

CHAPTER VI
PREPARATION AND STUDY OF SERICIN-G-PLA CLAY AEROGEL
WITH ACRYLIC ACID ASSISTED BY PLASMA TECHNIQUE

6.1 ABSTRACT

The aim of this study was to prepare sericin-g-PLA clay aerogel with acrylic acid by freeze-drying. Due to clay aerogel formed fragile materials hence sericin-g-PLA and acrylic acid were employed to improve the mechanical properties. Sericin (Nang Lai)-g-PLA clay aerogel with acrylic acid was prepared by varying acrylic acid and clay contents in 2, 4, 6 and 8 wt% and plasma treatment times in 15, 30, 60 and 120 s in order to study the effect of acrylic acid and clay contents and plasma treatment times to the properties of the aerogel. The mechanical and mechanical-thermal properties were investigated by universal testing machine (LLOYD) and dynamic mechanical analysis (DMA) in compression mode, respectively. The thermal properties were investigated by Thermogravimetric-Differential Thermal Analyzer (TG-DTA). The mechanical and thermal properties directly depend on acrylic acid and clay contents and plasma treatment times. By increasing clay content, the mechanical properties were improved but thermal properties were dropped due to the oxidation of Ferric ion effect. Moreover, the increasing of acrylic acid content also improved the mechanical properties of the aerogels.

Keywords: Sericin-g-PLA; Clay aerogel; Mechanical properties

6.2 INTRODUCTION

The smectite clay such as sodium montmorillonite and bentonite are extensively used to develop polymer clay nanocomposites due to their characteristic properties such as high surface area, high aspect ratio and relatively low cost. When layered silicate clay pass through the environmental friendly process called freeze-drying, clay powder can be rearranged to the “house of cards” structure and this

material is called “clay aerogel” (Bandi, 2006). Clay aerogel is the high porosity, low density, lightweight materials which is in the formed 3 dimension structure. This porous structure makes clay aerogels suitable for wide range applications like absorbent materials, insulator materials or biomedical materials. However, neat clay aerogel is fragile and exhibited low mechanical properties. To overcome this problem the combination with polymeric materials is required (Bandi, 2006, Pojanavaraphan, 2010). Graft copolymerization is a useful technique for modifying the properties of synthetic and natural polymers, and graft copolymers have been used as a stabilizer of emulsion and dispersion, sorption agents, biomedical materials and also improving properties materials of the composites.

In this study, the sericin-g-PLA clay aerogel with acrylic acid was prepared by freeze-drying. Sericin-g-PLA, synthetic grafted copolymers, was employed to improve the mechanical properties of the aerogels because of the fragility of neat clay aerogel. Acrylic acid was also used to enhance the mechanical properties of the aerogels by using plasma to initiate the crosslinking reaction. The sericin-g-PLA clay aerogel with acrylic acid was prepared by varied of acrylic acid and clay contents and plasma treatment times in order to study the effect of acrylic acid, clay and plasma treatment on the properties of the aerogels. The aerogels were studied on mechanical, mechanical-thermal, and thermal properties by using universal testing machine, DMA, and TG-DTA, respectively.

6.3 EXPERIMENTAL

6.3.1 Materials

Silk cocoon (*Bombyx mori*); Nang Lai (NL) was purchased from local sericulture in Thailand. Sodium-bentonite was supported from Thai Nippon Co.,Ltd, Thailand. The bentonite is a commercial sodium activated bentonite (Mac-Gel© (GRADE SAC)) with cationic exchange capacity (CEC) of 49.74 meq/100 g clay and used without extra modification. L-lactide monomer (CAS No. 4511-42-6) (99.5% purity) was purchased from Shenzhen Brightchina Industrial Co., Ltd. Stannous (II) octoate (CAS No. 301-10-0) used as catalyst was purchased from Sigma Aldrich Corp., Japan. Acrylic acid (AA) (CAS No. 79-10-7) used as cross-

linked agent was purchased from Sigma Aldrich Corp., USA with molecular weight 72.06 g/mol.

6.3.2 Extraction of Silk Sericin

Silk sericin was extracted by using hot water degumming process. Silk cocoons were rinse with water to eliminate contaminated matter. 20 g of silk cocoons were cut into small pieces (about $5 \times 5 \text{ mm}^2$) and mixed with 300 ml of purified water. Silk cocoons were autoclaved under pressure of 0.8-0.9 atm at 120 °C for 60 min. The silk fiber (fibroin) was filtered out to obtain the sericin aqueous solution. Then, Silk sericin solution was frozen in the glass shells at -40 °C for 12 hr and this glass shell was attached in a freeze-dryer maintained at -110 °C for 48 hr under vacuum to obtain silk sericin powder.

6.3.3 Preparation of PLA

Stannous (II) octoate ($\text{Sn}(\text{Oct})_2$) (0.2 wt%) was added into lactide monomers and stirred at 400 rpm, 140 °C for 10 hr. After 10 hr of synthetic, the synthesized PLA was cooled down to the room temperature. Then, PLA was grinded into powder.

6.3.4 Preparation of Sericin-g-PLA

Stannous (II) octoate ($\text{Sn}(\text{Oct})_2$) (0.2 wt%) was added into sericin (Nang Lai) powder (2 wt%). Then, they were mixed with lactide monomers (98 wt%) in glass reactor and stirred at 400 rpm, 140 °C for 10 hr. After 10 hr of mixing, the mixture was cooled down to the room temperature to get the sericin-g-PLA. Then, sericin-g-PLA was grinded into powder.

6.3.5 Preparation of Cross-linked Sericin-g-PLA with Acrylic Acid

Sericin-g-PLA powder (5 wt%) were dispersed in purified water of 50 mL and mixed with 4 mL acrylic acid for 1 hr. After that the mixtures were treated by plasma in air for 15, 30, 60, and 120 s and stirred for 15 min. Then, the mixtue was immediately frozen in petri dishes at -40 °C for 12 hr and attached to a freeze-dryer maintained at -110 °C for 48 hr to sublime the ice out.

6.3.6 Preparation of Clay Aerogel

Sodium-bentonite was dispersed in purified water under constant stirring for 3 hr. Then, the gel was immediately frozen in cylindrical glass shells at -40 °C

for 12 hr and attached to a freeze-dryer maintained at -110 °C for 48 hr to sublime the ice out.

6.3.7 Preparation of Sericin-g-PLA Clay Aerogel

Sericin-g-PLA powder (5 wt%) was dispersed in purified water for 1 hr and added into the dispersed Na-bentonite under constant stirring followed by continuous stirring for 2 hr. Then, the gel was immediately frozen in cylindrical glass shells at -40 °C for 12 hr and attached to a freeze-dryer maintained at -110 °C for 48 hr to sublime the ice out.

6.3.8 Preparation of Sericin-g-PLA Clay Aerogel with Acrylic Acid

Sericin-g-PLA powder (5 wt%) was dispersed in purified water and mixed with acrylic acid for 1 hr. The mixture was added into the dispersed Na-bentonite under constant stirring followed by continuous stirring for 2 hr. After that the gel was treated by plasma in air and stirred for 15 min. Then, the gel was immediately frozen in cylindrical glass shells at -40 °C for 12 hr and attached to a freeze-dryer maintained at -110 °C for 48 hr to sublime the ice out.

6.3.9 Characterizations

6.3.9.1 *Swelling Behavior*

The swelling behavior of cross-linked sericin-g-PLA with acrylic acid was studied by using conventional gravimetric procedure. The sample was dried in an oven at 60 °C over night and weighed to obtain weight of dry sample (W_1). The dry sample was immersed in water at 25 °C for 24 hr. The swollen sample was withdrawn, wiped to remove the excess water out, and reweighed (W_2). The swelling percentage was calculated as shown in Eq. 6.1.

$$\text{swelling percentage} = \frac{W_2 - W_1}{W_1} \times 100 \quad (\text{Eq. 6.1})$$

6.3.9.2 *Density Measurement*

The density of the aerogels was determined by mass and dimension measurement according to an equation:

$$\rho = \frac{M}{V} \quad (\text{Eq. 6.2})$$

where ρ is mass density (g/cm^3), M is mass of sample (g) and V is volume of sample (cm^3). Mass and volume was measured using Sartorius BS 224 S analytical balance and digital vernier caliper.

6.3.9.3 Thermogravimetric-Differential Thermal Analyser (TG-DTA)

Thermal stability of sericin-g-PLA clay aerogel with acrylic acid was examined by PERKIN-ELMER Pyris Daimond thermogravimetric analysis. The weight of sample was in the range of 5-7 mg and heated at the heating rate of 10 °C/min from 50-800 °C in nitrogen atmosphere with 20 ml/min of nitrogen flow rate.

6.3.9.4 Universal Testing Machine

The Young's modulus of sericin-g-PLA clay aerogel with acrylic acid was investigated by LLOYD Lrx Universal Testing Machine in compression mode with 500 N load cell at constant crosshead speed of 1 mm/min. The aerogels were prepared in the cylindrical shape with ~20 mm in diameter and height. Five samples of each composition were tested for reproducibility. The compressive modulus was calculated from the slope of the linear portion of the stress-strain curve.

6.3.9.5 Dynamic Mechanical Analysis (DMA)

DMA analyze was carried out by using a dynamic-mechanical analyzer GABO EPLEXOR QC 25 instrument. The testing temperature was set from -50 to 150 °C, heating rate 2 °C/min, 1 Hz for frequency. The aerogels were prepared in the cylindrical shape with ~20 mm in diameter and height. The compression mode was used.

6.4 RESULTS AND DISCUSSION

6.4.1 Swelling Behavior

Swelling studies of cross-linked sericin-g-PLA with acrylic acid synthesized using various plasma treatment times showed in Figure 6.1. The results showed that the increase of plasma treatment time from 15 s to 30 s, the swelling

percentage was decreased around 10%. This is attributed to an increase of crosslink density which arises from intercrosslinking or reaction between carboxyl groups of acrylic acid and hydroxyl group of sericin (Figure 6.2). This behavior affected the concentration of the ionic carboxyl groups of acrylic acid, which in turn decreased the swelling capacities (Ayman and Rasha, 2003). Moreover, the swelling percentage was increased to 420% and 430% when plasma treatment time was 120 s and 60 s, respectively. This is due to molecules degraded into lower Mw chain which led to an increase of the swelling capacities (Wan *et al.*, 2006).

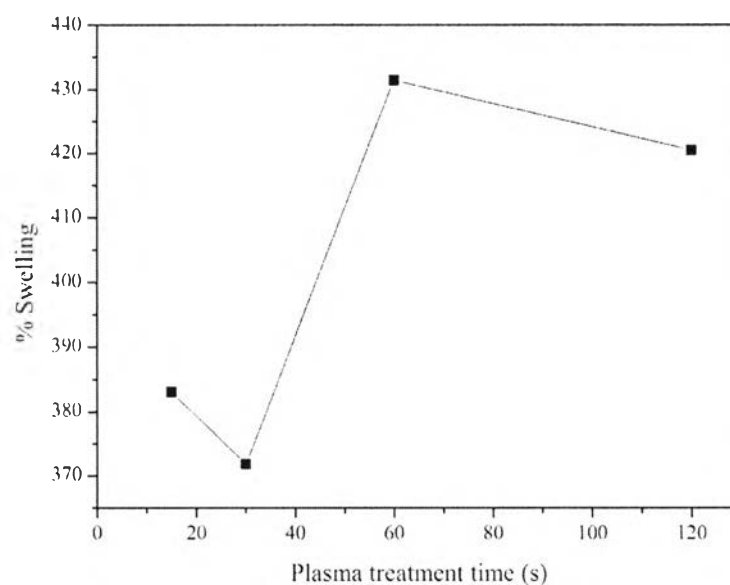


Figure 6.1 Swelling percentage of cross-linked sericin-g-PLA with acrylic acid in water as a function of plasma treatment time.

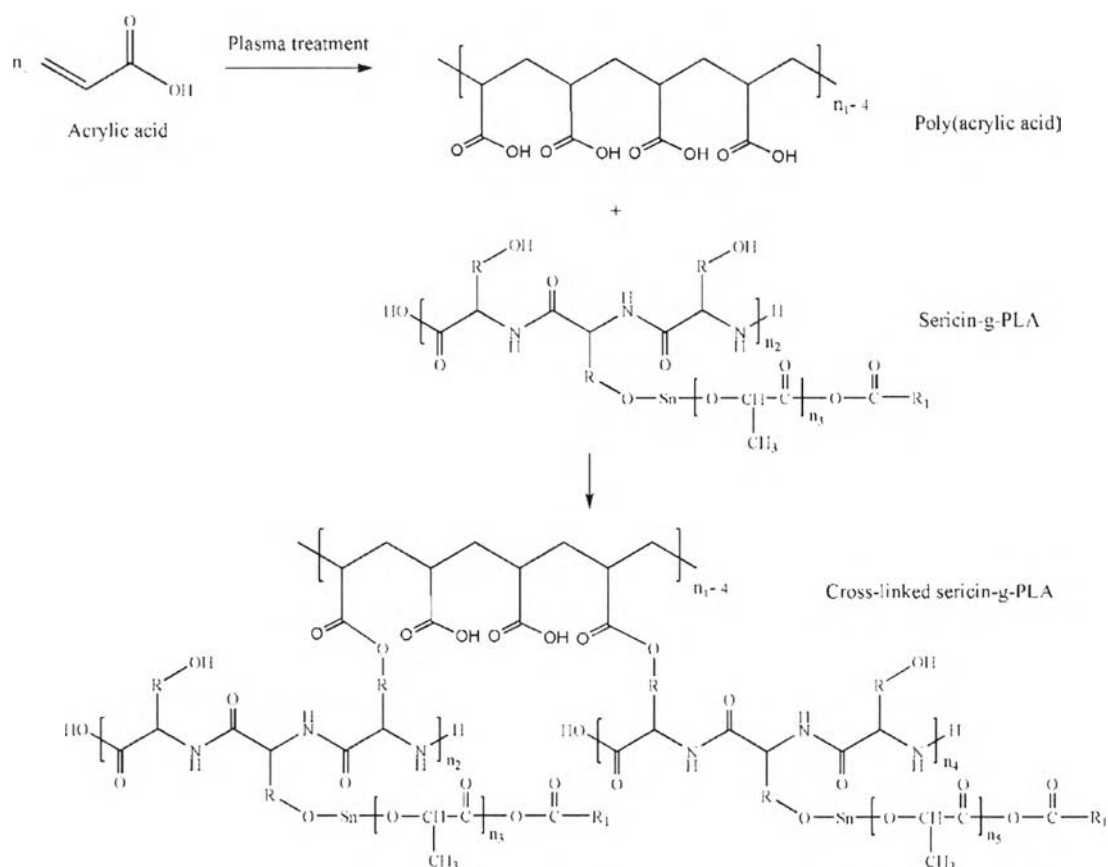


Figure 6.2 Purposed cross-linked mechanism of sericin-g-PLA with acrylic acid.

6.4.2 Density

The density of the clay aerogels are showed in Table 6.1. Neat clay aerogel exhibited low density material with bulk density of 0.05 g/cm^3 . The cooperation of clay aerogel with polymeric material was increased the density of the clay aerogels. Sericin-g-PLA clay aerogels presented the density ranged between 0.09 to 0.12 g/cm^3 depended on the composition of the aerogels. This is due to polymeric material was fulfilled the cavity between layers of clay lead to the denser materials.

Table 6.1 Density of the clay aerogels

Samples	Density (g/cm ³)
Clay aerogel 6 wt% (C6)	0.05±0.004
C6 with sericin-g-PLA 5 wt% (C6G5)	0.09±0.003
C6G5 with AA 2 wt% (plasma time 30 s)	0.11±0.003
C6G5 with AA 4 wt% (plasma time 30 s)	0.11±0.002
C6G5 with AA 6 wt% (plasma time 30 s)	0.10±0.007
C6G5 with AA 8 wt% (plasma time 30 s)	0.10±0.003
C6G5AA4 with plasma time 15 s	0.11±0.004
C6G5AA4 with plasma time 60 s	0.11±0.012
C6G5AA4 with plasma time 120 s	0.11±0.007
C2G5AA4 (plasma time 30 s)	0.10±0.006
C4G5AA4 (plasma time 30 s)	0.11±0.009
C8G5AA4 (plasma time 30 s)	0.12±0.011

6.4.3 Thermal Stability of Sericin-g-PLA Clay Aerogel with Acrylic Acid

The thermal stability of sericin (NL), PLA and sericin-g-PLA are shown in Figure 6.3. The weight loss of silk sericin was mainly occurred around 255 °C and the peak degradation temperature of silk sericin was around 300 °C. The silk sericin did not completely decompose at 900 °C (Srihanam *et al.*, 2009). PLA has the onset temperature of decomposition at 250.7 °C. In addition, when compared NL-g-PLA with PLA and NL, the decomposition onset temperature of NL-g-PLA was increased to 262.6 °C. This indicated that the grafted copolymer from NL and PLA was increased the decomposition onset temperature when compared to the neat PLA and silk sericin (NL).

The thermal stability of sericin-g-PLA clay aerogel with acrylic acid is shown in Figure 6.5 to 6.7. The loss in mass started at 130 °C, which is due to non-cross-linked acrylic acid (Figure 6.4) and evaporation of water (Horia and Abdel, 2012). The weight loss that starting from 240 to 350 °C was associated to anhydride formation and decarboxylation processes of poly(acrylic acid) (Mohamed *et al.*,

2012). Moreover, this step was associated with the decomposition of sericin and PLA which around 255 °C and 251 °C, respectively. The weight loss percentage of the sample increases with the increasing of acrylic acid contents. The difference of plasma treatment time are shown the close values of the weight loss percentage but at 30 seconds of plasma treatment time shows the lowest of the percentage of weight loss. The weight loss percentage of the sample decreases with the increasing of clay contents. The combination of bentonite clay into the organic materials should be enhanced the thermal stability of the composites but in sericin-g-PLA clay aerogel with acrylic acid system, increasing of clay contents showed slight decreased in decomposition onset temperatures. Morlat *et al.* (2004) suggested that the presence of ferric ion (Fe^{3+}) in octahedral sheet of clay could accelerate the thermal degradation of organic compound resulting in the reducing of thermal stability of the composite.

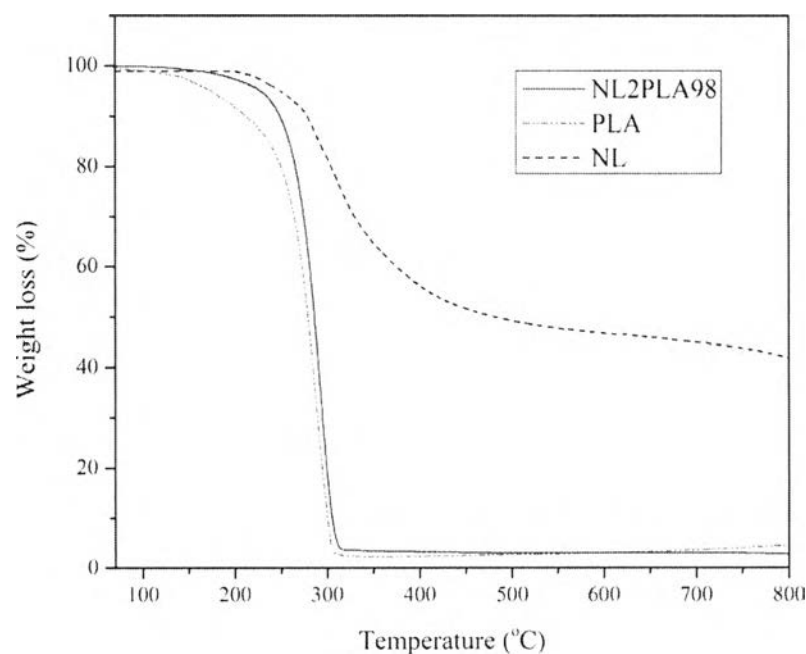
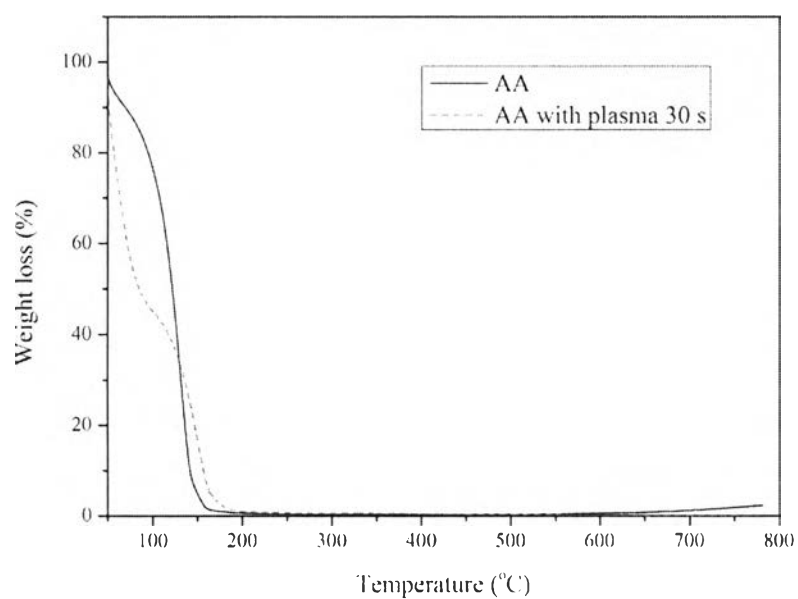


Figure 6.3 TGA curve of sericin (Nang Lai, NL), PLA and NL-g-PLA.

Table 6.2 Thermal stability of sericin (Nang Lai, NL), PLA and NL-g-PLA

Sample	T _d onset (°C)	Weight loss (%)
NL	255.5	51.3
PLA	250.7	97.1
NL2PLA98	262.6	96.6

**Figure 6.4** TGA curves of acrylic acid with and without plasma treatment.**Table 6.3** Thermal stability of acrylic acid with and without plasma treatment

Sample	T _d onset (°C)	Weight loss (%)
AA	109.6	90.4
AA with plasma 30 s	129.7	49.7

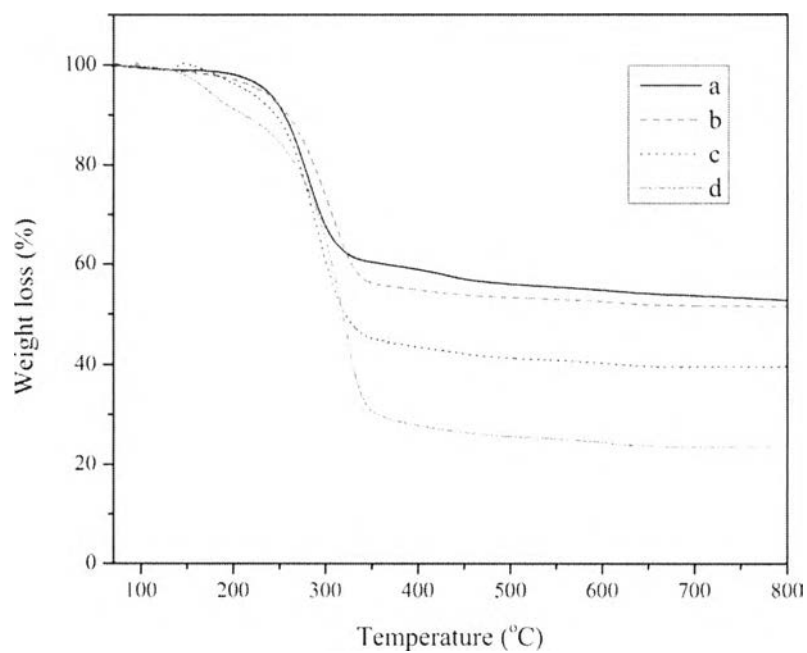


Figure 6.5 TGA curves of sericin-g-PLA clay aerogel with acrylic acid (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, and (d) 8 wt% (plasma treatment time 30 s and clay 6 wt%).

Table 6.4 Thermal stability of sericin-g-PLA clay aerogel with various acrylic acid contents (plasma treatment time 30 s and clay 6 wt%)

Acrylic acid content (wt%)	T _d onset (°C)	Weight loss (%)
2	243.0	40.1
4	257.5	45.8
6	250.2	58.2
8	262.5	74.1

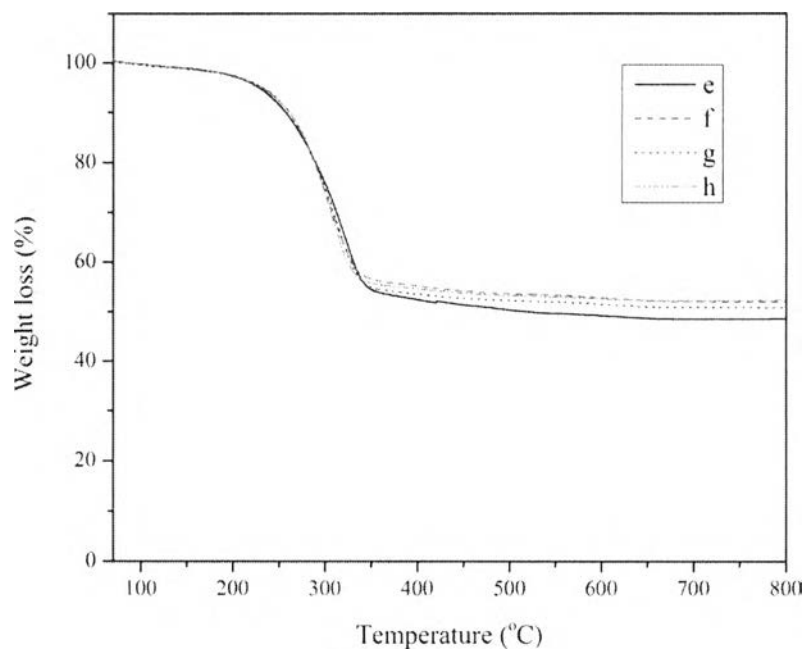


Figure 6.6 TGA curves of sericin-g-PLA clay aerogel with plasma treatment time (e) 15 s, (f) 30 s, (g) 60 s, and (h) 120 s (acrylic acid 4 wt% and clay 6 wt%).

Table 6.5 Thermal stability of sericin-g-PLA clay aerogel with various plasma treatment time (acrylic acid 4 wt% and clay 6 wt%)

Plasma treatment time (s)	T_d onset (°C)	Weight loss (%)
15	255.4	47.7
30	257.5	45.8
60	258.2	47.1
120	260.0	46.3

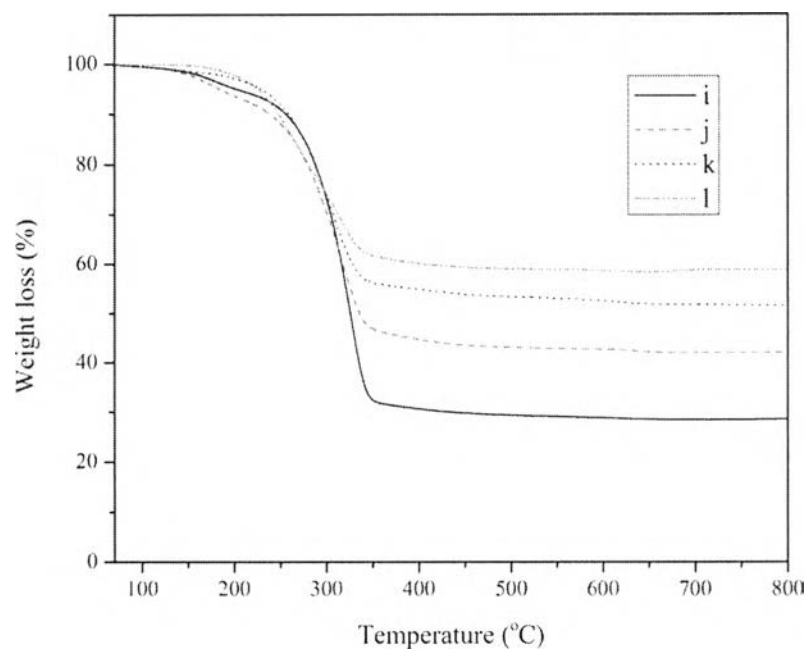


Figure 6.7 TGA curves of sericin-g-PLA clay aerogel with clay (i) 2 wt%, (j) 4 wt%, (k) 6 wt%, and (l) 8 wt% (acrylic acid 4 wt% and plasma treatment time 30 s).

Table 6.6 Thermal stability of sericin-g-PLA clay aerogel with various clay contents (acrylic acid 4 wt% and plasma treatment time 30 s)

Clay content (wt%)	T_d onset (°C)	Weight loss (%)
2	284.8	69.9
4	259.2	55.4
6	257.5	45.8
8	222.1	40.7

6.4.4 Mechanical Properties of Sericin-g-PLA Clay Aerogel with Acrylic Acid

The compressive properties of sericin-g-PLA clay aerogel with acrylic acid are characterized by using Lloyd universal testing machine. The crosslinking of the aerogels was induced by an addition of an acrylic monomer and treated with

plasma in order to initiate the reaction. The compressive stress-strain curves of the aerogels are shown in Figure 6.8 to 6.11. Table 6.8 to 6.10 summarized the mechanical properties of sericin-g-PLA clay aerogel with acrylic acid. Table 6.7 shows the Young's modulus of 6 wt% of clay aerogel and 6 wt% of clay aerogel with sericin-g-PLA, was 10 and 69 kPa, respectively. This indicates that the cooperation of clay aerogel with polymeric material was increased the mechanical properties of the clay aerogel (Pojanavaraphan *et al.*, 2008, Pojanavaraphan *et al.*, 2010). Moreover, the acrylic acid and clay content and plasma treatment time affected to the mechanical properties of the aerogels. Increasing of acrylic acid content from 2 to 4 wt%, the Young's modulus increased from 130 to 267 kPa. According to Pojanavaraphan *et al.*, 2010A, the cross-linked network can dissipated energy efficiently under apply load hence mechanical properties can be improved. In the case of 6 and 8 wt% of acrylic acid, stiffness and Young's modulus were dropped from 4 wt% of acrylic acid. When acrylic acid content increased, the acceleration of hydrolysis of amino acid in sericin and PLA was strongly increased hence the mechanical properties was fallen down. According to Feng *et al.*, 2014, the particles could be disrupted with a size reduction resulted from hydrolysis; at low pH, the molecules are protonated and will be collapsed, thus the particles will be shrunk and aggregated. In addition, the mechanical properties of the aerogels with plasma treatment time from 15 to 120 seconds showed the same trend as acrylic acid. Increasing clay contents from 2 to 6 wt%, the Young's modulus increased from 97 to 267 kPa due to the high reinforcing efficiency of clay bentonite. In case of 8 wt% of clay, the stiffness and Young's modulus were dropped from 6 wt% of clay because the clay gel dispersion was too viscous and difficult to process resulting in an inhomogeneous dispersion of the aqueous clay gel precursor. When compared between clay aerogel and sericin-g-PLA clay aerogel with acrylic acid that treated by plasma, the mechanical properties of the aerogels were improved by addition polymer material and crosslinking agent that treated by plasma.

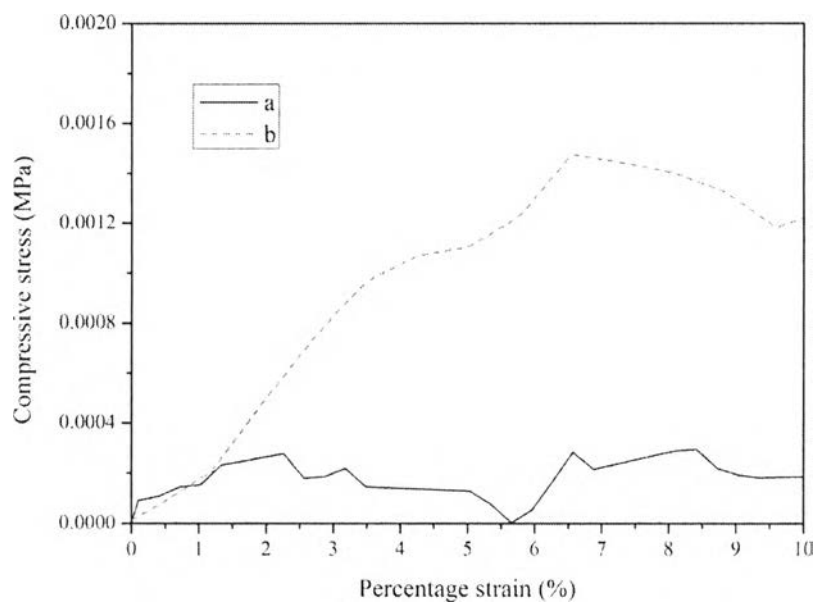


Figure 6.8 Stress-strain curves of (a) 6 wt% of clay aerogel and (b) 6 wt% clay of aerogel with 5 wt% of sericin-g-PLA.

Table 6.7 Mechanical properties of clay aerogel and sericin-g-PLA clay aerogel

Samples	Young's modulus (kPa)	Stiffness (kN/m ²)
Clay aerogel 6 wt% (C6)	10.22±1.31	0.11±0.03
C6 with sericin-g-PLA 5 wt%	68.90±6.52	0.72±0.07

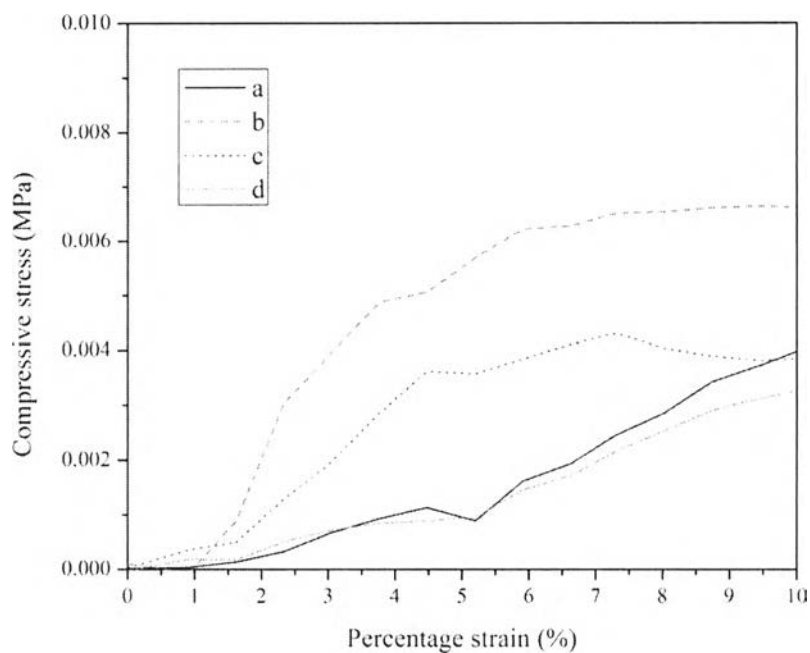


Figure 6.9 Stress-strain curves of sericin-g-PLA clay aerogel with acrylic acid (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, and (d) 8 wt% (plasma treatment time 30 s and clay 6 wt%).

Table 6.8 Effect of acrylic acid content on mechanical properties of sericin-g-PLA clay aerogel with acrylic acid

Acrylic acid content (wt%)	pH	Young's modulus (kPa)	Stiffness (kN/m ²)
2	2.77	130.32±35.21	2.05±0.67
4	2.65	267.42±26.22	3.03±0.45
6	2.49	143.48±17.48	1.50±0.32
8	2.38	88.31±7.64	1.39±0.78

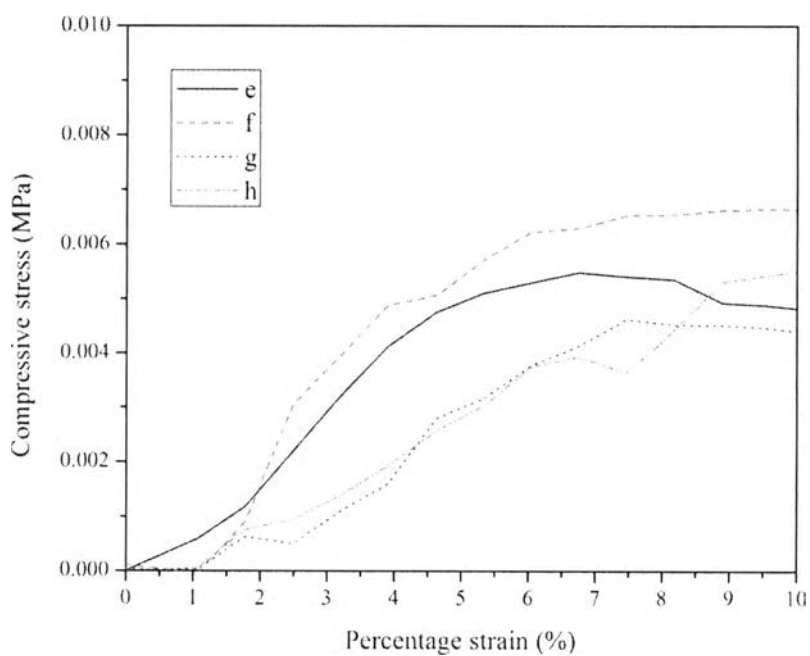


Figure 6.10 Stress-strain curves of sericin-g-PLA clay aerogel with plasma treatment time (e) 15 s, (f) 30 s, (g) 60 s, and (h) 120 s (acrylic acid 4 wt% and clay 6 wt%).

Table 6.9 Effect of plasma treatment time on mechanical properties of sericin-g-PLA clay aerogel with acrylic acid

Plasma treatment time (s)	Young's modulus (kPa)	Stiffness (kN/m ²)
15	147.48±46.95	1.54±0.76
30	267.42±26.22	3.03±0.45
60	182.04±30.83	1.91±0.45
120	157.77±45.64	1.65±0.66

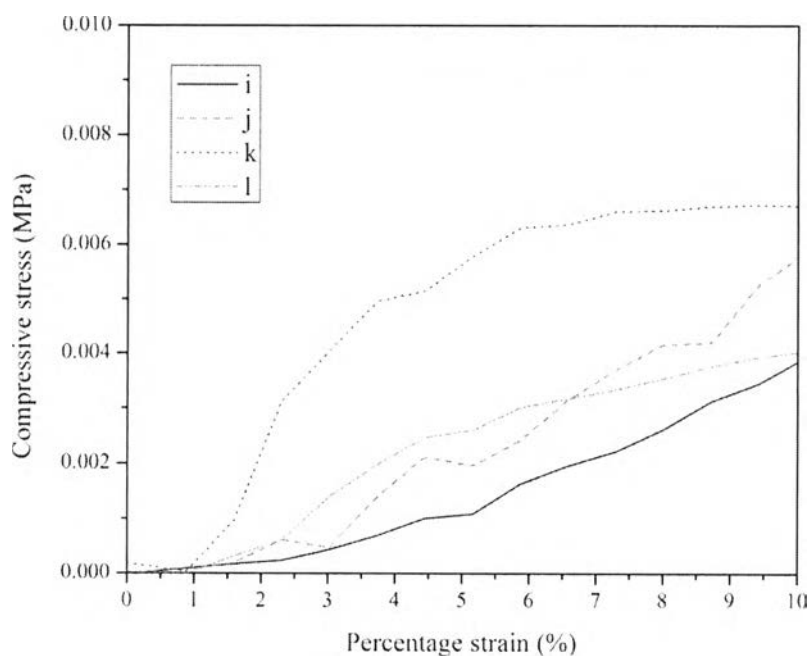


Figure 6.11 Stress-strain curves of sericin-g-PLA clay aerogel with clay (i) 2 wt%, (j) 4 wt%, (k) 6 wt%, and (l) 8 wt% (acrylic acid 4 wt% and plasma treatment time 30 s).

Table 6.10 Effect of clay content on mechanical properties of sericin-g-PLA clay aerogel with acrylic acid

Clay content (wt%)	Young's modulus (kPa)	Stiffness (kN/m ²)
2	97.42±9.11	1.02±0.36
4	154.72±42.21	1.62±0.44
6	267.42±26.22	3.03±0.45
8	177.80±47.24	1.86±0.69

6.4.5 Dynamic Mechanical Properties

The dynamic mechanical properties are characterized by using a dynamic-mechanical analyzer GABO EPLEXOR QC 25 instrument. According to Wu *et al.*,

2012, the range of the dynamic modulus value between the highest temperature and the lowest temperature were larger in tension mode than in compression mode. The reason for this is that the load in tension was primarily resisted by bonding strength, while the aggregate structure could support the major portion of the applied load in compression through interlocking actions between aggregate particles. The storage modulus and loss modulus of copolymers in compression mode which depend on temperature are shown in Figure 6.12 to 6.17. The difference in storage modulus of the aerogel results in the difference of stiffness. In the case of 4 wt% of acrylic acid and 6 wt% of clay content and 30 seconds of plasma treatment time, the storage modulus was the highest. These indicate that the aerogel has the highest of stiffness on the maximum storage modulus (Sriya *et al.*, 2013).

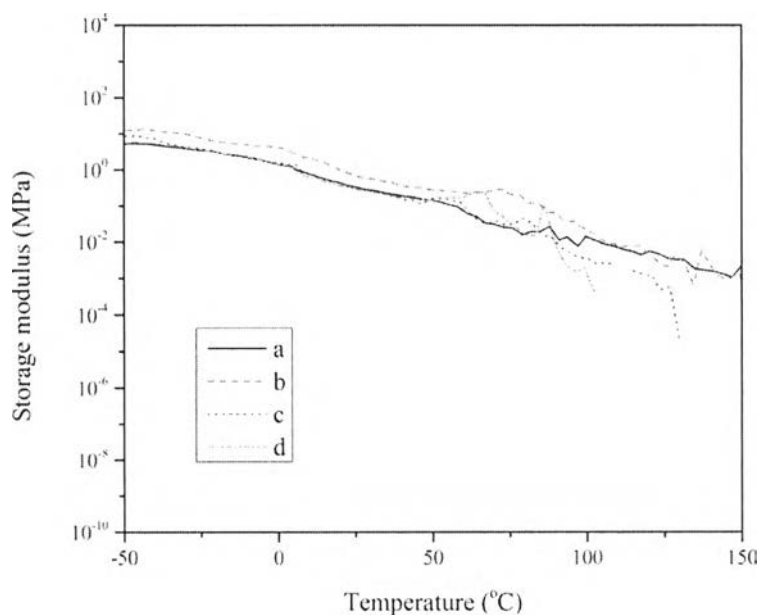


Figure 6.12 The storage modulus of sericin-g-PLA clay aerogel with acrylic acid (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, and (d) 8 wt% (plasma treatment time 30 s and clay 6 wt%).

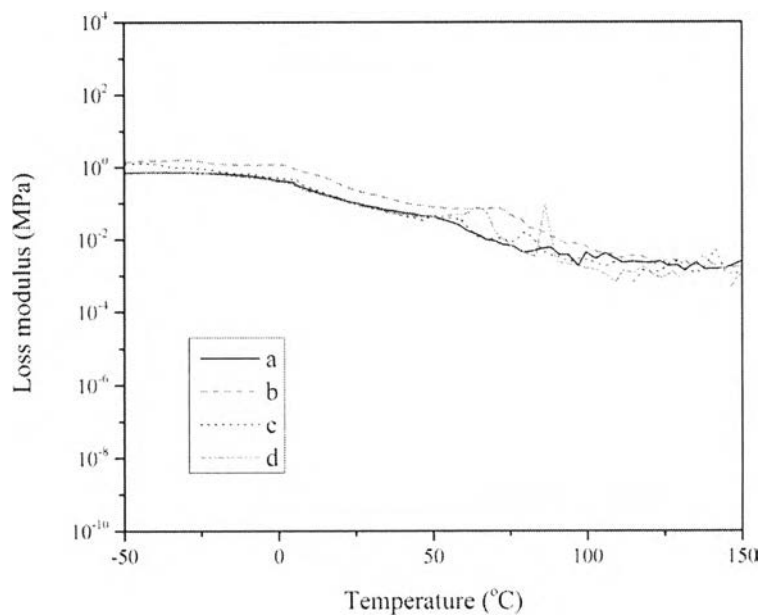


Figure 6.13 The loss modulus of sericin-g-PLA clay aerogel with acrylic acid (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, and (d) 8 wt% (plasma treatment time 30 s and clay 6 wt%).

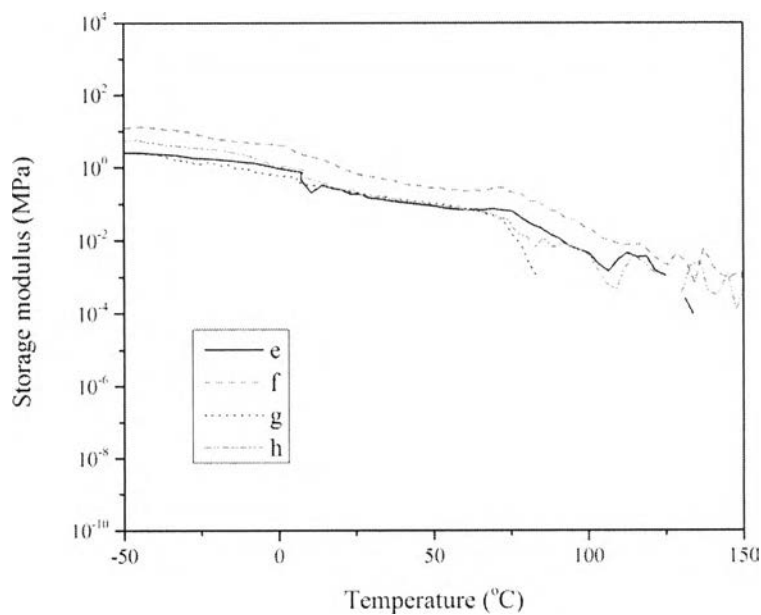


Figure 6.14 The storage modulus of sericin-g-PLA clay aerogel with plasma treatment time (e) 15 s, (f) 30 s, (g) 60 s, and (h) 120 s (acrylic acid 4 wt% and clay 6 wt%).

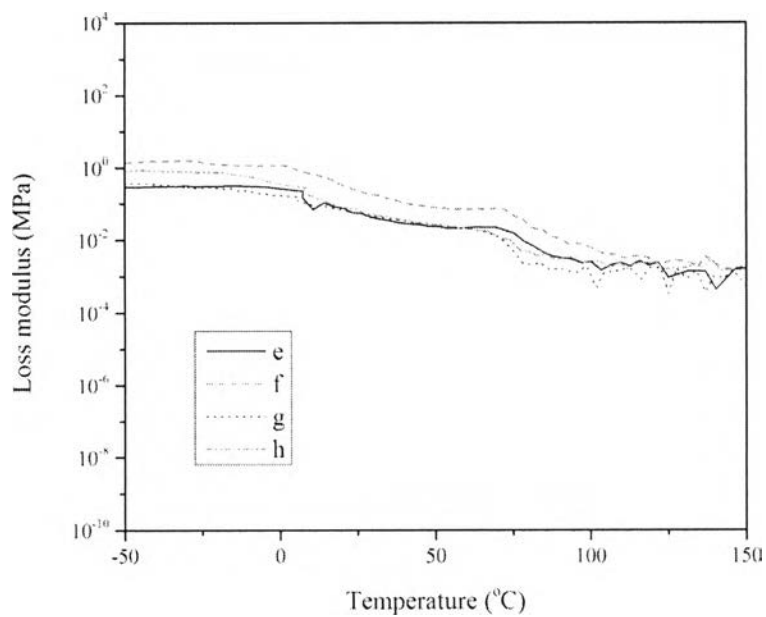


Figure 6.15 The loss modulus of sericin-g-PLA clay aerogel with plasma treatment time (e) 15 s, (f) 30 s, (g) 60 s, and (h) 120 s (acrylic acid 4 wt% and clay 6 wt%).

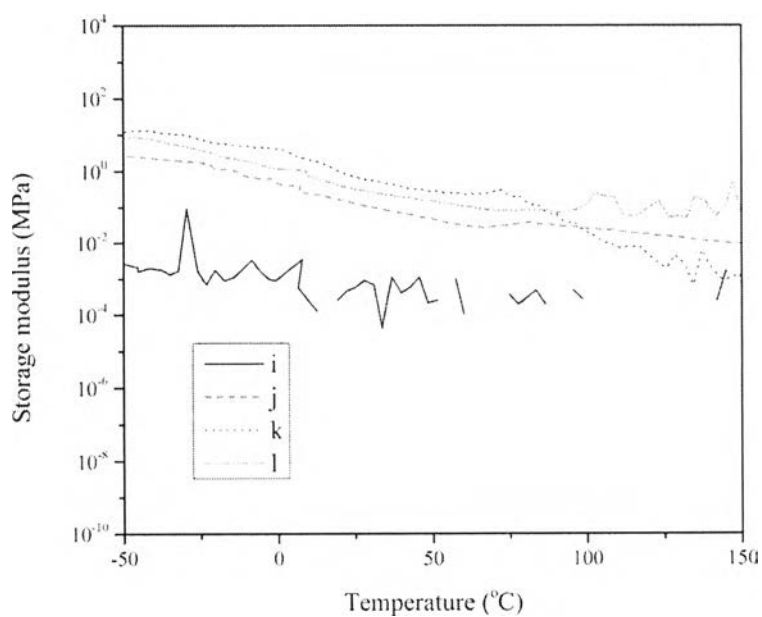


Figure 6.16 The storage modulus of sericin-g-PLA clay aerogel with clay (i) 2 wt%, (j) 4 wt%, (k) 6 wt%, and (l) 8 wt% (acrylic acid 4 wt% and plasma treatment time 30 s).

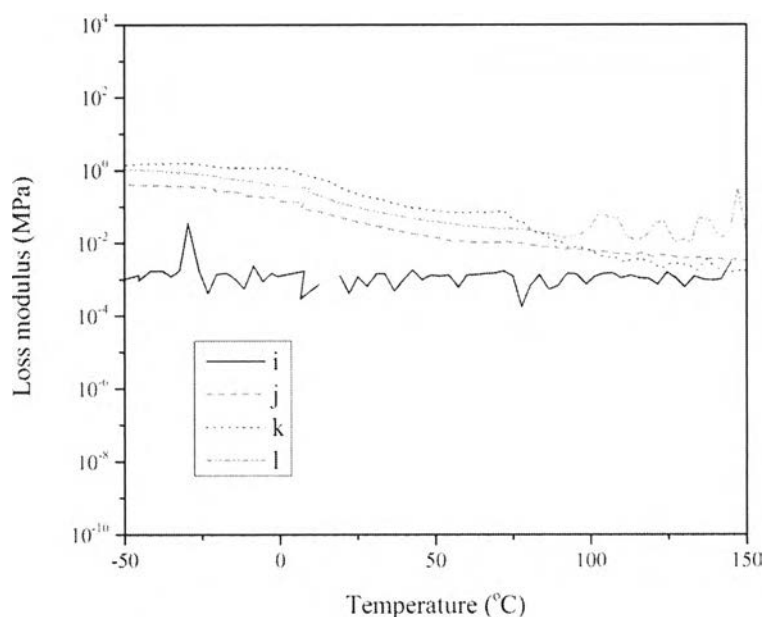


Figure 6.17 The loss modulus of sericin-g-PLA clay aerogel with clay (i) 2 wt%, (j) 4 wt%, (k) 6 wt%, and (l) 8 wt% (acrylic acid 4 wt% and plasma treatment time 30 s).

6.5 CONCLUSIONS

The novel sericin-g-PLA clay aerogel with acrylic acid were successfully prepared freeze-drying technique, the environmental friendly single step process. The properties of the aerogels mainly depended on acrylic acid, clay contents and plasma treatment times. The mechanical properties can be improved by increasing acrylic acid and clay loading. Increasing of acrylic acid content, was improved the thermal properties of the aerogels. TGA study notified that the ferric ion in clay sheet accelerated the decomposition of sericin-g-PLA/acrylic acid resulting in the decreasing of the decomposition onset temperature. Moreover, plasma treatment time at 30 s was highly enhanced the thermal and mechanical properties of the aerogels.

6.6 ACKNOWLEDGEMENTS

The authors thank the Center of Excellence on Petrochemical and Materials Technology and the government budget 2013 for the financial support.

6.7 REFERENCES

- Ayman, M. A., and Rasha, A. M. (2003) Effect of chemical crosslinking on swelling Parameters of modified poly(vinyl alcohol) Hydrogel, International Journal of Polymeric Materials, 52, 623-636.
- Bandi, S. (2006) High performance blends and composites: part (I) clay aerogel/polymer composites. Ph.D. Thesis, Department of macromolecular science and engineering, Case Western Reserve University, Ohio, USA.
- Feng, N., Dong, J., Han, G., and Wang, G. (2014) Polymer nanoparticles based on pyrene-functionalized poly(acrylic acid) for controlled release under photo and pH stimulation, Macromolecular Journals, 35, 721-726.
- Horia, M. M., and Abdel, W. M. (2012) Radiation synthesis of acrylic acid/polyethyleneimine interpenetrating polymer networks (IPNs) hydrogels and its application as a carrier of atorvastatin drug for controlling cholesterol, European Polymer Journal, 48, 1632-1640.
- Lee, S.W., Park, J.W., Park, C.H., Kim, H.J., and Eom, Y.G. (2013) UV-curing behaviors and mechanical properties of UV-cured polylactic acid (PLA). J. Korean Wood Sci. & Tech., 41(2), 134-140.
- Mohamed, R.B., Inas, H.H., Keiji, M., Masami, T., and Takeshi, M. (2012) An efficient strategy of managing irrigation water based on formulating highly absorbent polymer–inorganic clay composites. Journal of Hydrology, 470-471, 193-200.

- Morlat, S., Mailhot, B., Gonzalez, D., and Gardette, J.L. (2004) Photo-oxidation of polypropylene/montmorillonite nanocomposites.1. Influence of nanoclay and compatibilizing agent. Chemistry of Materials, 16, 377-383.
- Pojanavaraphan, T., and Magaraphan, R. (2008) Prevulcanized natural rubber latex/clay aerogel nanocomposites. European Polymer Journal, 44, 1968-1977.
- Pojanavaraphan, T., Schiradi, D.A., and Magaraphan, R. (2010) Mechanical, rheological, and swelling behavior of natural rubber/montmorillonite aerogels prepared by freeze-drying. Applied Clay Science , 50, 271-279.
- Pojanavaraphan, T., Magaraphan, R., Chiou, B., and Schiraldi, D.A. (2010A) Developpe of biodegradable foamlike materails based on casein and sodium montmorillonite clay. Biomacromolecules, 11, 2640-2646.
- Srihanam, P., Srisuwan, Y., and Simcheur, W. (2009) Characteristics of silk fiber with and without sericin component: A comparison between Bombyx mori and Ohilosamia ricini silks. Pakistan Journal of Biological Sciaences, 12(11), 872-876.
- Sriya, D., Fahmida, I., Lan, M., Sanjoy, K.B., Ronald, C.H., and Micah, J.G. (2013) Rheology and morphology of pristine graphene/polyacrylamide gels. Acs Appl. Mater. Interfaces, 5, 8633-8640.
- Wan, Y., Tu, C., Yang, J., Bei, J., Wang, S. (2006) Influences of Ammonia Plasma Treatment on Modifying Depth and Degradation of Poly(L-Lactide) Scaffolds. Biomaterials, 27, 2699-2704.
- Wu, H., Huang, B., and Shu, X. (2012) Characterizing viscoelastic properties of asphalt mixtures utilizing loaded wheel tester (LWT). Road Materials and Pavement Design, 81, 139-165.