiber mats content. Interestingly, incorporation of the nylon 4,6 as-spun fiber increased in the Young's modulus of films from 54.31 MPa to 145.75 MPa at the percent fiber content about 13.43 wt.% and further increased with the increasing in the amount of nylon 4,6 content. In contrast, the decreasing in the elongation at break was obtained with increasing in the amount of nylon 4,6 fibers as shown in Figure 7.5 c). For the prediction of the tensile modulus of the composite, the Halpin-Tsai model was applied:

$$P_c = P_m \left(\frac{1 + \zeta \eta f}{1 - \eta f} \right) \quad ; \text{ where } \eta = \frac{\left(\frac{P_f}{P_m} \right) - 1}{\left(\frac{P_f}{P_m} \right) + \zeta}$$

Assume: $\zeta = 2 + 40f^{10}$ where ζ was a geometry parameter

Where P_c , P_m , and P_f were the properties of composite, matrix, and fiber, respectively. f was a volume fraction of the fiber in the composite.

The Halpin-Tsai model was compared with the experimental data which was shown in the Figure 7.6. This result shows that the Halpin-Tsai can be applied and predicted the properties of the composite well.

Figure 7.7 shows the crystallization behavior of neat PVA, nylon 4,6 as-spun fiber mats, and all composites. After deconvolution, neat PVA show four characteristic peaks at the position of $2\theta = 11.6^\circ$, 17.05° , 19.65° , and 21.20° correspond to 100, 001, 101, and 101 reflections, respectively which is also observed by J.D. Cho *et al.* in 1999 [9]. Usually, crystalline phases of nylons are composed of the stacking of hydrogen bonded sheets with chains in a fully extended conformation [10]. Nylon 4,6 as-spun fibers show two characteristic peaks at the position of $2\theta = 20.50$ and 22.70° which are typical reflections of 200 and 202/002 for the nylon 46 monoclinic form, correspond to the d-spacing of 4.33 Å and 3.91 Å, respectively. Generally, the d-spacing of nylon 4,6 are 0.37 and 0.44 nm which are typical corresponding to reflections of 200 and 202/002 for the nylon 4,6 monoclinic form [11-13]. This result is consistent with observation by Michel M. *et al* in 1999 [2], he found that the wide angle X-ray scattering (WAXS) pattern of electrospun nylon-4,6 nanofibers exhibited two peaks at $2\theta = 20.5^\circ$ and $2\theta = 24.0^\circ$ which correspond to d-spacing of 4.33 Å and 3.70 Å (based on α_1 -radiation) or 4.34 Å and 3.71 Å. (based on α_2 -radiation), respectively. And also in 1977, Gaymans *et al* [14] found that d-spacing of nylon 4,6 electrospun fibers are 3.74 Å (d_{010}) and 4.30 Å (d_{100}). However, C. Ramesh (1998) [15] founded that nylon 4,6 appears only one characteristic peak at the position of $2\theta = 21.23^\circ$ but on cooling process from T_c , the characteristic peaks of nylon 4,6 will split into two peaks at temperature about 150°C . This might be explained that the electrostatic force during the electrospinning process can change the crystal structure of the nylon 4,6. In the case of composites the XRD patterns are look similar but the characteristic peaks of the nylon 4,6 will shift from the position of $2\theta = 20.50^\circ$ and 22.70° to $2\theta = 21.00^\circ$ and 23.20° which corresponded to the d-spacing of 4.33 Å and 3.91 Å and 4.23 Å and 3.83 Å, respectively. This can be explained by the incorporation of water molecules during the solution casting

because these two spacing correspond to the intersheet distance and hydrogen bonded interchain distance within the sheet, respectively [16].

7.5 CONCLUSION

The nylon 4,6 nanofiber mats were fabricated by using the electrospinning process and the average diameter of the as-spun fibers was 116 nm. The as-spun fibers were prepared the composites films by solution casting of Poly(vinyl alcohol) (PVA) which the concentration was fixed at 7.5 %wt/v. The percent loaded of the nylon 4,6 was controlled by the amount of the PVA solution casting in which varied from 3 to 7 ml. With the incorporation of the nylon 4,6 fiber mats, the tensile strength increased about 10% as compare to that of PVA films. Young's modulus of the composite films was also increased about 168% at the fiber content of 13.43 wt% and trend to further increasing with the amount of the nylon 4,6 fibers loaded. The tensile modulus of nylon 4,6 fiber/PVA composite films was fitted and predicted by using the relationship from the Halpin-Tsai model. The result shows that this composite can be predicted by the Halpin-Tsai.

7.6 ACKNOWLEDGEMENTS

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7.7 REFERENCES

- [1] Studies on the Structure and Properties of Nylon 4,6 Fiber. 1. Dimensional Stability Kazushige Kudo, Masatsugu Mochizuki, Shunichi Kiriya, Masaharu Watanabe, And Matsuo Hiram1
- [2] Transparent Nanocomposites with Ultrathin, Electrospun Nylon-4,6 Fiber Reinforcement**By Michel M. Bergshoef and G. Julius Vancso* *Adv. Mater.* 1999, 11, No. 16 1362-1365
- [3] Encyclopedia of Polymer Science and Engineering, Vol. 11 (Ed: J.Kroschwitz), Wiley, New York 1985, p. 371
- [4] A review on polymer nanofibers by electrospinning and their applications in nanocomposites Zheng-Ming Huang*, Y.-Z. Zhang, M. Kotakic, S. Ramakrishna, *Composites Science and Technology* 63 (2003) 2223–2253
- [5] Electrostatic deposition of nanofibers for sensor application Ana Neilde Rodrigues da Silva, Rogerio Furlan, Idalia Ramos, Jorge Juan Santiago-Avilés *Mat. Res. vol.8 no.1 São Carlos Jan./Mar. 2005*
- [6] Bergshoef M M and Vancso G J 1999 *Adv. Mater.* 11 1362
- [7] Electrospun polymer nanofibres with small diameters Chaobo Huang, Shuiliang Chen, Chuilin Lai, Darrell H Reneker, Haiyan Qiu, Ying Ye and Haoqing Hou *Nanotechnology* 17 (2006) 1558–1563
- [8] Jeffrey W. Gilman, David L. VanderHart, and Takashi Kashiwagi' *Materials and Test for Hazard Prevention, American Chemical Society, ACS Symposium Series 599, August 21-26, 1994*
- [9] X-ray Analysis and Molecular Modeling of Poly(vinyl alcohol)s with Different Stereoregularities J. D. Cho, W. S. Lyoo, S. N. Chvalun, and J. Blackwell *Macromolecules* 1999, 32, 6236-6241
- [10] Structure and characterization of nylon 4,6, Takeshi Yamanobe, Yoshihito Kurihara, Hiroki Uehara, Tadashi Komoto *Journal of Molecular Structure*, 2007, 80–87, 829.
- [11] E.D. Atkins, M. Hill, S.K. Hong, A. Keller, S. Organ, *Macromolecules* 25 (1992) 917.

- [12] Q. Zhan, Z. Zhan, H. Zhang, Z. Mo, *J. Polym. Sci. Part B: Polym. Phys.* 40 (2002) 1784.
- [13] K. Kubo, T. Yamanobe, T. Komoto, I. Ando, T. Shiibashi, *J. Polym. Sci. B27* (1989) 929.
- [14] R. J. Gaymans, T. E. C. van Utteren, J. W. A. van den Berg, J. Schuyer, *J. Polym. Sci., Polym. Chem. Ed.* 1977, 15, 537.
- [15] New Crystalline Transitions in Nylons 4,6, 6,10, and 6,12 Using High Temperature X-ray Diffraction Studies C. Ramesh *Macromolecules* 1999, 32, 3721-3726
- [16] Structure and characterization of nylon 46 Takeshi Yamanobe, Yoshihito Kurihara, Hiroki Uehara, Tadashi Komoto *Journal of Molecular Structure* 829 (2007) 80–87

Table 7.1 Surface area and porosity of nylon 4, 6 nanofibers

Samples	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (Å)
Nylon 4,6 nanofibers	34.22	0.1222	142.8

Table 7.2 The composition of nylon 4,6 as-spun fibers from TGA

Sample	% Nylon (wt.%)	% PVA (wt.%)	Moisture Content (wt.%)	% ash (wt.%)
Pure PVA (7.5 %wt/v)	0.00	100.00	12.70	10.23
Nylon 4,6 fibers	100.00	0.00	1.46	2.99
N46 + 3 ml PVA	19.04	62.14	9.31	9.51
N46 + 4 ml PVA	14.66	62.84	10.87	11.63
N46 + 5 ml PVA	11.18	68.17	10.60	10.04
N46 + 6 ml PVA	9.07	66.72	10.77	13.43
N46 + 7 ml PVA	7.15	67.25	10.84	14.76

Table 7.3 The Bulk density, weight fraction and volume fraction of nylon 4,6 as-spun fibers

Sample	Density (g / cm ³)	Weight Fraction	Volume Fraction
Pure PVA (7.5 %wt/v)	1.10±0.05	0.0000	0.0000
Nylon 4,6 fibers	0.21±0.01	1.0000	1.0000
N46 + 3 ml PVA	1.17±0.04	0.1343	0.4497
N46 + 4 ml PVA	1.24±0.03	0.1040	0.3794
N46 + 5 ml PVA	1.20±0.04	0.0880	0.3372
N46 + 6 ml PVA	1.22±0.02	0.0713	0.2881
N46 + 7 ml PVA	1.21±0.07	0.0613	0.2559

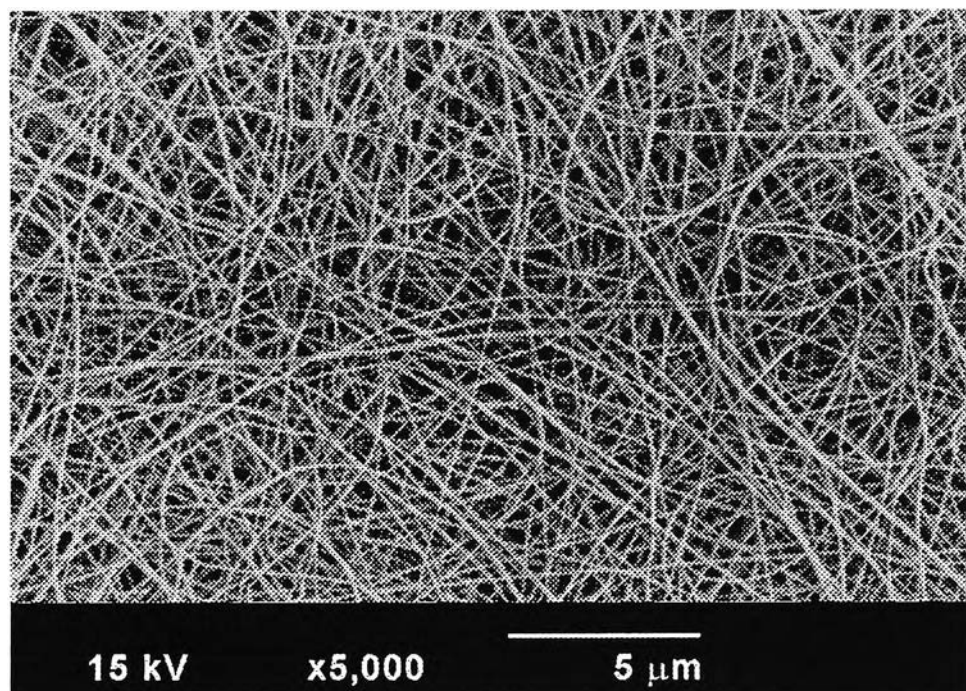


Figure 7.1 SEM micrograph of the Nylon 4,6 nanofiber mats.

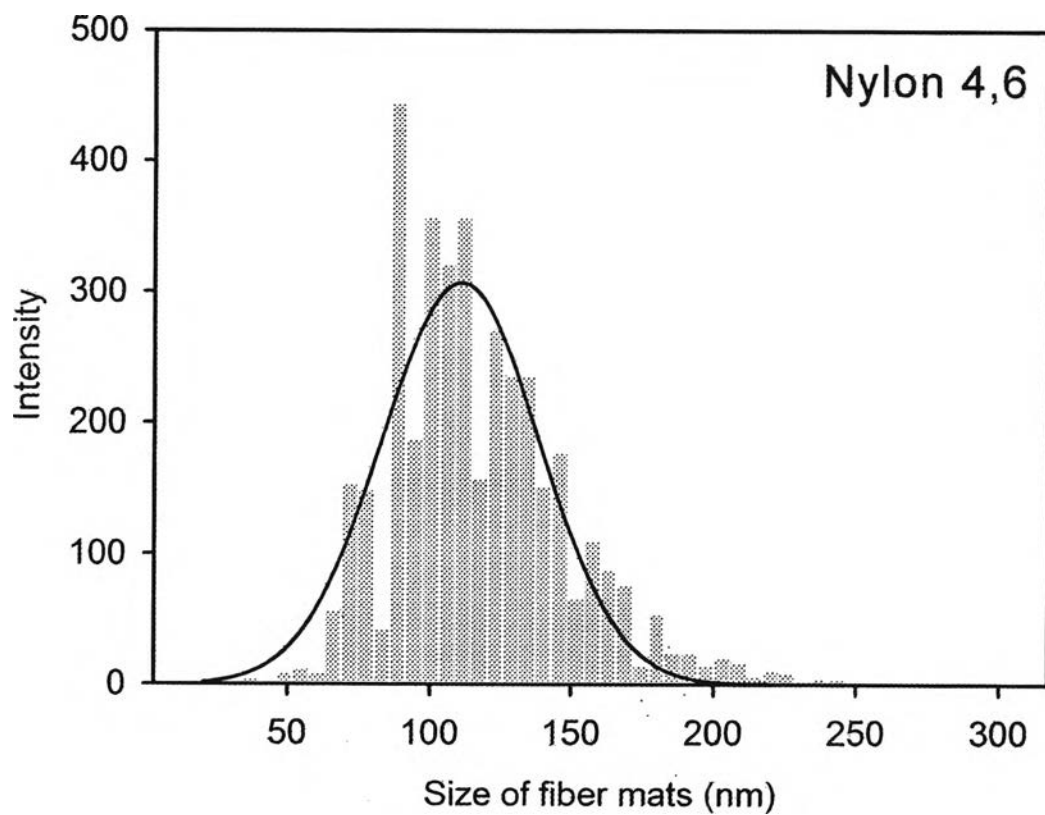


Figure 7.2 Size distribution of nylon 4,6 nanofibers.

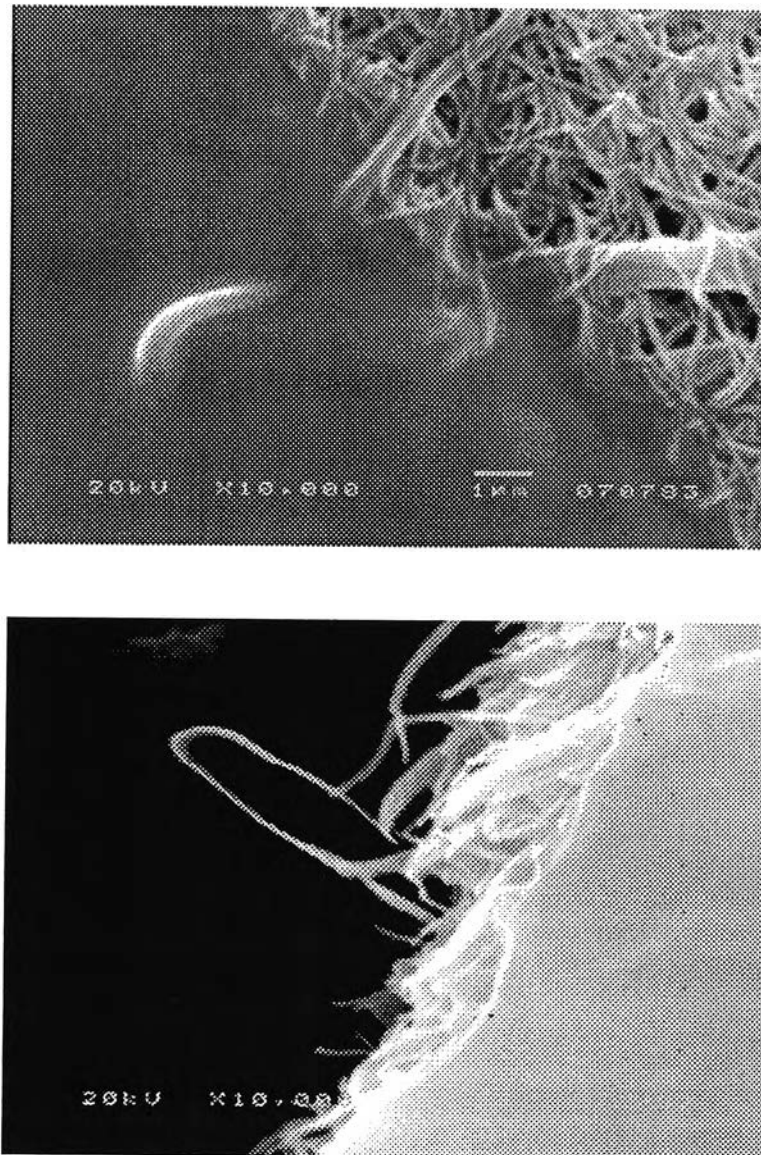


Figure 7.3 SEM images show the fiber formation of nylon 4,6 in the composite films.

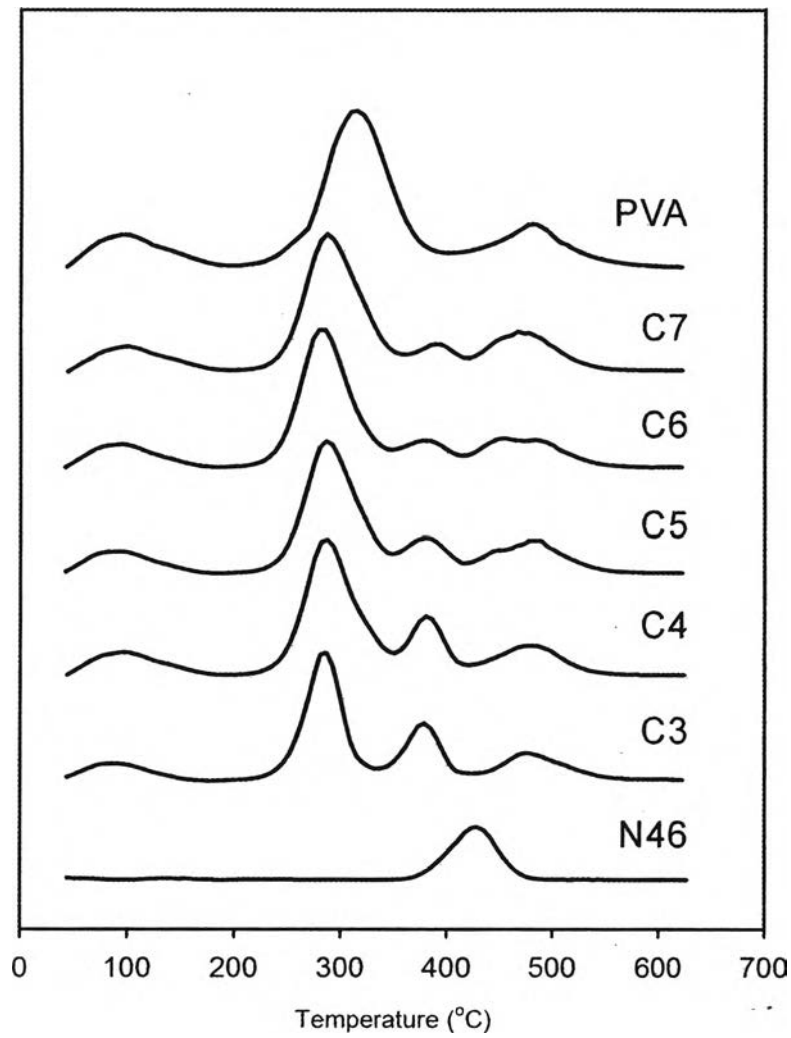


Figure 7.4 Derivative TGA curve of nylon 4,6 as-spun fibers, PVA films, and all composites.

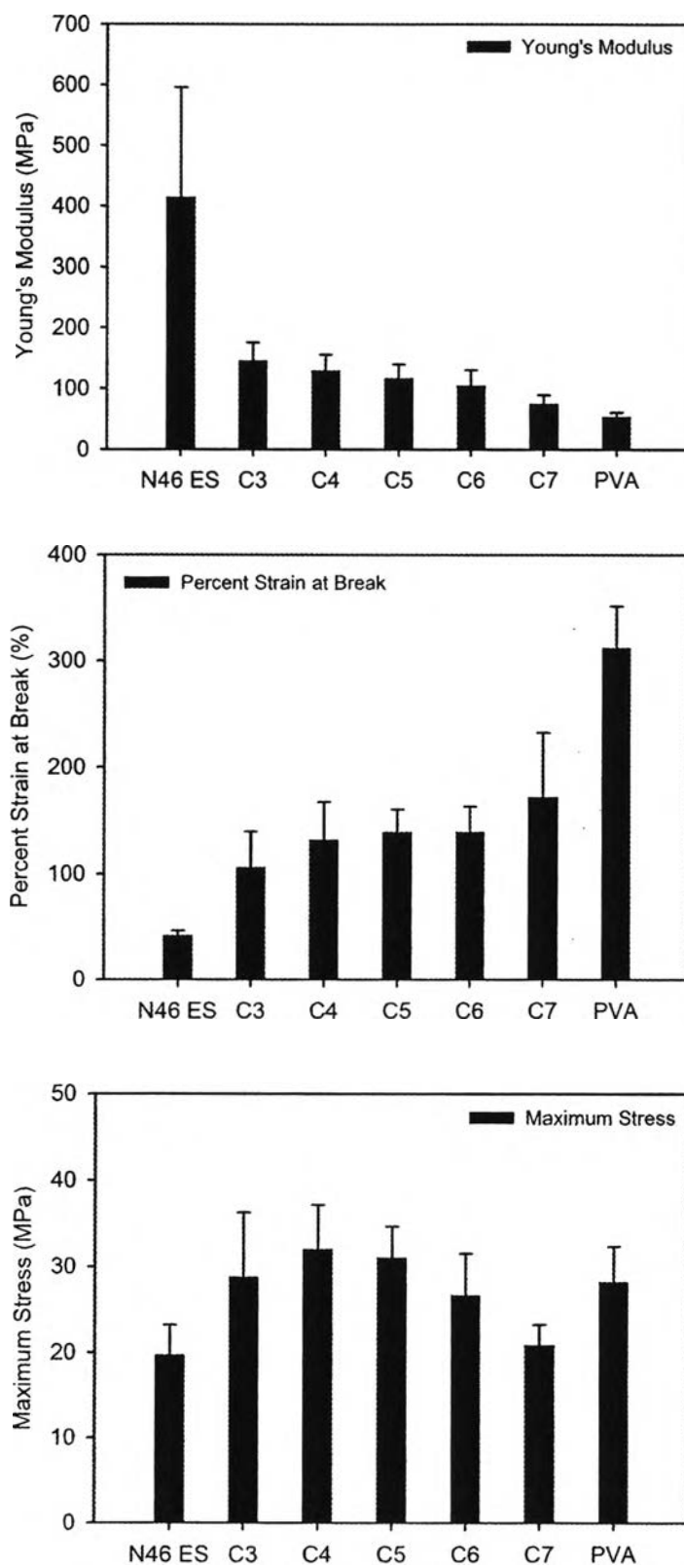


Figure 7.5 Tensile properties of the nylon 4,6 composites.

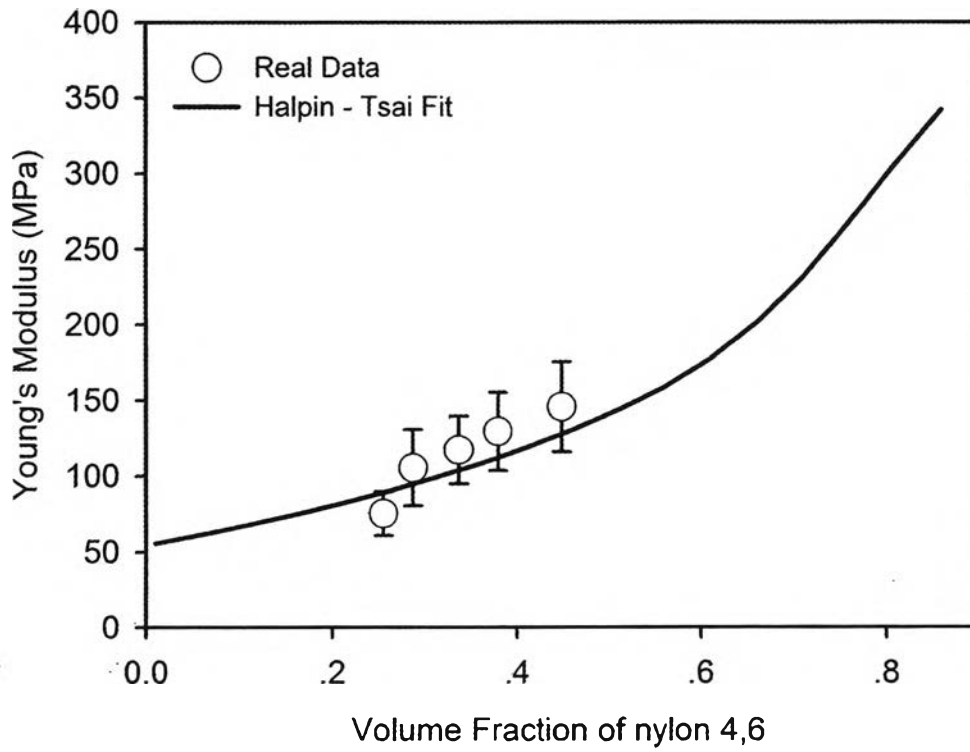


Figure 7.6 The experiment data was fitted by using the Halpin-Tsai model.

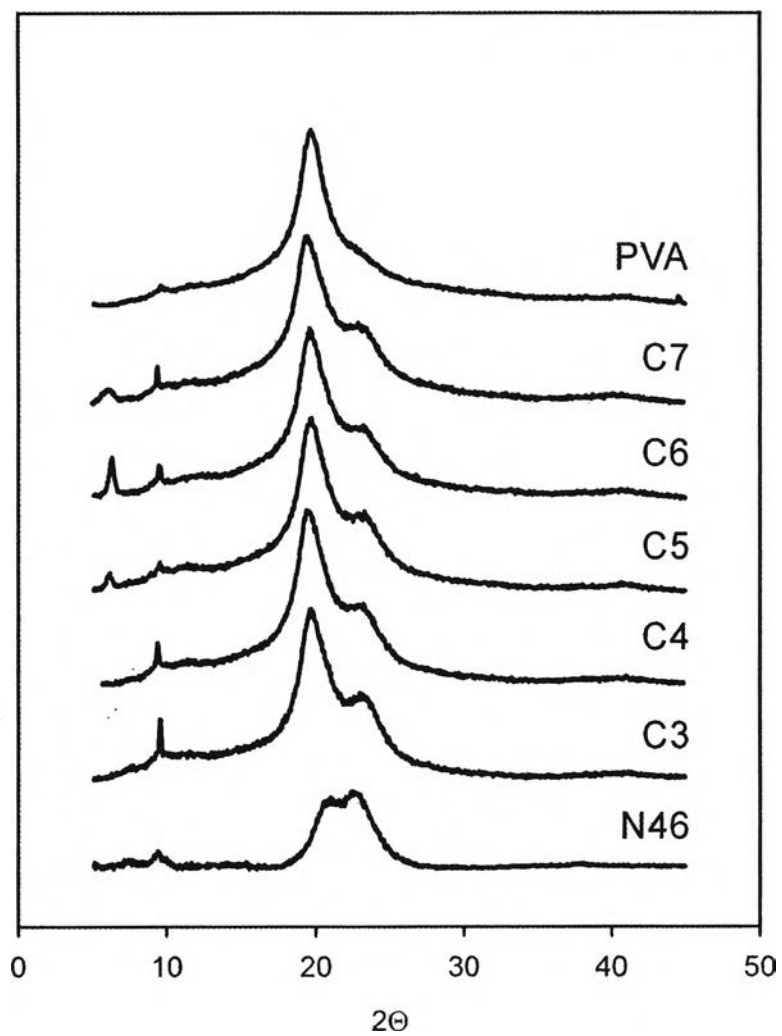


Figure 7.7 XRD results of nylon 4,6 as-spun fibers, PVA film, and all composites.