



CHAPTER IV

THE EFFECT OF MOLECULAR WEIGHT ON STRUCTURE AND MECHANICAL PROPERTIES OF POLYCAPROLACTONE

4.1 Abstract

Polycaprolactone (PCL) is biodegradable polyester, it is very tough and has melting point around 60°C. PCL becomes soft in warm water and can be shaped, therefore it is proper for use as boil and bite mouth guard. Before using PCL as mouth guard materials, the proper molecular weight should be concerned at this point. This work aims to study the effect of molecular weight on structure and mechanical properties of PCL in order to choose the appropriate one. The different molecular weights affected the mechanical properties and crystallization behavior of PCL. Impact strength of PCL increased as molecular weight increased. The morphology of each molecular weight was examined after impact testing, lower molecular weight showed higher roughness of surface. The different molecular weight did not affect the thermal stability and melting temperature of PCL. However, the lowest molecular weight PCL ($M_w \sim 17,000$) showed the highest crystallinity and T_c onset.

Keyword : Polycaprolactone, Molecular weight, Structure, Mechanical properties

4.2 Introduction

Mouth guards are plastic dental appliances (*Ja cobs, A.G. et al. 1967 and Kawakami, M. et al. 1987*) which is worn to provide a degree of protection for both the mouth's soft tissues (lips, cheeks, gums, tongue) and hard tissues (teeth and jaw bones). The most important criterion of mouth guards is the fit of its shape to the teeth. Custom mouth guards are the best types of mouth protectors that are individually made for an athlete. A well-designed custom mouth guard provide the greatest level of protection for an athlete as compared to the other types of mouth guards. However, custom mouth guards are difficult to make and have very high cost.

This research tries to make the mouth guard with fit shape, easy making, and suitable cost. Polycaprolactone (PCL) is the material chosen in this work, it is biodegradable polyester and very tough. The interesting property of PCL is its melting temperature about 60°C which is the temperature of warm water, it becomes soft and can be shaped around this temperature. Therefore, we can use this property to make boil and bite mouth guard with fit shape for each person. Although PCL is very tough but to use it as mouth guard materials, the mechanical properties should be concerned.

Polycaprolactone has been studied for many years. In 1989, *Sieverding, L.D.* studied about polycaprolactone modeling and molding compositions. In this work, polycaprolactone was expected to use as modeling materials which are softened and upon cooling, solidifies to a stiff material that retains the shape. High molecular weight polycaprolactone had been determined to develop certain deficiencies for this application when it was repeatedly worked in the melt. Two years later in 1991, dental impression process using polycaprolactone molding composition was studied by *Oxman, J.D. et al.* They blending high molecular weight (MW~40,000) and low molecular weight (MW~500-10,000) PCL at various compositions. The blends showed the improvement of modulus which is higher than the pure of high molecular weight PCL. The data showed that the composition had a sharp melting point at temperatures that would be acceptable in the mouth. At body temperature (~ 38°C), the molding composition exhibited solidity, usefully high modulus, and low plasticity.

The above reasons bring about this part of research. This chapter was focused on the effect of molecular weight on the structure and mechanical properties of PCL for choosing the appropriate one to use as mouth guard materials. The different molecular weight PCL in this chapter were synthesized by ring-opening polymerization of ϵ -caprolactone (*Storey, R.F., et al. 2001, Penczek, S. et al. 2007, and Kowalski, A. et al. 2007*) with the different monomer/catalyst mole ratio.

4.3 Experimental

4.3.1 Materials

ϵ -caprolactone ($C_6H_{10}O_2$) and tin (II) 2-ethylhexanoate ($Sn(Oct)_2$) were supplied by Fluka and Sigma using as monomer and catalyst, respectively. Toluene

(A.R. grade), chloroform (A.R. grade), and methanol (commercial grade) using as solvent for polymerization, dissolution, and precipitation, respectively were supplied by Labscan. Tetrahydrofuran (HPLC grade) for mobile phase of GPC was supplied by Burdick & Jackson.

4.3.2 Methodology

a) Synthesis of Different Molecular Weight PCL

ϵ -CL and stannous octoate with monomer/catalyst mole ratio at 2000, 4000, 6000, 8000, and 10000 were weighed into flask. All of them were dissolved in toluene 50 ml.

$[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$	Wt. of $\epsilon\text{-CL}$	Wt. of $\text{Sn}(\text{Oct})_2$
2000	130 g	0.231 g
4000	130 g	0.115 g
6000	130 g	0.077 g
8000	130 g	0.058 g
10000	130 g	0.046 g

The reaction was done under nitrogen atmosphere at 120°C for 24 h. After the reaction was completed, the product was dissolved in chloroform and then precipitated in cold methanol, and dried under vacuum at 40°C. The yield can be calculated by

$$\% \text{Yield} = \frac{\text{wt. of PCL}}{\text{wt. of } \epsilon\text{-CL}} \times 100$$

b) Preparation of Specimens for Testing The Mechanical Properties

The crude polymers obtained from solution ring-opening polymerization 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.

4.3.3 Characterization

a) Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of synthesized PCL was obtained using a Nicolet Nexus 670 FTIR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} . Specimen was prepared into film by solution casting in chloroform.

b) Gel Permeation Chromatography (GPC)

The different molecular weights of synthesized PCL were examined by GPC Shimadzu Model in THF solvent as the mobile phase, Waters Styragel THF Column, and RID-10A detector. The THF solvent was filtrated with MN 615 \varnothing 155 mm filter paper under the vacuum. The crude polymers were dissolved in THF at the concentration 0.5 wt% and filtrated with 0.45 mm diameter of cellulose acetate filter before injecting into the column. The conditions of this machine were 40°C column temperature, 1 ml/min flow rate, and 30 min run time. Molecular weight and molecular weight distribution of PCL were calculated in reference to a polystyrene calibration.

c) X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the crystal structure of synthesized PCL. 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. The specimens were observed on the 2θ range of 5 – 30 degree with scan speed 1 degree/min and scan step 0.01 degree.

d) 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 10ml/min.

e) 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.

f) 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.

g) 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.

h) Dynamic Mechanical Analysis (DMA)

DMA analyses were carried out by using a dynamic mechanical analyzer NETZSCH DMA 242 instrument. The specimen was 10 × 60 × 3 mm³ (width × length × 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.

i) Scanning Electron Microscope (SEM)

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

4.4 Results and Discussion

4.4.1 Chemical Analysis

The ring-opening polymerization of ϵ -caprolactone can be confirmed by IR spectra as shown in Figure 4.1. We can easily identify strong peak for carbonyl stretching mode at 1732 and 1169 cm^{-1} for the symmetric C-O-C stretching modes of the ester group. One of them is the characteristic peak of the chain such as 3441 cm^{-1} for hydroxyl end group of PCL. The peak at 1294 cm^{-1} is assigned to the backbone C-C and C-O stretching modes in the crystalline PCL (*Elzein, T. et al. 2004*).

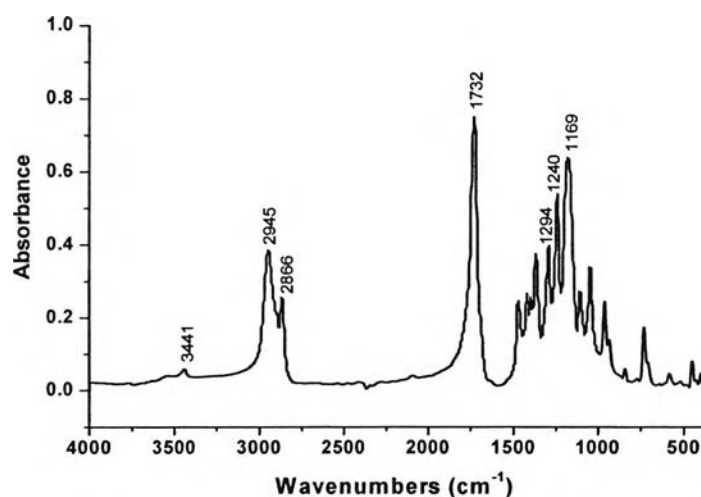


Figure 4.1 IR spectrum of polycaprolactone obtained by solution ring-opening polymerization.

Table 4.1 Characterization for IR spectrum of PCL

Position (cm^{-1})	Vibration mode
2945	Asymmetric CH_2 stretching
2866	Symmetric CH_2 stretching
1732	Carbonyl stretching
1294	C-O and C-C stretching in the crystalline phase
1240	Asymmetric COC stretching
1169	Symmetric COC stretching

4.4.2 Yield of PCL

After extraction the crude sample with metanol to remove non-reacted ϵ -caprolactone, % yield of all products was calculated by using following equation and shown in Table 4.2.

$$\% \text{Yield} = \frac{\text{wt. of PCL}}{\text{wt. of } \epsilon\text{-CL}} \times 100$$

Table 4.2 % yield of reacted ϵ -caprolactone after extraction the crude sample with methanol

Samples	$[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$	% Yield
PCL-A	2000	84.62
PCL-B	4000	81.48
PCL-C	6000	82.76
PCL-D	8000	78.26
PCL-E	10000	79.31

4.4.3 Molecular Weight Measurement

Molecular weight and molecular weight distribution of the resulting polymers were measured by using the gel permeation chromatography (GPC). GPC was carried out in tetrahydrofuran (THF) using a THF column with a refractometer index detector. Molecular weight and molecular weight distribution of these polymers were calculated in reference to a following polystyrene calibration in Figure 4.2 with the equation of calibration curve.

$$\text{Log } M_w = -0.5152t_R + 13.718$$

The different molecular weights of synthesized PCL are caused by monomer/catalyst ($\epsilon\text{-CL}/\text{Sn}(\text{Oct})_2$) mole ratio. M_w , M_n , and molecular weight distribution are shown in Table 4.3. The molecular weight at lower $[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$ exhibits higher molecular weight than the higher one.

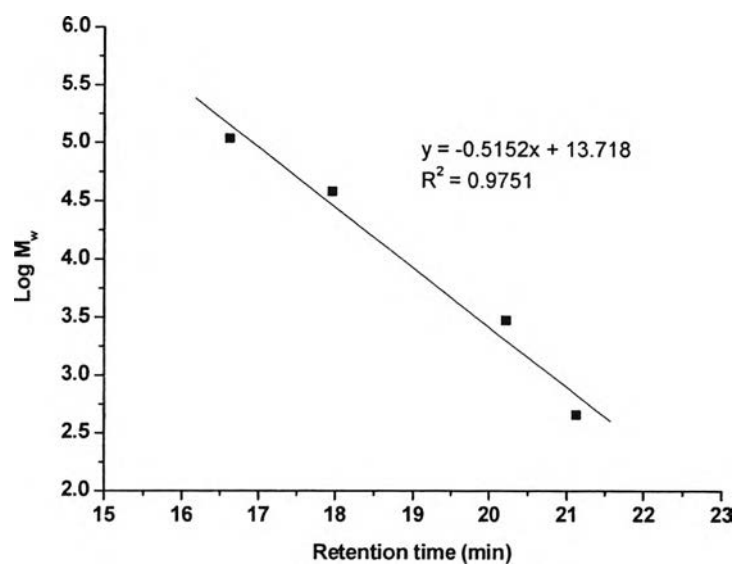
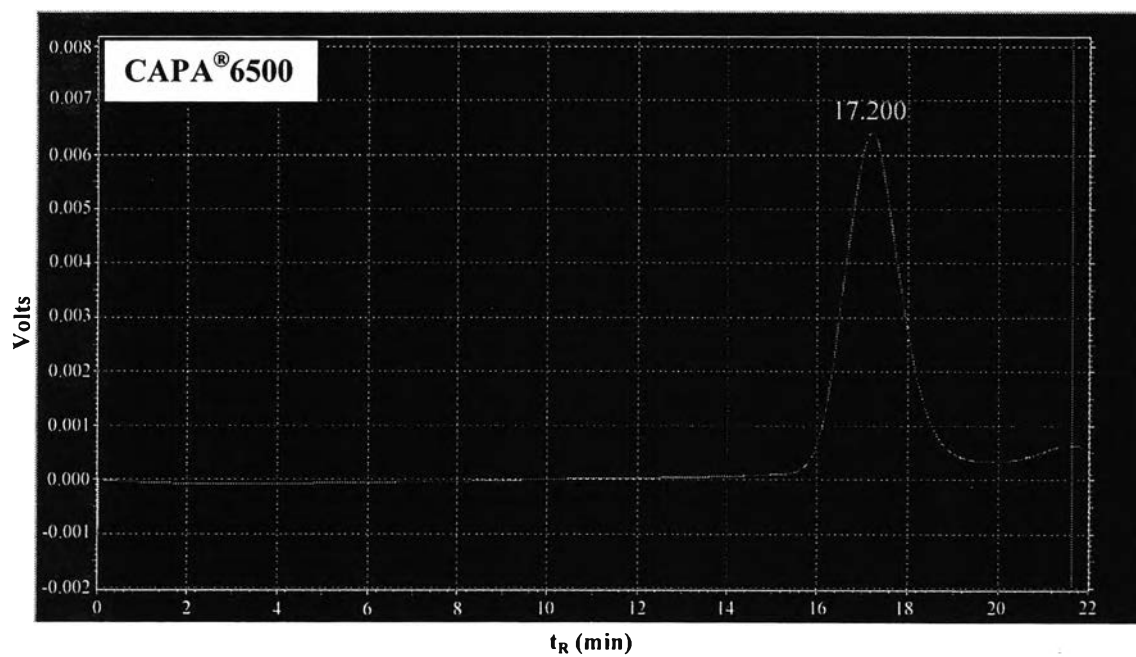
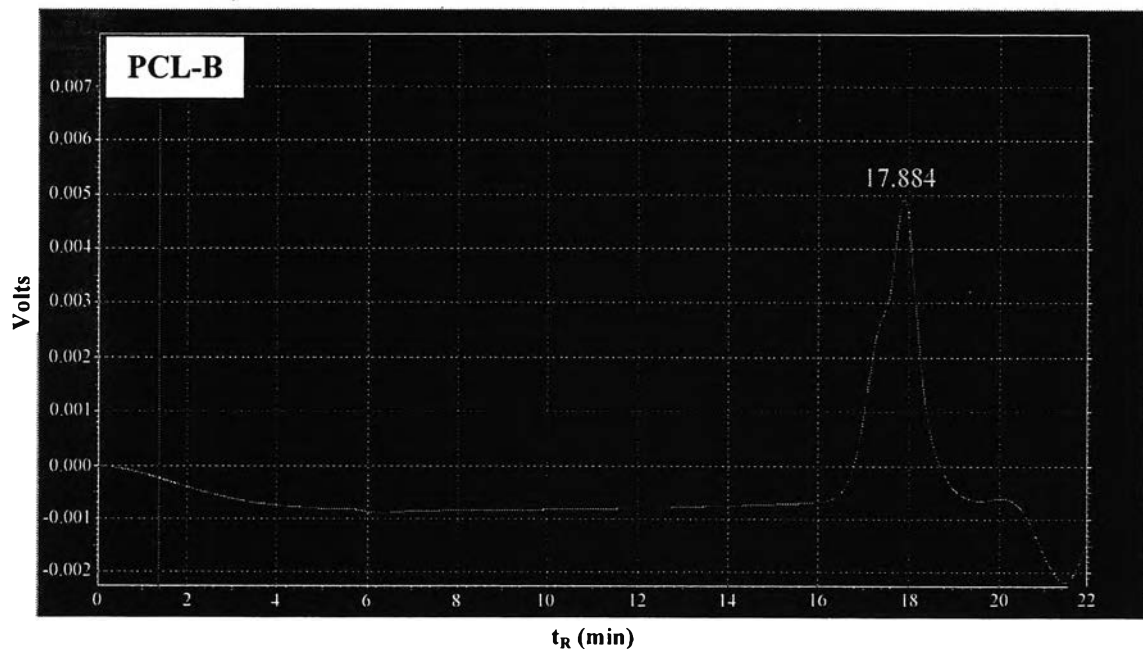
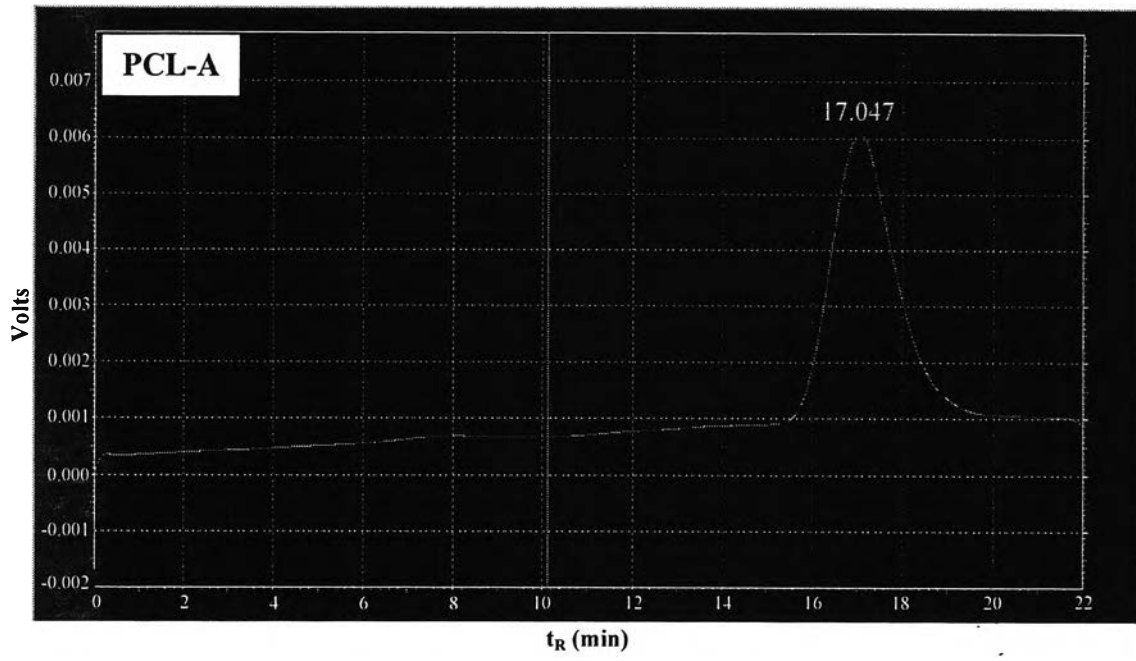
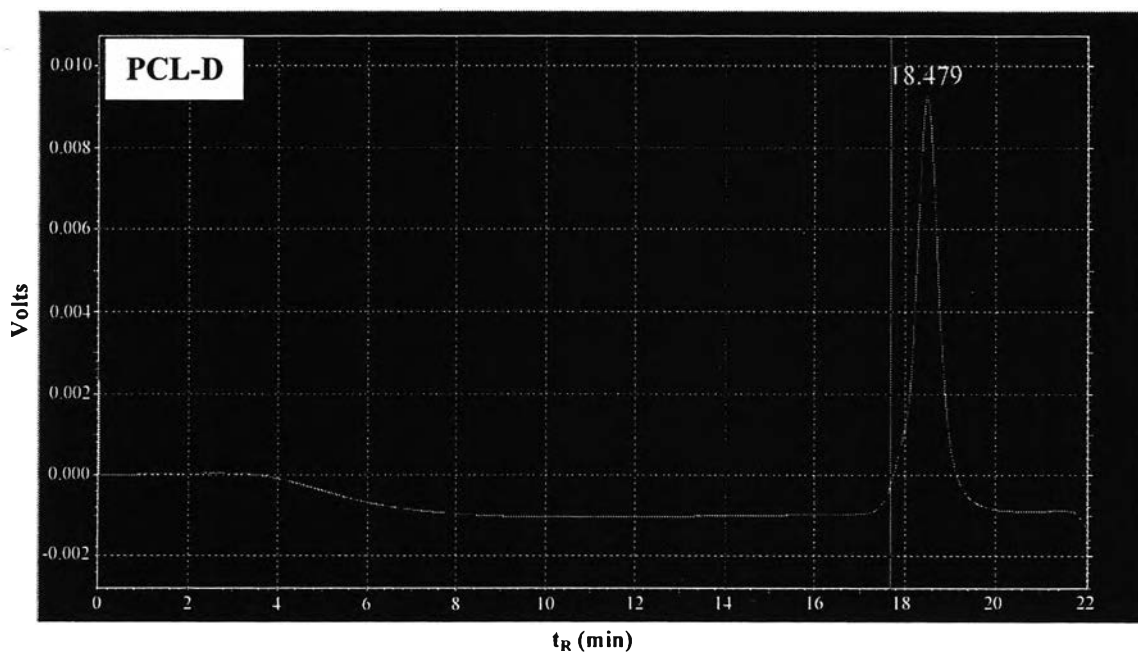
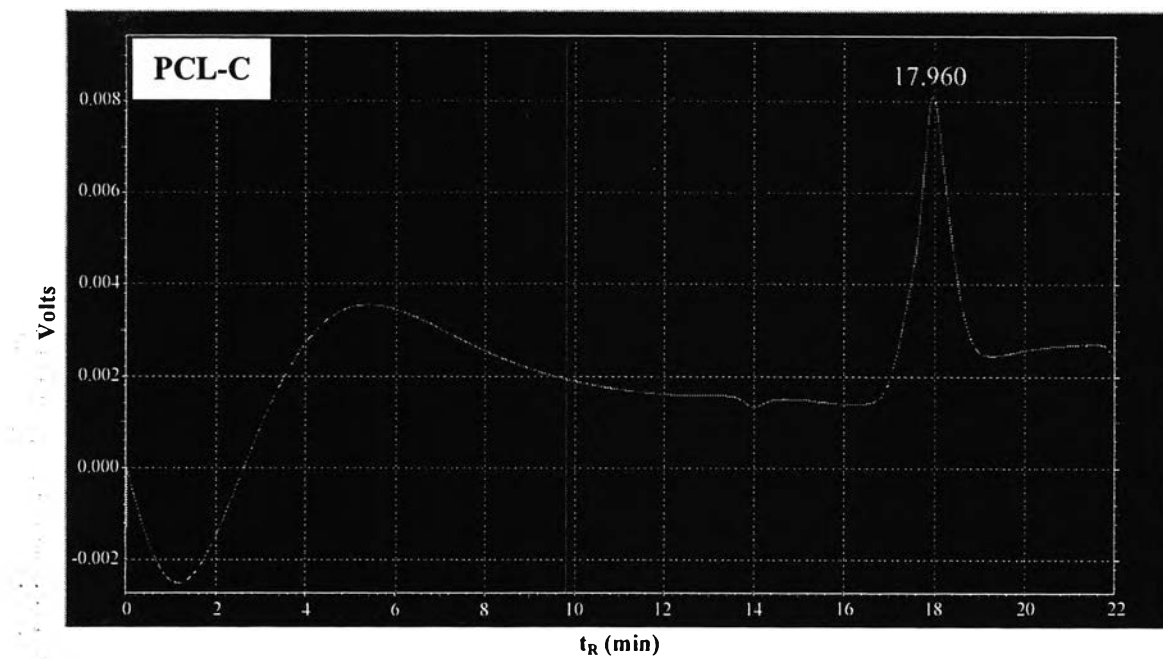


Figure 4.2 The polystyrene calibration for the calculation of molecular weight.







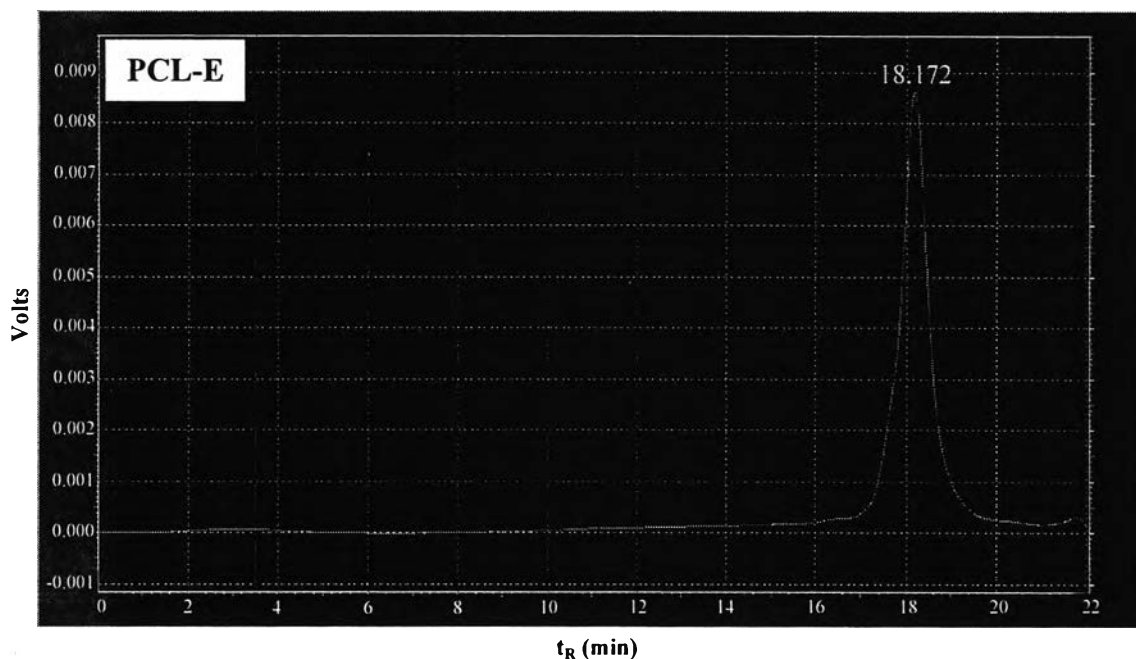


Figure 4.3 Chromatogram of different molecular weight PCL (0.5 wt% of PCL, THF solvent as a mobile phase, Waters Styragel THF Column, RID-10A detector, 1ml/min flow rate, and 30 min run time).

Table 4.3 Molecular weight and molecular weight distribution of PCL synthesized by using solution ring-opening polymerization

Samples	t_R	$[\epsilon\text{-CL}]/$ $[\text{Sn}(\text{Oct})_2]$	Wt. of $\text{Sn}(\text{Oct})_2$	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	$M_w/$ M_n
CAPA [®] 6500	17.200	-	-	8.42	5.21	1.62
PCL-A	17.047	2000	0.231 g	9.58	4.92	1.94
PCL-B	17.884	4000	0.115 g	4.36	3.17	1.37
PCL-C	17.960	6000	0.077 g	3.27	2.66	1.23
PCL-D	18.479	8000	0.058 g	1.70	1.43	1.19
PCL-E	18.172	10000	0.046 g	2.47	1.99	1.25

As results in Table 4.3 and Figure 4.4, molecular weight of PCL increases when $[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$ decreases and exhibits the highest one at $[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$ of 2000. Catalyst concentration increases the molecular weight of

PCL due to high concentration of catalyst can improve the reactivity of the reaction (Hyon, S.H. et al. 1997). The ring-opening polymerization of cyclic monomers is an equilibrium reaction; in the equilibrium state, besides the polymer the monomer and a homologous series of cyclic oligomers are observed. During polymerization back-biting and/or end-biting reactions may occur upon which the ring-chain equilibrium is established. This is the reason for a decrease of molecular weight when catalyst content decreases.

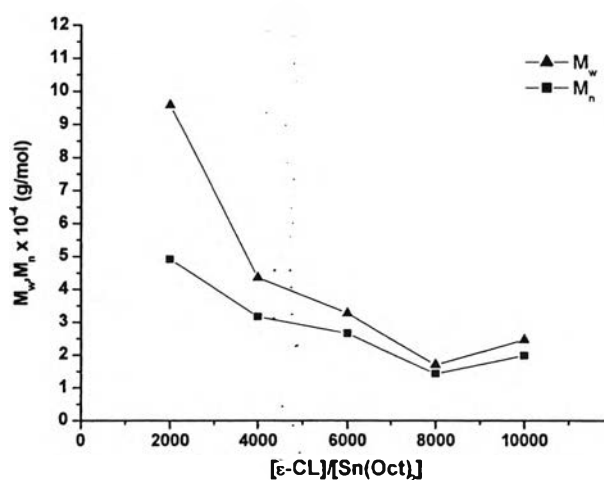


Figure 4.4 The effect of $[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$ on M_w and M_n of synthesized PCL.

4.4.4 Structural Properties

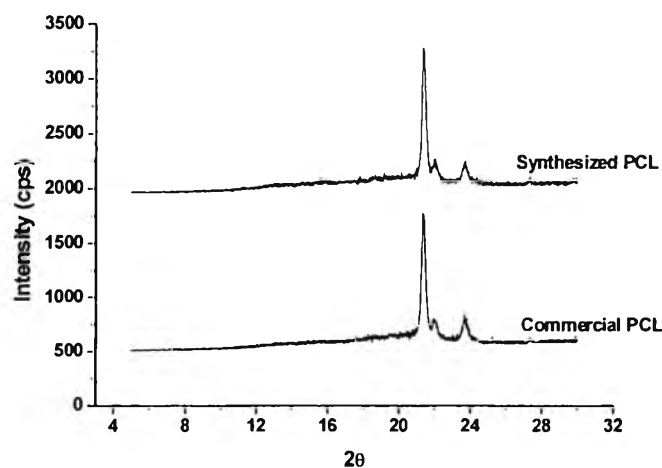


Figure 4.5 XRD patterns of commercial PCL (CAPA[®]6500) and PCL-A with the highest molecular weight synthesized from the solution ring-opening polymerization.

XRD patterns in Figure 4.5 are the comparison between commercial PCL (CAPA[®]6500) and PCL-A with the highest molecular weight synthesized from the solution ring-opening polymerization. Commercial PCL exhibits a sharp crystalline peak at $2\theta = 21.38, 21.96,$ and 23.73 . (Wei, Z. *et al.* 2009 and Rezgui, F. *et al.* 2005). Synthesized PCL also exhibits the crystalline peak close to the commercial one at $2\theta = 21.39, 21.99,$ and 23.74 . The same crystal structure from XRD patterns confirms the success of ring-opening polymerization of PCL.

4.4.5 Thermal Analysis

Thermal behavior of the different molecular weight PCL was carried out by DSC measurement. Results of each molecular weight PCL are shown in Figure 4.6 for second heating and Figure 4.7 for cooling. Second heating of the samples from -20 to 100°C with a constant heating rate of $10^{\circ}\text{C}/\text{min}$ displays only melting peak at temperature about 55°C (Chun, Y.S. *et al.* 2000). The different molecular weights do not affect the melting temperature of PCL but they affect degree of crystallinity as shown in table 4.4. It shows that degree of crystallinity increases with a decreasing of molecular weight.

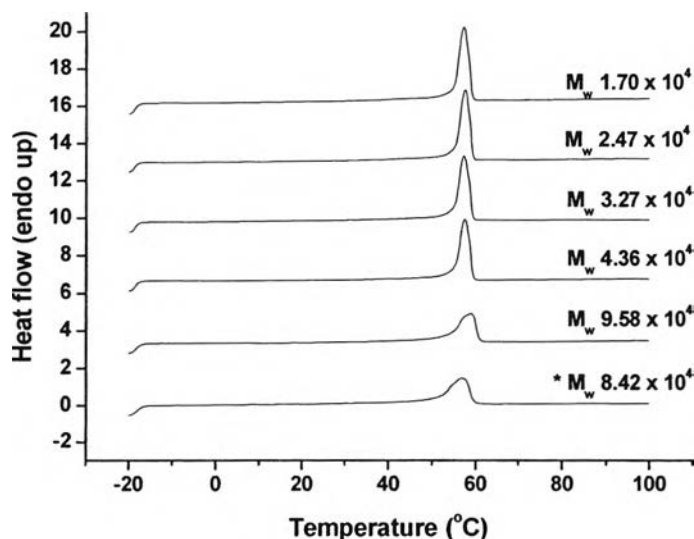


Figure 4.6 DSC-measurement of different molecular weight PCL (second heating at $10^{\circ}\text{C}/\text{min}$ heating rate), *CAPA[®]6500.

Table 4.4 T_m , T_c , and degree of crystallinity of different molecular weight PCL

Samples	$M_w \times 10^{-4}$ (g/mol)	ΔH_m (J/g) ^a	Degree of crystallinity ^b	T_m (°C)	T_c (°C)
CAPA [®] 6500	8.42	54.1955	39.85	56.9	27.6
PCL-A	9.58	54.6922	40.21	58.9	25.1
PCL-B	4.36	66.4482	48.86	57.5	28.5
PCL-C	3.27	70.9940	52.20	57.2	28.8
PCL-D	1.70	77.7839	57.19	57.2	31.5
PCL-E	2.47	71.8478	52.83	57.5	30.8

^a Melting enthalpy

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

The cooling of each sample shows the effect of molecular weight on crystallization temperature. Crystallization temperature shifts to higher temperature when molecular weight increases because PCL of low molecular weight has shorter chain so it can readily crystallize compared to high molecular weight of PCL.

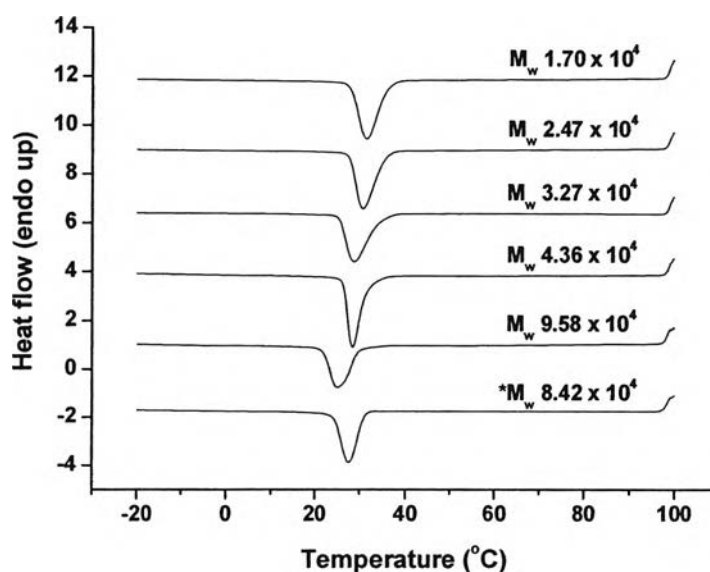


Figure 4.7 DSC-measurement of different molecular weight PCL (cooling at 10°C/min cooling rate) *CAPA[®]6500.

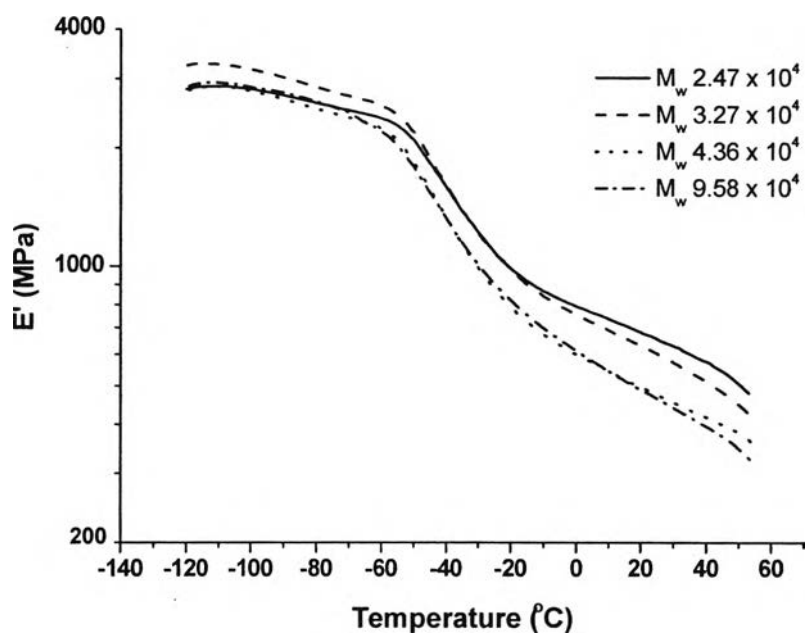
Thermal stability of different molecular weight PCL was investigated by TGA but it does not show any significant changes at all. The degradation temperature (T_d) of PCL was observed at about 410°C (*Ruseckaite, R.A. et al. 2003*) and T_d onset at about 372°C as shown in Table 4.5.

Table 4.5 Thermal stability of different molecular weight PCL

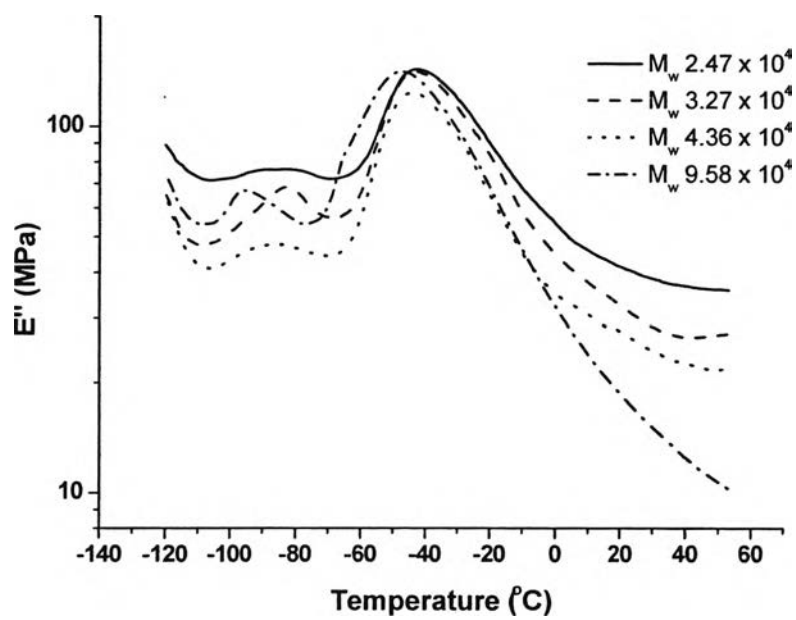
Samples	$M_w \times 10^{-4}$ (g/mol)	T_d onset (°C)	T_d (°C)	Char residue (%)
CAPA [®] 6500	8.42	369.1	410.0	0.8
PCL-A	9.58	372.4	410.2	0.8
PCL-B	4.36	369.9	410.7	0.7
PCL-C	3.27	372.1	410.9	0.6
PCL-D	1.70	374.4	411.3	0.7
PCL-E	2.47	376.4	411.7	0.8

4.4.6 Dynamic Mechanical Analysis

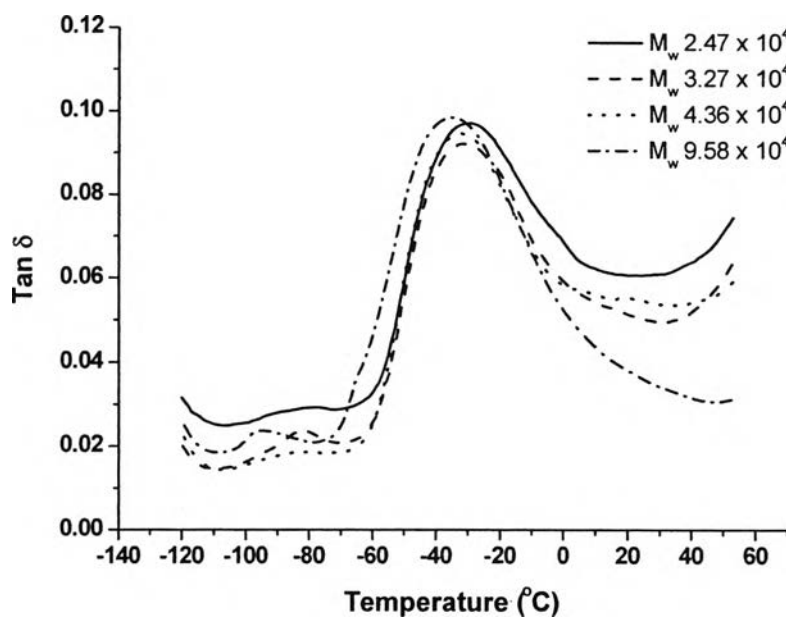
The DMA results for the different molecular weight PCL are presented in Figures 4.8. PCL-D or PCL with the lowest molecular weight ($M_w \sim 1.70 \times 10^4$) does not present in this figure because it is too brittle to clamp before the test. Figures 4.8 (a) and (b) show the storage modulus (E') and the loss modulus (E'') of different molecular weight PCL as the function of temperature. The storage modulus drops drastically between -60°C and -20°C from 2200-2500 MPa to 800-1000 MPa which is its glass-transition region, and gradually decreases between 0°C and 55°C from 600-800 MPa to 300-500 MPa. The storage modulus of PCL in the temperature range of 0 to 55°C increases when molecular weight decreases. PCL of $M_w 2.47 \times 10^4$ and 3.27×10^4 g/mol exhibit higher storage modulus than PCL of $M_w 4.36 \times 10^4$ and 9.58×10^4 g/mol because they have lower molecular weight distribution as shown in Table 4.3. The decreasing of storage modulus with the increasing of molecular weight distribution can be described by the plasticizing effect. The low molecular weight PCL in high molecular weight distribution system acts as a plasticizer to reduce the storage modulus.



(a)



(b)



(c)

Figure 4.8 DMA results of different molecular weight PCL (a) E' , (b) E'' , and (c) $\tan \delta$ as the function of temperature.

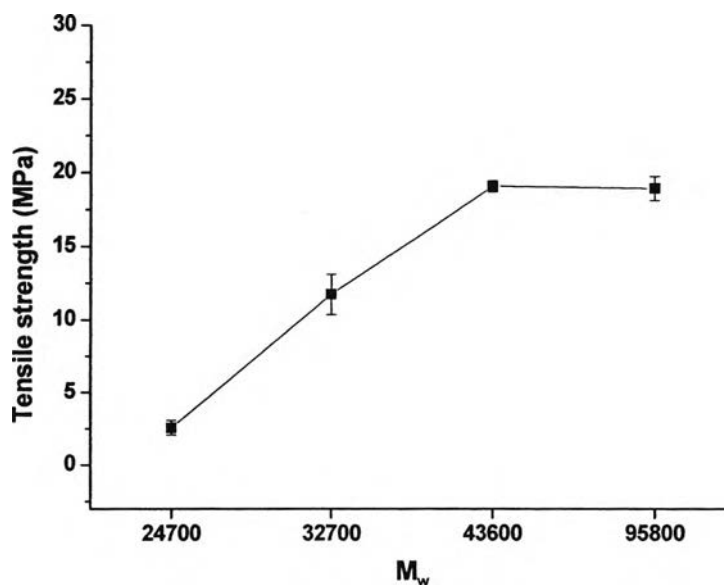
The glass-transition temperature taken at the maximum of $\tan \delta$ peaks does not significantly change for all molecular weight as shown in Table 4.6. However, PCL with the highest molecular weight shows the lowest glass transition temperature at -34.5°C , this causes by the effect of molecular weight distribution. PCL-A has higher molecular weight than the others and also has higher molecular weight distribution. The low molecular weight in PCL-A acts as the plasticizer and causes the decreasing of glass transition temperature. Therefore, it can be concluded that the glass-transition temperature of PCL does not depend on the molecular weight but depend on molecular weight distribution.

Table 4.6 Glass transition temperature of different molecular weight PCL

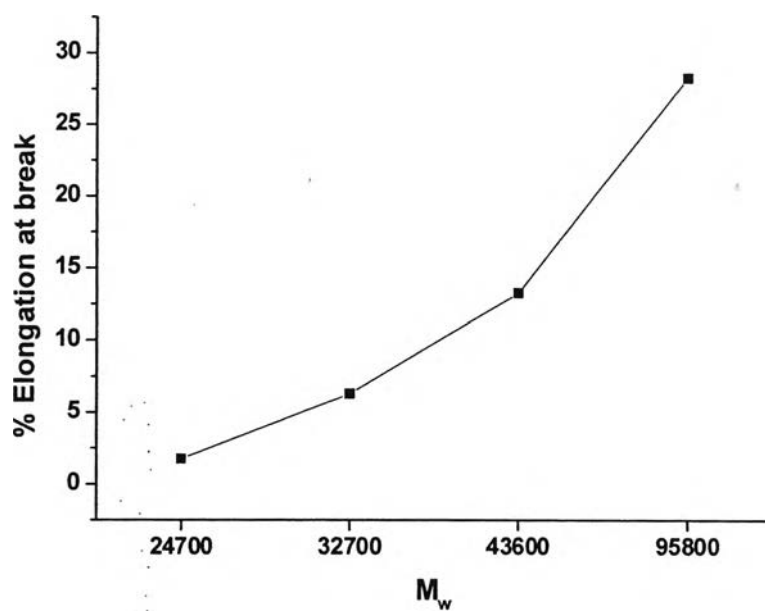
Samples	$M_w \times 10^{-4}$ (g/mol)	T_g ($^{\circ}\text{C}$)
PCL-A	9.58	-34.5
PCL-B	4.36	-31.7
PCL-C	3.27	-31.5
PCL-D	1.70	-
PCL-E	2.47	-30.0

4.4.7 Mechanical Properties

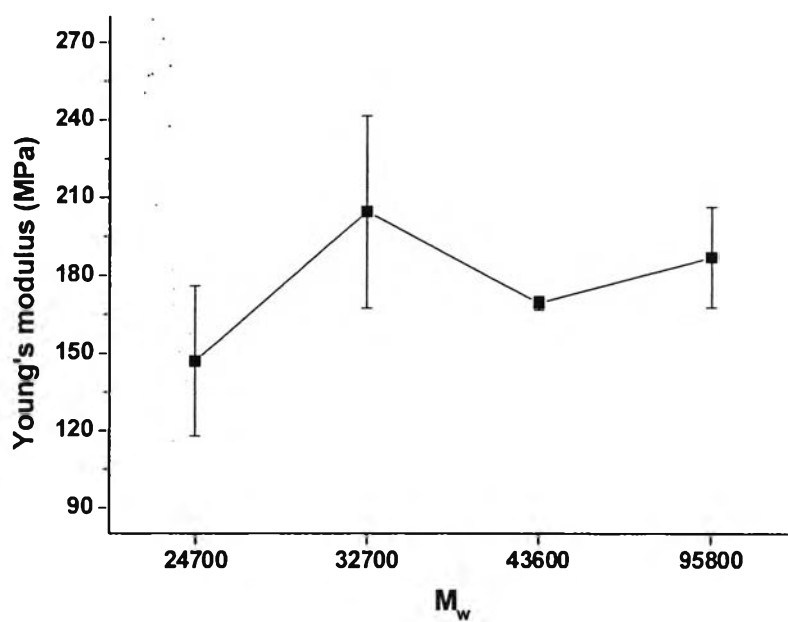
Tensile properties of different molecular weight PCL are shown in Figure 4.9. Tensile strength, %elongation at break, and Young's modulus were observed for tensile properties. The lowest molecular weight synthesized PCL ($M_w \sim 17000$) cannot be examined for tensile properties because it is very brittle so that it cannot be prepared for tensile testing. The results show tendency clearly for %elongation at break which increases when molecular weight increases. The observation of tensile strength shows the improvement of high molecular weight compared to the lowest one. The improvement is caused by the entanglement of the chains. Young's modulus does not show significant changes between each others (Grosvenor, M.P. et al. 1996).



(a)



(b)



(c)

Figure 4.9 Tensile properties of different molecular weight PCL (a) tensile strength, (b) % elongation at break, and (c) Young's modulus.

PCL with different molecular weights were tested for impact strength and tensile properties to study the effect of molecular weight on these mechanical properties. The impact strength of each molecular weight is shown in Figure 4.10, it increases as molecular weight increases. This situation can be described by the different chain sizes of PCL, the higher molecular weight means the longer chain of PCL. When specimens absorb some energy from the pendulum load, the entanglement of long chain causes higher energy dissipation than short chain. Therefore, the impact strength is affected by the different molecular weights of PCL by showing the highest impact strength at M_w 95800.

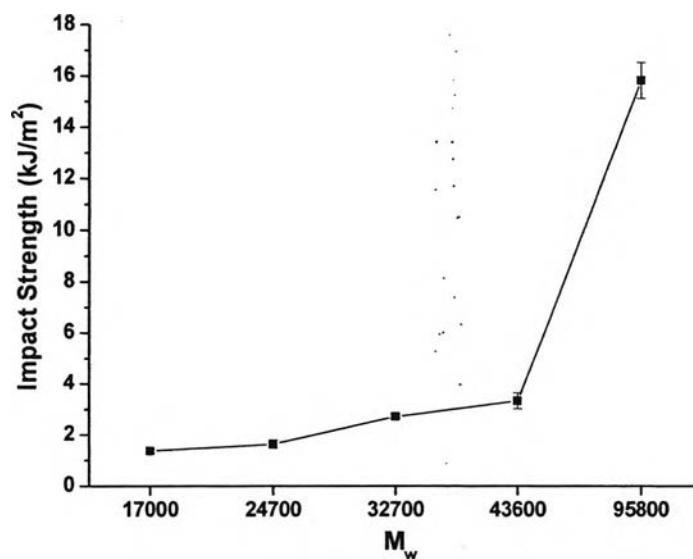


Figure 4.10 Impact strength of different molecular weight PCL.

4.4.8 Morphological Characterization

Figure 4.11 represents to the fractured surface of PCL with various molecular weights. The morphological study was observed after impact testing. The fracture of high molecular weight PCL shows the smooth crack whereas the sharp crack is observed in low molecular weight PCL. The sharp crack of low molecular weight exhibits the brittleness of PCL which is increased when molecular weight decreases. The sharp crack represented by white edge is caused by cracking of grain boundary of crystal. Lower molecular weight PCL shows higher amount of cracking that corresponds to degree of crystallinity and brittleness of the sample.

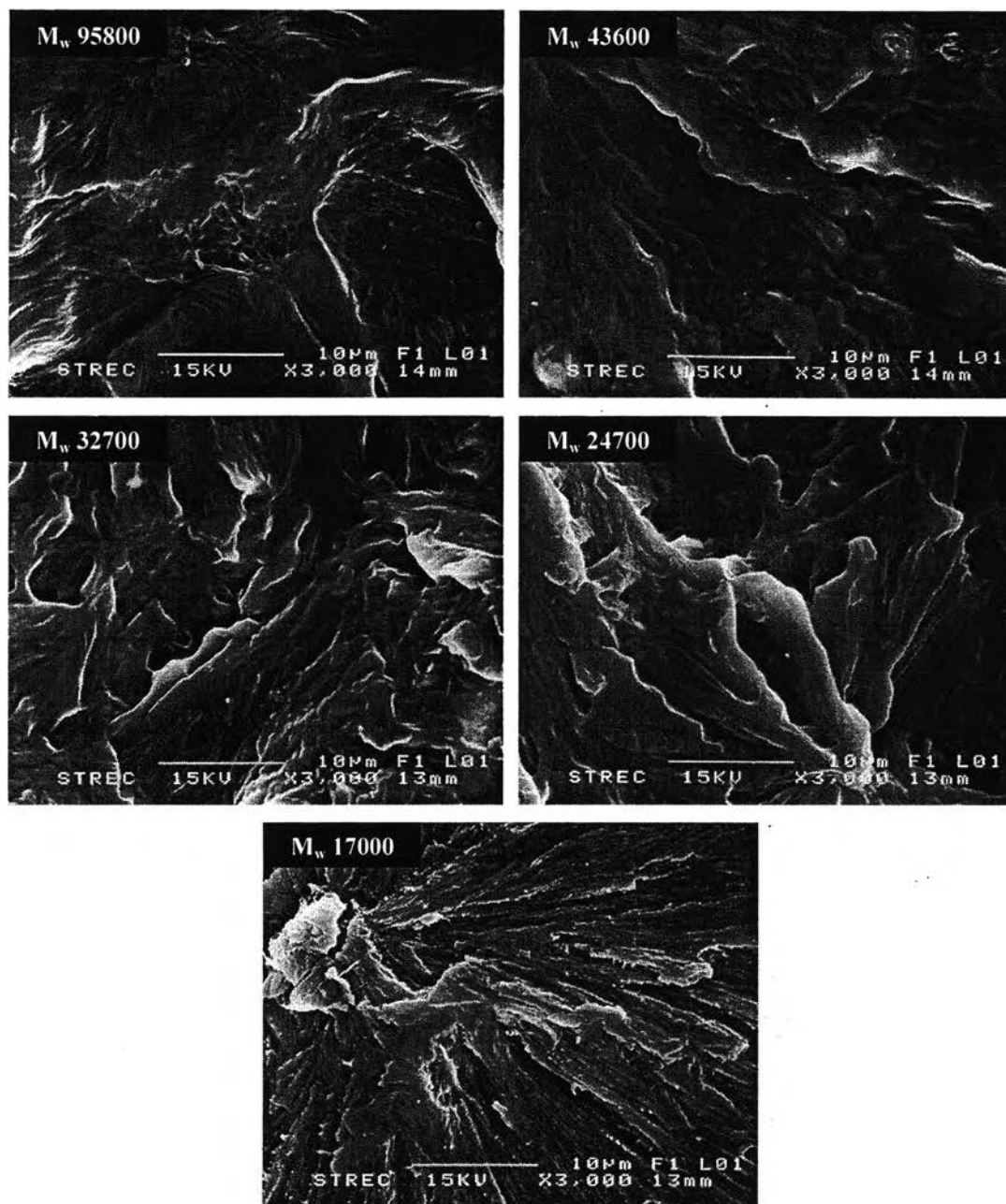


Figure 4.11 SEM images of fractured surface of different molecular weight PCL after impact testing.

4.5 Conclusion

The effect of molecular weight on structure and mechanical properties were studied to consider the best one for use as mouth guard materials. Each molecular

weight PCL was synthesized by solution ring-opening polymerization in different $[\epsilon\text{-CL}]/[\text{Sn}(\text{Oct})_2]$. All synthesized PCL were confirmed by FTIR which occurs the strong peak for carbonyl stretching mode at 1732 cm^{-1} and 1169 cm^{-1} for the symmetric C-O-C stretching modes of the ester group. Each synthesized PCL showed different molecular weights and was further tested for other properties. The highest molecular weight PCL was compared to commercial one for XRD pattern and exhibited the same crystal structure. As results, the mechanical properties of PCL were affected by molecular weight. Higher molecular weight showed higher impact strength and higher %elongation at break for tensile properties. The storage modulus of PCL from DMA showed higher value at lower molecular weight. Although low molecular weight had higher modulus but it was too brittle to use for any applications.

The molecular weight affected some properties of PCL but to use it as mouth guard materials, mechanical properties should be concerned. Two important properties, impact strength and modulus were improved when molecular weight increased. Therefore, PCL using as mouth guard material should has high molecular weight.

4.6 Acknowledgement

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