

CHAPTER V
THE EFFECT OF ORGANOCLAY CONTENT ON STRUCTURE AND
MECHANICAL PROPERTIES OF POLYCAPROLACTONE NANOCLAY
NANOCOMPOSITES

5.1 Abstract

Polycaprolactone (PCL) is polyester having suitable properties for using as mouth guard materials. It has high toughness and can be shaped over teeth at warm water temperature. Molecular weight of PCL affects its properties, high molecular weight PCL has better mechanical properties. Therefore, high molecular weight is appropriate for use as mouth guard materials. This work tries to improve the modulus and mechanical properties of PCL by adding rigid part into PCL system. The rigid part is organoclay, therefore this work aims to study the effect of organoclay content on structure and mechanical properties of PCL nanoclay nanocomposites. Bentonite was modified by Stepanex SP-90 surfactant before adding to PCL. The organoclay content at 1, 3, 5, and 7 wt% were investigated. The modulus of PCL nanocomposites were higher than that of the pure one and thermal stability were also enhanced. The results of impact testing showed the decreasing of impact strength when organoclay content increased. Morphological study after impact testing showed moderate compatibility of organoclay and PCL.

Keyword : Polycaprolactone, Nanocomposites, Structure, Mechanical properties

5.2 Introduction

As we know that PCL is suitable for making mouth guard materials from the previous chapter, the important properties that should be concerned later is mechanical properties of PCL. This chapter tries to modify PCL by adding the rigid part into its system. The rigid part in this work is bentonite modified by stepanex SP-90 surfactant. Organomodified clay is expected to has higher interlayer spacing and to improve the compatibility between PCL and clay. In 1997, *Jimenez, G. et al.* studied

structure and thermal/mechanical properties of PCL-clay blend. They prepared nanocomposites between organically modified clay and PCL by solvent cast blended with chloroform. These nanocomposites were investigated by DMA resulting in the increasing of storage modulus (E') when organically modified clay increased. As results for the isothermal crystallization, the small amount of clay (5, 10%) in the blend accelerates the crystallization of PCL while a large clay content (15, 20%) delays it. The increasing of modulus is good for mouth guard materials because mouth guard should be strong enough to sustain its shape when absorb some energy.

Polymer nanocomposites can be prepared by various techniques (*Ray, S.S. et al. 2003, Kiersnowski, A. et al. 2004, and Zeng, Q.H. et al. 2005*). Two techniques of nanocomposite preparation, casting and intensive were compared by *Luduena, L.N. et al.* in 2007. The solvent choice and evaporation procedure for casting method is of crucial importance since it could produce holes during its evaporation, which is the case of dichloromethane in their study. With the conditions (150 rpm, 10 min, 100°C) in intensive mixing, the mechanical properties were superior to those of the films obtained by casting. This can be associated to the shear forces developed in the intensive mixer. For this technique the highest modulus was obtained for 5 wt% of organoclay content. In addition, the absence of solvent, which can produce environmental problems is another advantage for the intensive mixing technique.

This part of research aims to modify PCL by adding organoclay to its structure. PCL nanoclay nanocomposites were prepared by intensive mixing by using twin-screw extruder to avoid the problem of solvent remaining in the nanocomposites. The effect of organoclay content on the structure and mechanical properties of these nanocomposites was studied in this part.

5.3 Experimental

5.3.1 Materials

Polycaprolactone (PCL) pellets were received from Perstorp UK Ltd. Organomodified clay was prepared from bentonite and stepantex SP-90 surfactant, supplied by Thai Nippon Chemical Industry Co., Ltd. and Sunny World Co., LTD., respectively.

5.3.2 Methodology

a) Preparation of Organoclay

300 g of Na-Bentonite was swollen in water for 24 h. Stepantex SP-90 was dissolved in methanol at 80°C for 30 min. The swollen clay was mixed with Stepantex SP-90 solution and kept at 80°C for 2 h with vigorously stirring. After that the mixture was homogenized at 80°C for 1 h. The sediment was filtrated and washed with hot water several times to remove the excess salts and surfactant. Dry in a vacuum oven at 100°C overnight. Ground into powder and screen through a mesh #325.

b) Preparation of Nanocomposites

PCL and 7 wt% organoclay, prepared for masterbatch were melt blended in a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm; the processing conditions were the following: temperature (°C): 80, 90, 100, 100, 100, and 95°C from hopper to die, respectively and the screw rotation is 20 rpm. PCL and 7 wt% organoclay were premixed in a tumble mixer before introducing into the twin-screw extruder then extruded through a single strand die, followed by solidified with cold water and pelletized. The obtained pellets were dried in oven. After the preparation of masterbatch, it was dilute to 1, 3, and 5 wt% organoclay PCL nanocomposites.

c) Preparation of Specimens for Testing The Mechanical Properties

PCL nanoclay nanocomposites obtained from intensive mixing by twin screw extruder were prepared into sheet with 1.5 mm and 3 mm thickness by using a Wabash compression moulding machine with preheating for 5 min, followed by heating for 5 min at a force of 15 tons. The operating temperatures of mould were maintained at 100°C and cooled down to room temperature. After that these sheets were cut into rectangular-shape for investigating the tensile properties, impact strength, and dynamic mechanical properties.

5.3.3 Characterization

a) X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the crystal structure of PCL nanoclay nanocomposites. X-ray diffraction patterns were measured on a Bruker AXS Model D8 Advance with Ni-filtered Cu K_{α} radiation operated at 40 kV and 30 mA. Both film and powder samples were observed on the 2θ range of 5 – 30 degree with scan speed 1 degree/min and scan step 0.01 degree.

b) Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from -20 to 130°C, cooled down from 130 to 0°C, and second heat from -20 to 130°C at a rate of 10°C/min under N₂ atmosphere with a flow rate of 10 ml/min.

c) Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a TGA Q50 TA instrument. Each specimen was loaded on the platinum pan and heated from 30 to 600°C at a heating rate of 10°C/min under flow of N₂ 90 ml/min.

d) Tensile Testing

Tensile tests were performed using Instron tensile testing machine. The specimens were prepared according to the ASTM D638 standard. The grips moved apart at a constant speed of 250 mm/min, then the tensile stress, modulus, and strain were tested at least five samples of each condition.

e) Izod Impact Testing

The sheets of sample were cut into the specimen shape following the ASTM D256 (notched IZOD type), then tested the impact strength by the ZWICK 5113 Pendulum Impact Tester with the pendulum load of 21.6 J. At least five samples were tested of each condition.

f) Dynamic Mechanical Analysis (DMA)

DMA analyses were carried out by using a dynamic mechanical analyzer NETZSCH DMA 242 instrument. The specimen were $10 \times 60 \times 3 \text{ mm}^3$ (width \times length \times thickness). The testing temperature was -120 to 55°C, heating rate at 3°C/min, and frequency 1 Hz under a dual-cantilever bending mode.

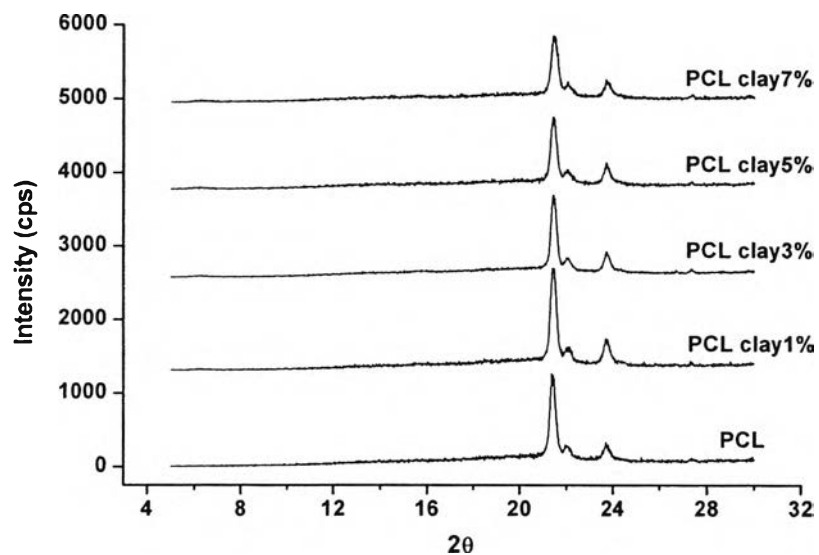
g) Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL JSM-6400 Scanning Microscope to observe surface morphology of PCL nanoclay nanocomposites. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

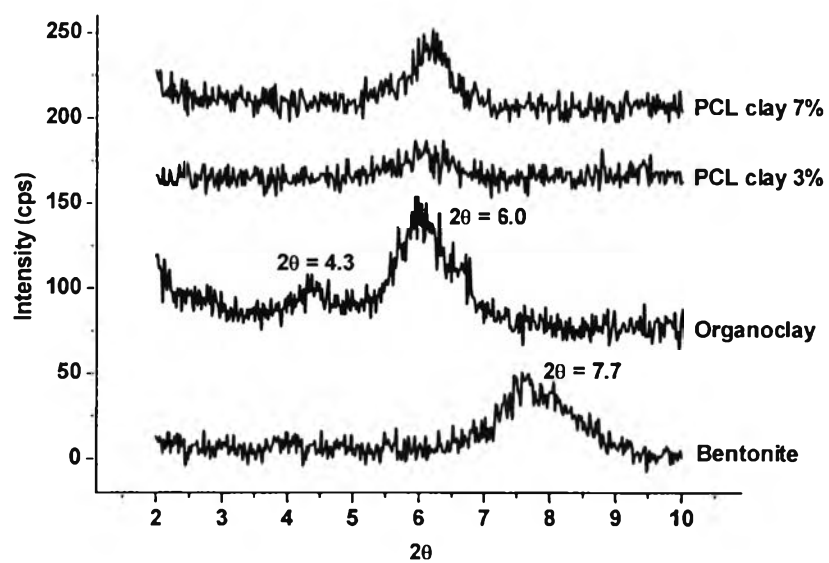
5.4 Results and Discussion

5.4.1 Structural Properties

XRD patterns of pure PCL and PCL nanoclay nanocomposites are shown in Figure 5.1 (a). As results, XRD patterns of pure PCL and PCL nanoclay nanocomposites show the same characteristic peak at $2\theta = 21.38, 21.96,$ and 23.73 (Homminga, D. et al. 2006, Wei, Z. et al. 2009, and Rezgui, F. et al. 2005). Organoclay does not affect the crystallization behavior of PCL. Organoclay shows the increasing of interlayer spacing from 1.15 nm to 1.47 and 2.05 nm calculated from Bragg's law ($n\lambda = 2d\sin\theta$) (Luduena, L.N. et al. 2007). There are two types of order in this organoclay. The disappearance of 2θ at 4.3 as shown in Figure 5.1 (b) indicates that some parts of PCL nanoclay nanocomposites exhibits the exfoliated structure. This is caused by the disorder of layered silicate at $2\theta = 4.3$, PCL can intercalate into organoclay until the exfoliation occurs. However, 2θ at 6.0 does not disappear or shift to the another position that means some part of this composite show the microstructure. It can be concluded that this composite is the mixture between exfoliated structure and microstructure.



(a)



(b)

Figure 5.1 XRD patterns (a) Pure PCL and PCL nanoclay nanocomposites with various contents of organoclay at $2\theta = 5 - 30$, (b) Bentonite, Organoclay, PCL nanoclay nanocomposites with 3 and 7 wt% of organoclay at $2\theta = 2 - 10$.

5.4.2 Thermal Analysis

DSC measurement of PCL nanoclay nanocomposites shows the results in Figure 5.2 and Figure 5.3 for second heating and cooling, respectively. Second heating of the samples from -20 to 100°C with a constant heating rate of 10°C/min exhibits only melting peaks at temperature about 55°C. The various contents of organoclay do not affect the melting behavior but affect the degree of crystallinity of PCL by the reduction of the degree of crystallinity compared to the pure one (*Lepoittevin, B. et al. 2002*).

The crystallization temperature of PCL nanoclay nanocomposites at various organoclay contents were observed from 100 to -20°C at constant cooling rate of 10°C/min. Crystallization temperature of PCL increases from 21.30°C to around 27-29°C after the addition of organoclay and slightly increases when organoclay content increases (*Homminga, D. et al. 2006*). The small amount of organoclay (1, 3, 5, and 7%) behaves as a nucleating agent of PCL so PCL added by organoclay can crystallize easier than the unfilled PCL. The addition of organoclay affects only the crystallization temperature due to the effect of nucleating agent from organoclay but it does not relate to the degree of crystallization presented in Table 5.1.

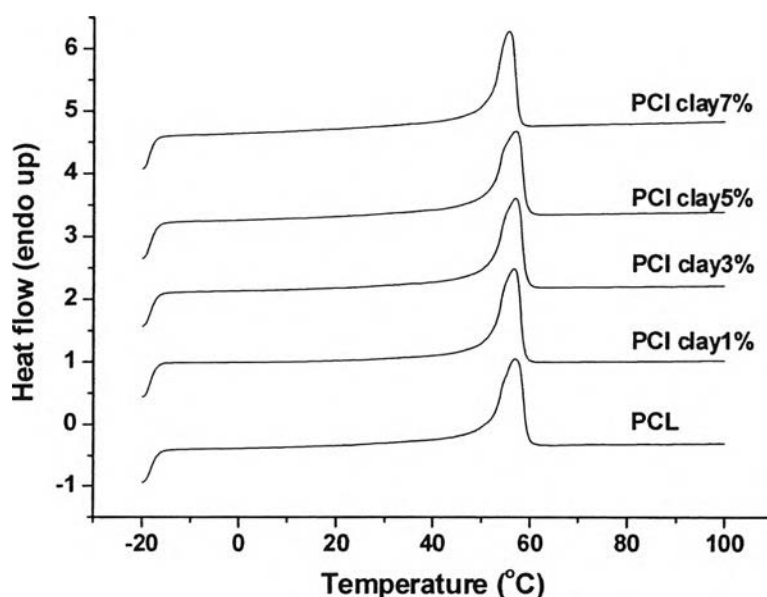


Figure 5.2 DSC-measurement of PCL nanoclay nanocomposites (second heating at 10°C/min heating rate).

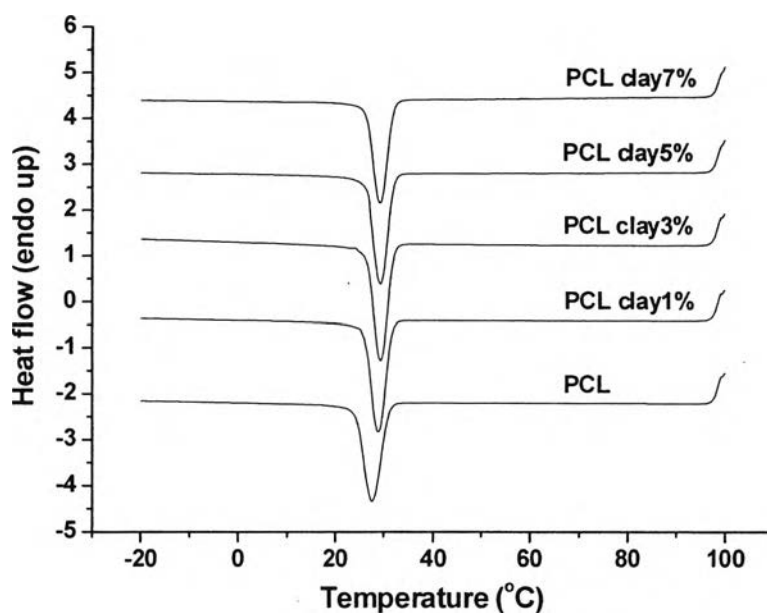


Figure 5.3 DSC-measurement of PCL nanoclay nanocomposites (cooling at 10°C/min cooling rate).

Table 5.1 T_m , T_c , and degree of crystallinity of PCL nanoclay nanocomposites

Samples	ΔH_m (J/g) ^a	Degree of crystallinity ^b	T_m (°C)	T_c (°C)
Pure PCL	54.1955	39.85	56.9	27.6
PCL clay 1%	51.7781	38.07	56.7	29.3
PCL clay 3%	52.4505	38.57	57.0	29.0
PCL clay 5%	52.1864	38.37	57.0	29.3
PCL clay 7%	48.6282	35.76	55.5	29.1

^a Melting enthalpy

^b ΔH_m for 100% crystalline PCL = 136 J/g (Lepoittevin, B. et al. 2002)

Thermal stability of PCL nanoclay nanocomposites was investigated by TGA. The addition of organoclay can enhance the thermal stability of PCL. T_d onset and char residue of each sample are displayed in Table 5.2 which shows the slight

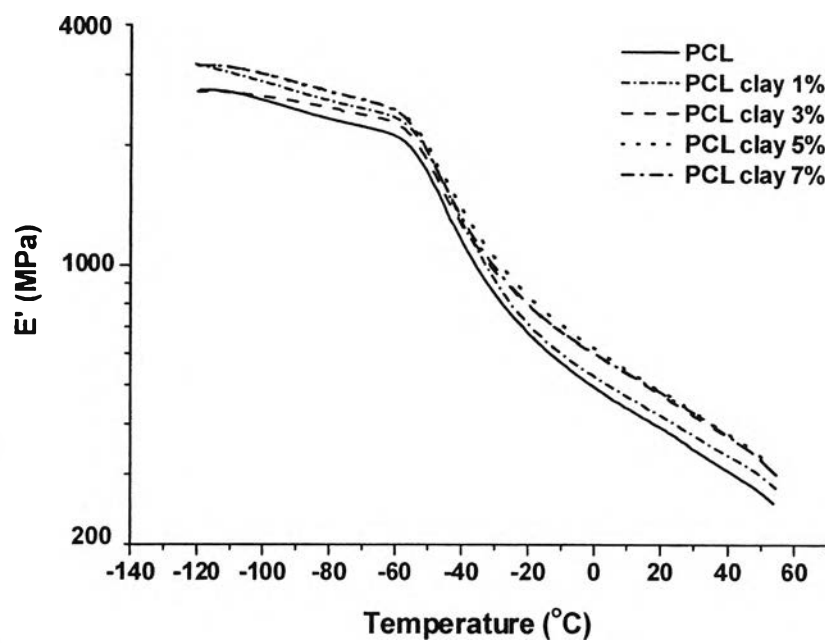
increase when organoclay content increases (Pandey, J.K. et al. 2005). PCL with higher organoclay content exhibits higher char residue than PCL with lower organoclay content due to the higher remained inorganic component in PCL nanoclay nanocomposites.

Table 5.2 Onset of degradation temperature of PCL nanoclay nanocomposites

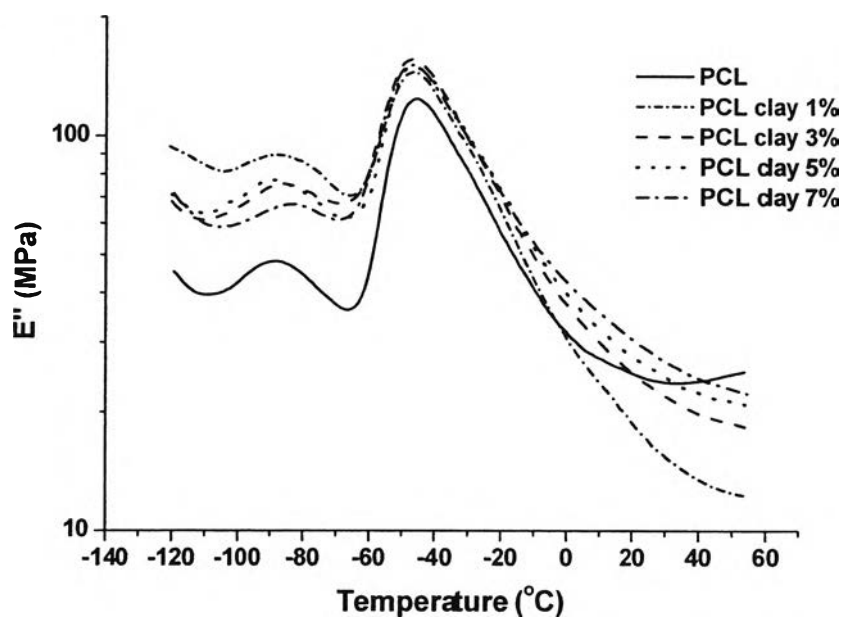
Samples	T _d onset (°C)	Char residue (%)
Pure PCL	369.07	0.8
PCL clay 1%	371.64	1.3
PCL clay 3%	372.99	3.0
PCL clay 5%	374.11	4.3
PCL clay 7%	375.93	5.8

5.4.3 Dynamic Mechanical Analysis

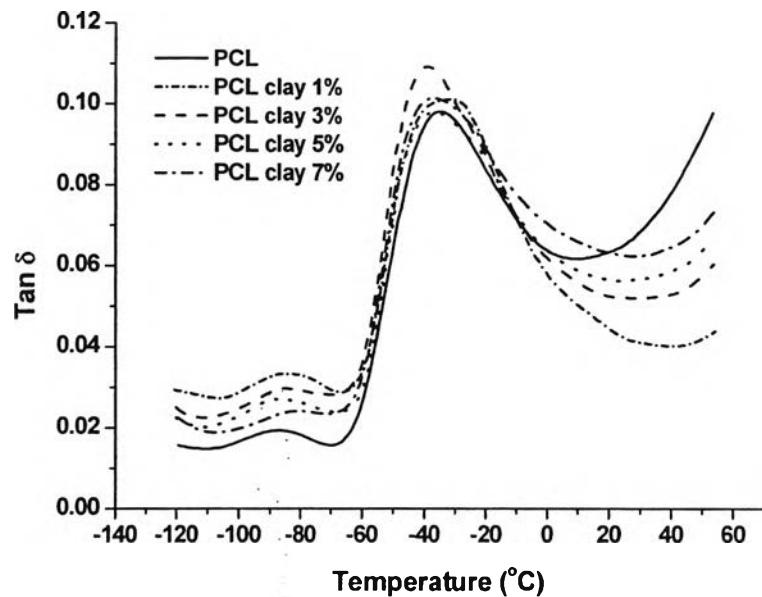
PCL nanoclay nanocomposites at various organoclay content were examined for dynamic mechanical properties from temperature of -120 to 55°C. The results are shown in Figure 5.4 (a) storage modulus, (b) loss modulus, and (c) tan δ . The storage modulus of PCL nanoclay nanocomposites drops drastically between temperature -60°C and -20°C from 2350-2500 MPa to 700-850 MPa which is its glass-transition region, and gradually decreases between 0°C and 55°C from 500-600 MPa to 250-300 MPa. In these plots, a low-temperature transition, which corresponds to the relaxation of local motions of methylene units in the main chain, can be observed at about temperature 90°C (Jimenez, G. et al. 1997). The temperature that should be concerned for mouth guard materials is the temperature in the range of 20 to 50°C because mouth guard materials will be used at room temperature, body temperature, and warm water temperature. As results for the temperature in this range, the storage modulus of PCL increases when organoclay is added and increases when organoclay content increases. The glass-transition temperature observed at the maximum of tan δ peaks does not show significant change for all contents of added organoclay.



(a)



(b)



(c)

Figure 5.4 DMA results of PCL nanoclay nanocomposites (a) E' , (b) E'' , and (c) $\tan \delta$ as the function of temperature.

5.4.4 Mechanical Properties

Impact strength and tensile properties of PCL nanoclay nanocomposites were tested for study the effect of organoclay content. Figure 5.5 shows the impact strength of each organoclay content. The increasing of organoclay contents cause the drop of impact strength (*Chen, B. et al. 2008*). The decreasing of impact strength is caused by defects inside the specimen. Impact strength of PCL with 5 to 7% organoclay show the lowest impact strength by 30% loss. Figure 5.6 (a) and 5.6 (b) display tensile properties of PCL nanoclay nanocomposites. The %elongation at break and tensile strength of all specimens cannot be observed because they did not break even if the highest speed of 250 mm/min was tested. Therefore, the tensile testing was observed for maximum strength and Young's modulus of each specimen. Young's modulus is moderately increased as organoclay content increases. Maximum strength of all specimens were observed at yield point, it shows the highest value at 3% organoclay content (*Lepoittevin, B. et al. 2002 and Pantoustier, N. et al. 2002*).

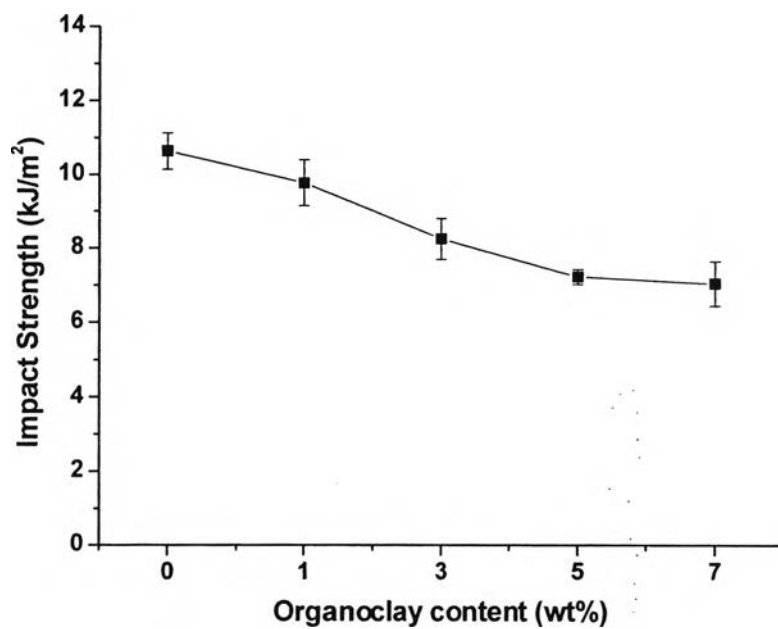
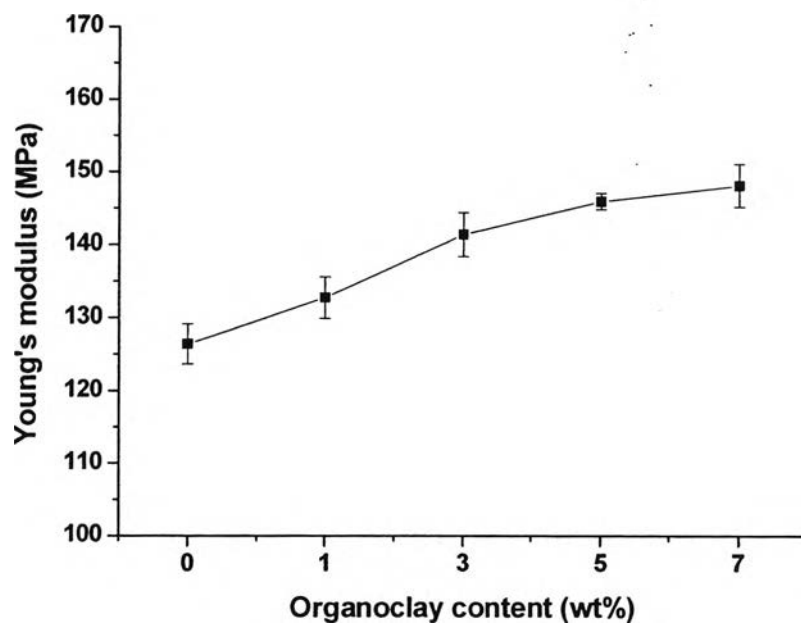
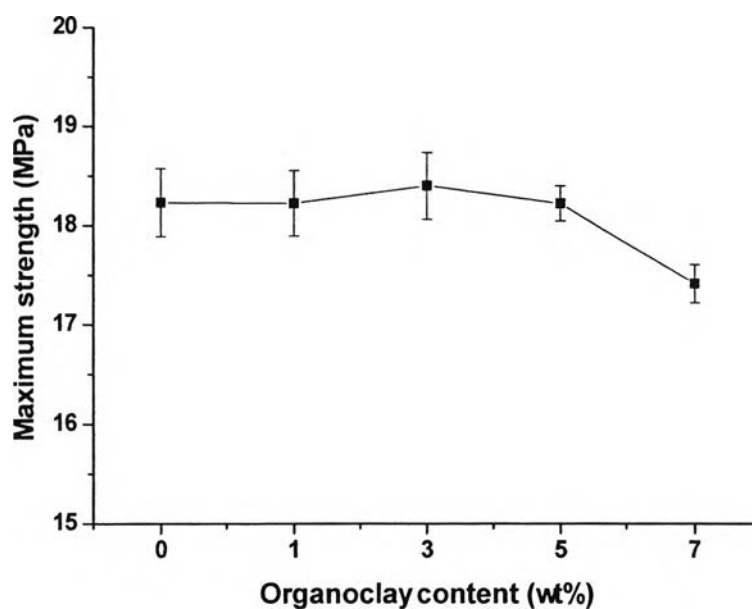


Figure 5.5 Impact strength of PCL nanoclay nanocomposites:



(a)

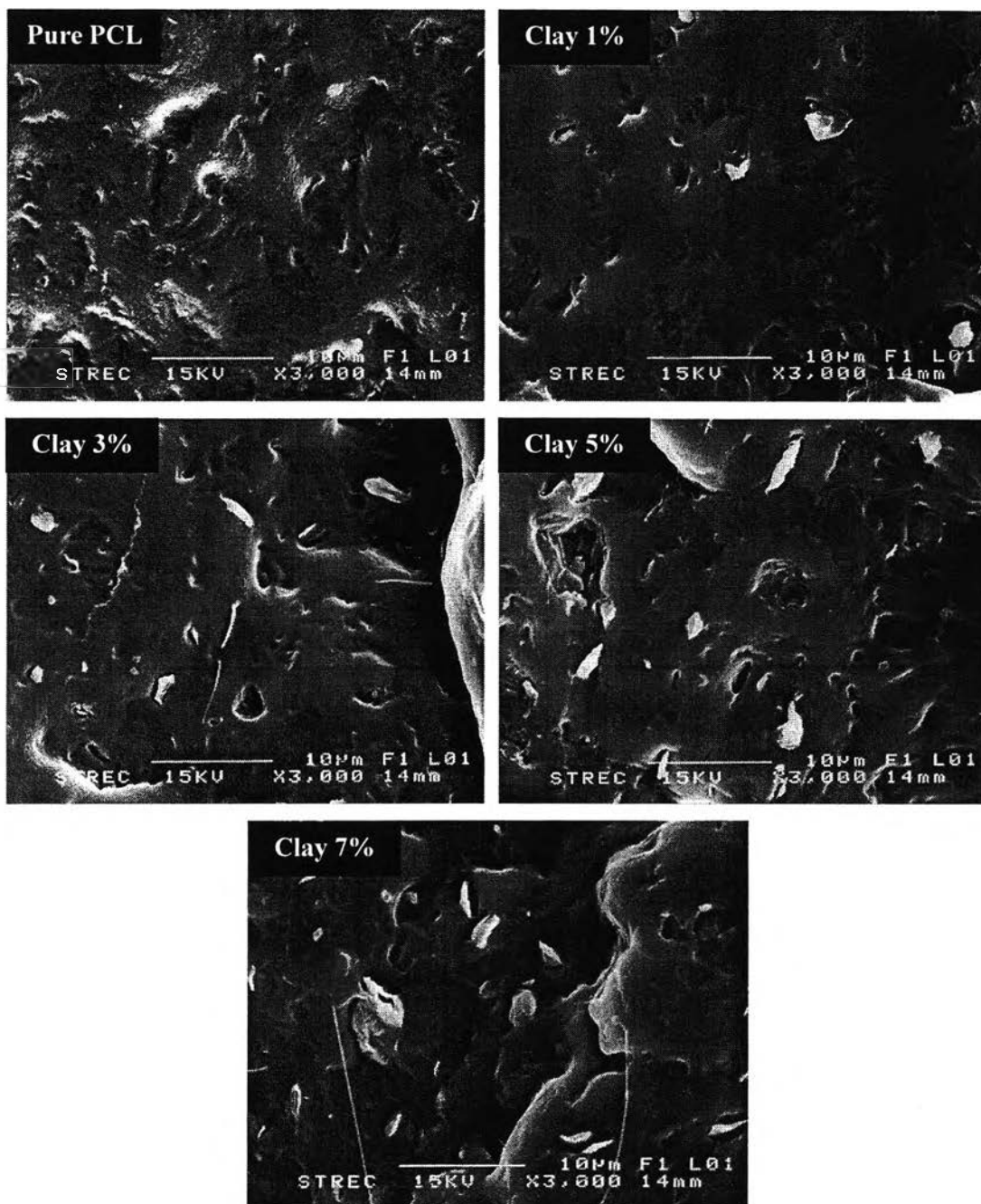


(b)

Figure 5.6 Tensile properties of PCL nanoclay nanocomposites (a) Young's modulus, (b) maximum strength.

5.4.5 Morphological characterization

The morphological study observed after impact testing is shown in Figure 5.7. Organoclays appear on and inside the surface of each nanocomposite, they disperse on the fractured surface of PCL. Voids occurring on the surface after impact testing is due to the lost of organoclay. The moderate compatibility of organoclay and PCL can be seen in these SEM images. Organoclays in these images are referred by the white plates, they show some good compatibility and some poor compatibility between PCL and themselves. Poor compatibility is determined by the area which contains organoclay surrounded by some voids and good compatibility is determined by the area which contains organoclay without any voids surround them.



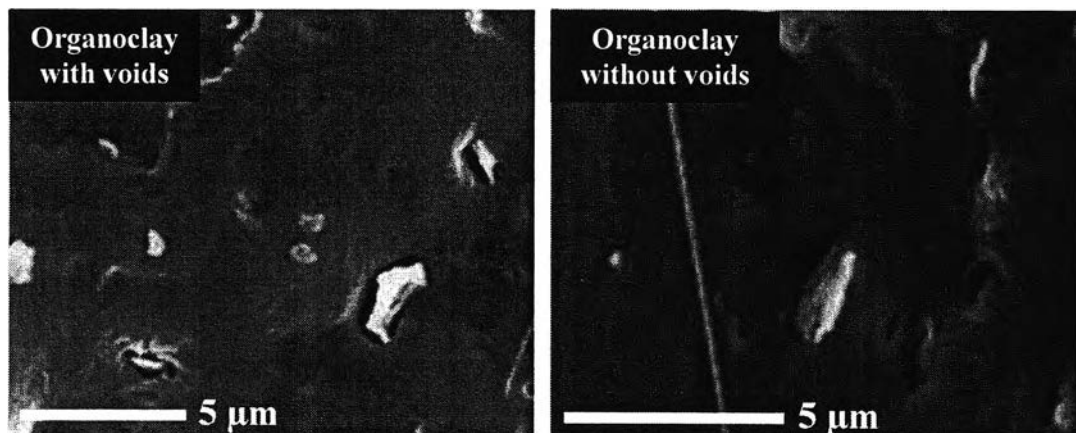


Figure 5.7 SEM images of fractured surface of PCL nanoclay nanocomposites after impact testing.

5.5 Conclusion

The effect of organoclay content on structure and mechanical properties were studied to consider the best one for use as mouth guard materials. The compatibility between organoclay and PCL was investigated by XRD pattern and SEM images. XRD patterns showed some exfoliated structure mixed with microstructure of organoclay and SEM images showed some compatibility between them. This could be concluded that the compatibility between organoclay and PCL was moderate. Impact strength of PCL nanoclay nanocomposites decreased when organoclay content increased. Young's modulus and storage modulus between 20 and 50°C increased when organoclay content increased. The addition of organoclay did not affect the melting behavior of PCL nanoclay nanocomposites but it could enhance the thermal stability.

However, the addition of organoclay could improve the modulus of PCL nanoclay nanocomposites at temperature range of 20 to 50°C which is the range of room temperature, body temperature, and warm water temperature that mouth guard materials will be used. PCL nanoclay nanocomposites with 3 wt% content of organoclay was more appropriate than the other content of organoclay for use as mouth guard materials.

5.6 Acknowledgement

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REFERENCES

- Chen, B. and Evans, J.R.G. (2008) Impact and tensile energies of fracture in polymer-clay nanocomposites. Polymer, 49, 5113-5118.
- Homminga, D., Goderis, B., Dolbnya, I., and Groeninckx, G. (2006) Crystallization behavior of polymer/montmorillonite nanocomposites. Part II. Intercalated poly(ϵ -caprolactone)/montmorillonite nanocomposites. Polymer, 47, 1620-1629.
- Jimenez, G., Ogata, N., Kawai, H., and Ogihara, T. (1997) Structure and thermal/mechanical properties of poly(ϵ -caprolactone)-clay blend. Journal of Applied Polymer Science, 64, 2211-2220.
- Kiersnowski, A. and Piglowski, J. (2004) Polymer-layered silicate nanocomposites based on poly(ϵ -caprolactone). European Polymer Journal, 40, 1199-1207.
- Kiersnowski, A., Dabrowski, P., Budde, H., Kressler, J., and Piglowski, J. (2004) Synthesis and structure of poly(ϵ -caprolactone)/synthetic montmorillonite nano-intercalates. European Polymer Journal, 40, 2591-2598.
- Lepoittevin, B., Devalckenaere, M., Pantoustier, N., Alexdandre, M., Kubies, D., Calberg, C., Jerome, R., and Dubois, P. (2002) Poly(ϵ -caprolactone)/clay nanocomposites prepared by melt intercalation: mechanical, thermal and rheological properties. Polymer, 43(14), 4017-4023.
- Lepoittevin, B., Pantoustier, N., Devalckenaere, M., Alexdandre, M., Calberg, C., Jerome, R., Henrist, C., Rulmont, A., and Dubois, P. (2003) Polymer/layered silicate nanocomposites by combined intercalative polymerization and melt intercalation: a masterbatch process. Polymer, 44, 2033-2040.
- Luduena, L.N., Alvarez, V.A., and Vazquez, A. (2007) Processing and micro structure of PCL/clay nanocomposites. Materials Science and Engineering A, 460-461, 121-129.
- Pandey, J.K., Raghunatha, Kuma, A.P., and Singh, R.P. (2005) An overview on the degradability of polymer nanocomposites. Polymer Degradation and Stability, 88, 234-250.
- Pantoustier, N., Lepoittevin B., Alexandre, M., Kubies, D., Calberg, C., Jerome, R., and Dubois, P. (2002) Biodegradable polyester layered silicate

- nanocomposites based on poly(ϵ -caprolactone). Polymer Engineering and Science, 42(9), 1928-1937.
- Ray, S.S. and Okamoto, M. (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. Progress in Polymer Science, 28, 1539-1641.
- Rezgiu, F., Swistek, M., Hiver, J.M., G'Sell, C., and Sadoun, T. (2005) Deformation and damage upon stretching of degradable polymers (PLA and PCL). Polymer, 46, 7370-7385.
- Wei, Z., Liu, Lian., Qu, Chao., and Qi, M. (2009) Microstructure analysis and thermal properties of L-lactide/ ϵ -caprolactone copolymers obtained with magnesium octoate. Polymer, 50, 1423-1429.
- Zeng, Q.H., Yu, A.B., Lu, G.Q., and Paul, D.R. (2005) Clay-based polymer nanocomposites: Research and commercial development. Journal of Nanoscience and Nanotechnology, 5, 1574-1592.