CHAPTER VI

THE EFFECT OF POLYCAPROLACTONE CONTENT ON STRUCTURE AND MECHANICAL PROPERTIES OF ETHYLENE VINYL ACETATE-graft-POLYCAPROLACTONE

6.1 Abstract

Polycaprolactone (PCL) using as mouth guard materials should has high molecular weight in order to exhibit good mechanical properties. Many previous researches modified PCL by adding fillers such as clay, starch, etc. and study the properties of those composites. This work tried another way to modify PCL by adding soft part into PCL system. EVA-g-PCL is the system of this method and it was investigated for the structure and mechanical properties. This work studied 3 compositions of EVA-g-PCL which are 1:1, 1:5, and 1:10 (EVA:ε-CL). As results, these graft copolymers had lower modulus and thermal stability of PCL phase decreased obviously from 370°C to around 300°C. These graft copolymers also showed the interesting property that is the decreasing of melting point from pure PCL and EVA, which bring about more viscoelasticity allowing better shaping of mouth guard materials at lower temperature

Keyword : Polycaprolactone, Ethylene vinyl acetate, Graft copolymer, Structure, Mechanical properties

6.2 Introduction

Polycaprolactone has suitable properties for making mouth guard materials and mechanical properties are the important point of those materials. The addition of organoclay is the first way to modify PCL to improve mechanical properties. The other way is the modification of its structure. In 2002, *Jiang, H. et al.* studied the system of graft copolymer between ethylene vinyl alcohol (EVOH) and PCL. EVOH is the backbone of this graft copolymer. Hydroxyl group of EVOH acted as an initiator of the ring-opening polymerization to open the ring of ε-caprolactone.

Melting temperature of EVOH-g-PCL showed the 20°C lower than that of pure PCL. The melting temperature of graft copolymer about 40°C is the proper temperature for shaping the mouth guard materials. This work brings about the idea of modifying of PCL by grafting method. The system of PCL graft copolymer with another materials has been widely studied by basic principle of the initiating group to start the ring-opening polymerization (*Chen, L. et al. 2005, Dubois, P. et al. 1999, Wang, C. et al. 2006, and Janata, M. et al. 2003*).

Ethylene vinyl acetate (EVA) is the interesting one because it approaches elastomeric materials in softness and flexibility; and can be processed like other thermoplastics. Graft copolymer of EVA with other polymer was used to studied in 2004 by *Cheng, S.K. et al.* They studied the system of EVA-g-PMMA, the results showed the improvement of toughness, impact strength, and higher elongation as increasing of EVA content. Although EVA is interesting for use as the backbone of graft copolymer but it does not contain hydroxyl group or other groups to initiate the ring-opening polymerization. Acetate group cannot be the initiator for opening lactone ring. However, this problem can be solved by replacing acetate group with hydroxyl group through transesterification. Due to the structure of EVA after transesterification called modified EVA look like EVOH, therefore the graft copolymer using modified EVA should exhibits the properties close to EVOH-g-PCL that was refered above.

This part of research aims to modify PCL by using EVA as backbone of graft copolymer and grafts EVA by PCL in different contents. The obtained graft copolymers were investigated in structure and mechanical properties.

6.2 Experimental

6.3.1 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. Ethylene vinyl acetate (EVA) was supplied by TPI Polene Public Co., Ltd. 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) and ethyl acetate for extraction of crude samples supplied by Burdick & Jackson and Labscan, respectively.

6.3.2 Methodology

a) Transesterification of EVA

EVA copolymer was partially hydrolyzed in a homogeneous medium. In a typical reaction, 10 g of EVA was solubilized in 100 ml of toluene at 70°C under stirring. 10 ml of a 2 wt% solution of sodium hydroxide in methanol was added and the reaction was carried out under reflux for 60 min. The polymeric material was precipitated into methanol and dried in a vacuum oven at 60°C for 24 h. The final product was called modified EVA

b) Synthesis of EVA-g-PCL

ε-CL, stannous octoate (monomer/catalyst mole ratio = 2000) and modified EVA as initiator were weighed into flask. EVA-g-PCL was synthesized into 3 weight ratios of 1:1, 1:5, and 1:10 (Modified EVA:ε-CL). Modified EVA was dissolved in 100 ml toluene then ε-CL and stannous octoate were added into flask. 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.

c) Soxhlet Extraction

The resulting graft copolymers obtained from the ring-opening polymerization were purified by extraction with ethyl acetate at the temperature about 190°C for 3 h to extract modified EVA, following by extraction with tetrahydrofuran at the temperature about 160°C for 3 h to extract the homopolymer PCL. After that the resulting yields were dried in vacuum oven at the temperature of 50°C. Then the extracted polymers were characterized by FTIR spectrometer for studying the chemical structure and calculating %yield by the following equation

$$\%\text{Yield} = \frac{\text{wt.of EVA} - \text{g} - \text{PCL}}{\text{wt.of Modified EVA} + \text{wt.of } \varepsilon - \text{CL}} \times 100$$

d) Preparation of Specimens for Testing The Mechanical Properties

EVA-g-PCL 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 investigation of the tensile properties, impact strength, and dynamic mechanical properties.

6.3.3 Characterization

a) Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of EVA, modified EVA, PCL, and EVA-g-PCL film were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1}. Specimens were prepared into film by solution casting using chloroform as a solvent.

b) X-ray Diffractometer (XRD)

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

c) 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 N_2 atmosphere with a flow rate of 10 ml/min.

d) 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 N_2 90 ml/min.

e) 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.

f) 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.

g) Dynamic Mechanical Analysis (DMA)

DMA analyses were carried out by using a dynamic mechanical analyzer NETZSCH DMA 242 instrument. The specimen was $10 \times 60 \times 3$ mm^3 (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.

h) Scanning Electron Microscope (SEM)

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

6.4 Results and Discussion

6.4.1 Chemical Analysis of Modified EVA

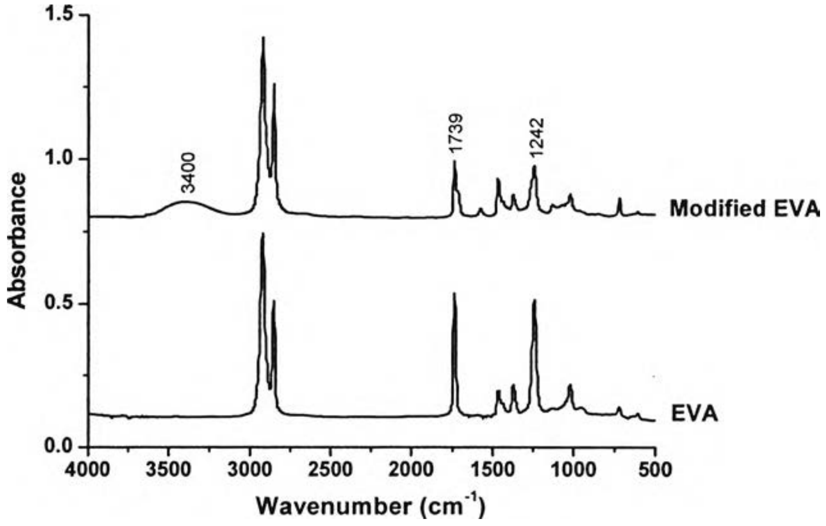
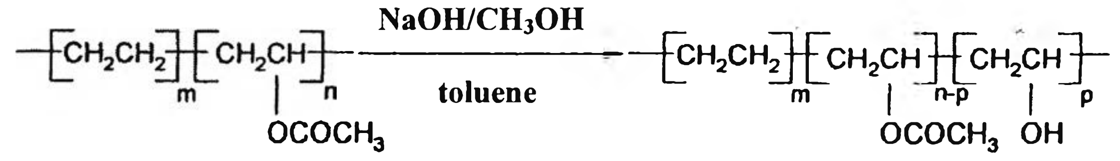


Figure 6.1 IR spectrum of EVA and modified EVA.



$$-\left[CH_2CH_2\right]_m\left[\underset{OCOCH_3}{\underset{|}{CH_2CH}}\right]_n- \xrightarrow[\text{toluene}]{NaOH/CH_3OH} -\left[CH_2CH_2\right]_m\left[\underset{OCOCH_3}{\underset{|}{CH_2CH}}\right]_{n-p}\left[\underset{OH}{\underset{|}{CH_2CH}}\right]_p-$$

Figure 6.2 Transesterification of EVA (*Garcia, F.G. et al. 2002*).

The transesterification of EVA in Figure 6.2 shows the modifying of acetate group to hydroxyl group. The success of modifying can be confirmed by the FT-IR in Figure 6.1 which shows the characteristic -OH group around 3250 – 3500 cm^{-1} (*Garcia, F.G. et al. 2002*). The other characteristics in IR spectrum which can confirm the success of modifying are the peak of carbonyl stretching and asymmetric C-O-C stretching at 1739 and 1242 cm^{-1}, respectively. The decreasing of these two peaks can be described by the partial disappearance of carbonyl group on vinyl acetate.

The modified EVA is the backbone polymer for the graft copolymer with PCL. Hydroxyl group of modified EVA acts as the intiator to start the ring-opening polymerization of ε-CL (*Jiang, H. et al. 2002 and Becquart, F. et al. 2006*).

6.4.2 Chemical Analysis of EVA-g-PCL

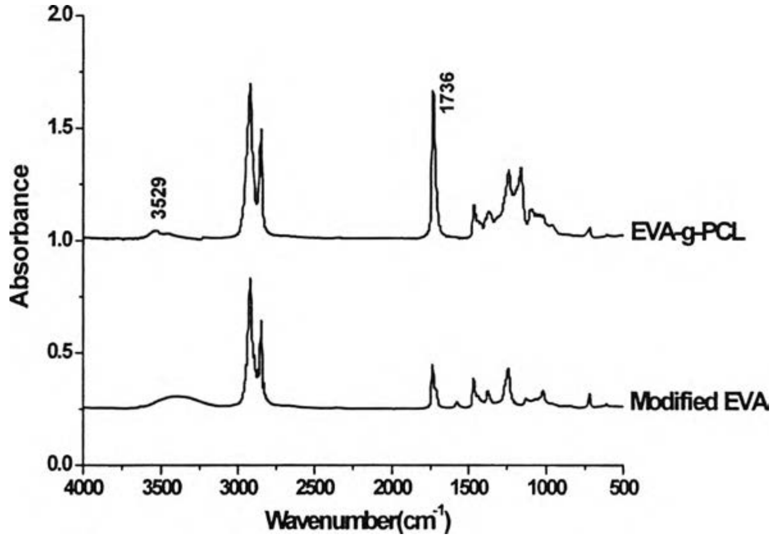


Figure 6.3 IR spectrum of modified EVA and EVA-g-PCL.

The grafting reaction occured through the ring-opening polymerization of ε-caprolactone. EVA-g-PCL can be confirmed by FTIR results showing new peak at 3529 cm^{-1} which is the characteristic peak of -OH group in PCL and ester carbonyl group of ε-CL skeleton at 1736 cm^{-1} (*Jiang, H. et al. 2002*).

6.4.3 Yield of EVA-g-PCL

After extraction the crude sample with ethyl acetate and tetrahydrofuran to remove non-reacted ε-caprolactone, % yield of all products was calculated by using following equation and shown in Table 6.1.

$$\%\text{Yield} = \frac{\text{wt. of EVA} - \text{g} - \text{PCL}}{\text{wt. of Modified EVA} + \text{wt. of } \varepsilon - \text{CL}} \times 100$$

Table 6.1 % yield of reacted EVA-g-PCL after extraction the crude sample with ethylene acetate and tetrahydrofuran

Samples	% Yield
EVA-g-PCL (1:1)	93.33
EVA-g-PCL (1:5)	69.67
EVA-g-PCL (1:10)	41.55

6.4.4 Structural Properties

The crude sample of graft copolymer was investigated by XRD as shown in Figure 6.4. A peak of EVA-g-PCL at 1:1 shows very low intensity that means its structure is close to an amorphous, which corresponds to its appearance that is translucent. EVA-g-PCL at higher content of PCL exhibits higher crystalline as shown by the increasing of intensity at 2θ ~ 24, their appearances are opaque. The increasing of crystalline of graft copolymer comes from only PCL phase The graft copolymer shows the shift of peak at 2θ = 21.38, 23.73 of 100% PCL (*Wei, Z. et al. 2009 and Rezgui, F. et al. 2005*) and EVA to the new peak at higher position.

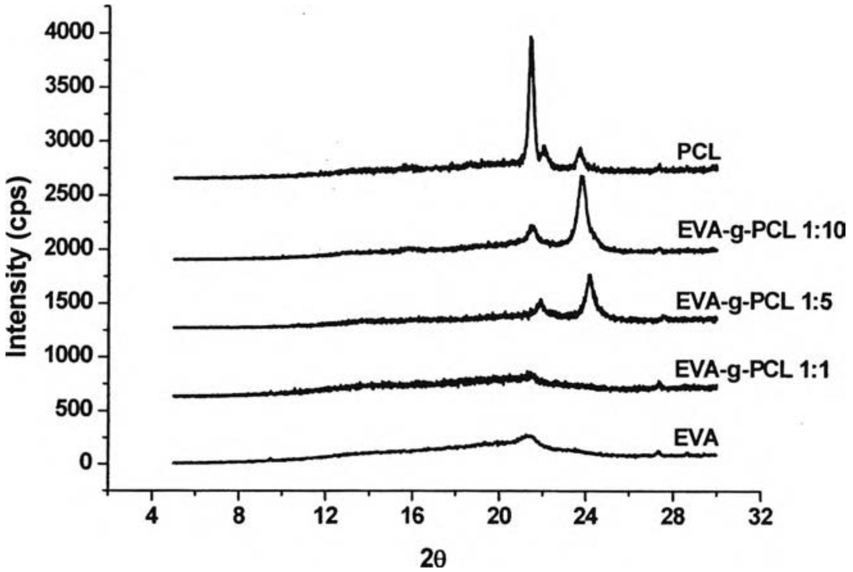


Figure 6.4 XRD patterns of PCL and EVA-g-PCL with various compositions synthesized from the solution ring-opening polymerization.

6.4.5 Thermal Analysis

Figure 6.5 and 6.6 represent the thermal behavior of crude sample of EVA-g-PCL at various contents of ε-CL. Figure 6.5 shows the shift of melting peak of the graft copolymers from 76.27°C of modified EVA and 58.87°C of PCL to the new positions. At high PCL content of the graft copolymer, T_m shifts to the lower temperature as shown in Table 6.2 which is interesting for use as boil and bite mouth guard materials because it must be immersed in the warm water before shaping to teeth. Temperature around 40 to 45°C is not too hot to shape in mouth. This interesting properties also showed in the graft copolymer of ethylene vinyl alcohol (EVOH) and ε-caprolactone (*Jiang, H. et al. 2002*). The shift of T_m to lower temperature is caused by the decreasing of crystal size of graft copolymer. EVA-g-PCL at weight ratio 1:1 shows no peak of T_m which corresponds to XRD result showing amorphous structure. The crystallization temperature is displayed in Figure 6.6 and Table 6.2. As a result, the crystallization at high content of PCL (1:5 and 1:10 of EVA:ε-CL), is retarded as shown by the decreasing of T_c. This situation can be described by the increasing of chain mobility of PCL dangling ends which are the side chains of graft copolymer that retard the crystallization.

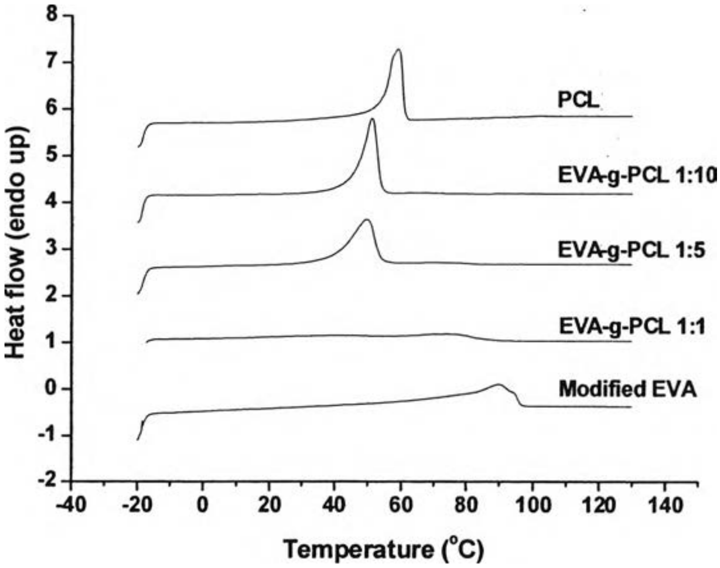


Figure 6.5 DSC-measurement of modified EVA, PCL and EVA-g-PCL at various compositions (second heating at 10°C/min heating rate).

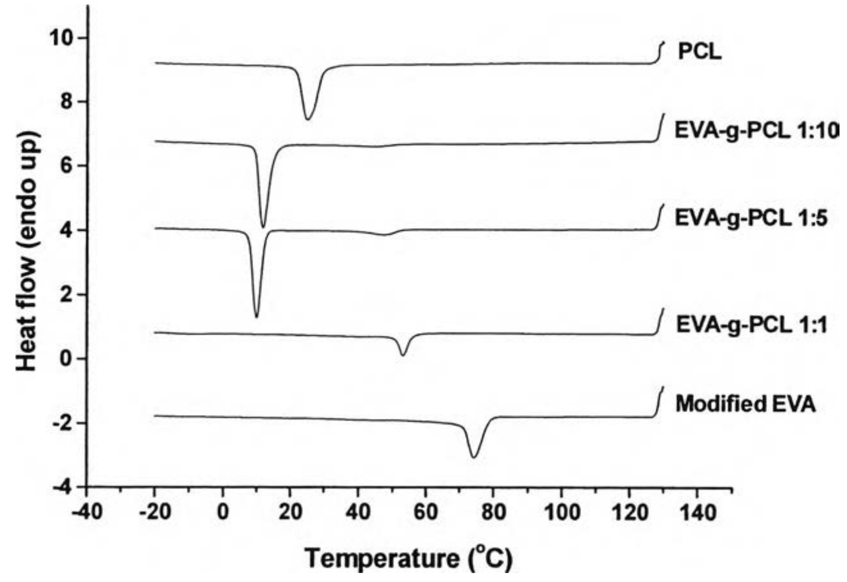


Figure 6.6 DSC-measurement of modified EVA, PCL and EVA-g-PCL at various compositions (cooling at 10°C/min cooling rate).

Table 6.2 Melting and crystallization temperature of modified EVA, PCL, and EVA-g-PCL

Samples	T_m (°C)		T_c (°C)	
	Onset	Peak	Onset	Peak
Modified EVA	76.3	89.5	77.6	73.3
PCL	54.2	58.9	29.8	25.1
EVA-g-PCL (1:1)	59.3	75.7	55.8	53.3
EVA-g-PCL (1:5)	39.9	49.7	12.4	10.0
EVA-g-PCL (1:10)	45.9	51.2	15.0	11.8

The thermal stability of each crude sample of graft copolymer was observed by TGA as shown in Figure 6.7 and Table 6.3. T_d onset of modified EVA increases after transesterification reaction of EVA due to the occuring of hydrogen bond from –OH group. T_d onset of pure PCL was observed at 372.4°C (*Ruseckaite, R.A. et al. 2003*). The thermal stability of PCL phase decreases but EVA phase increases when graft copolymer has high PCL content.

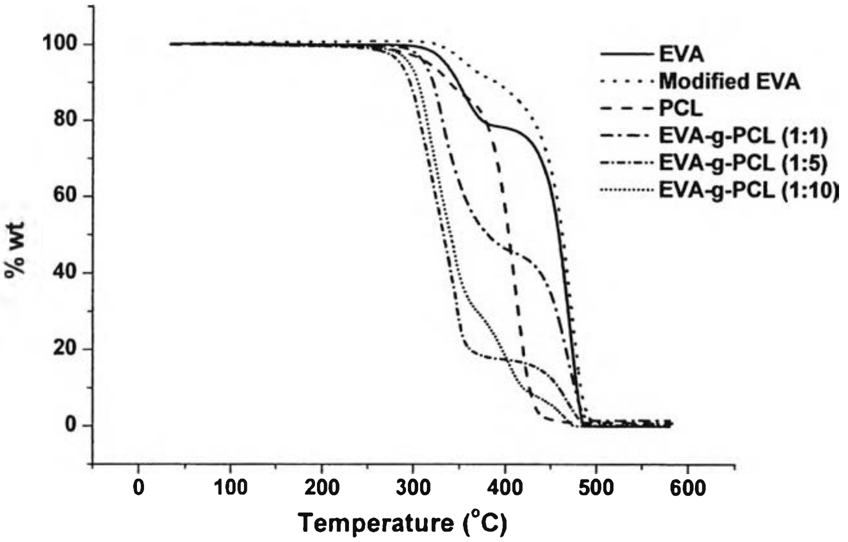


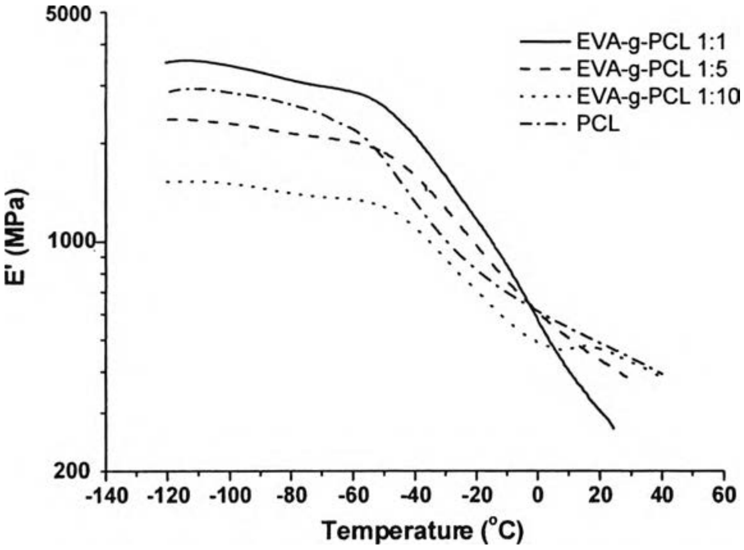
Figure 6.7 TGA curves of modified EVA, PCL, and EVA-g-PCL.

Table 6.3 Thermal stability of EVA, Modified EVA, PCL, and EVA-g-PCL

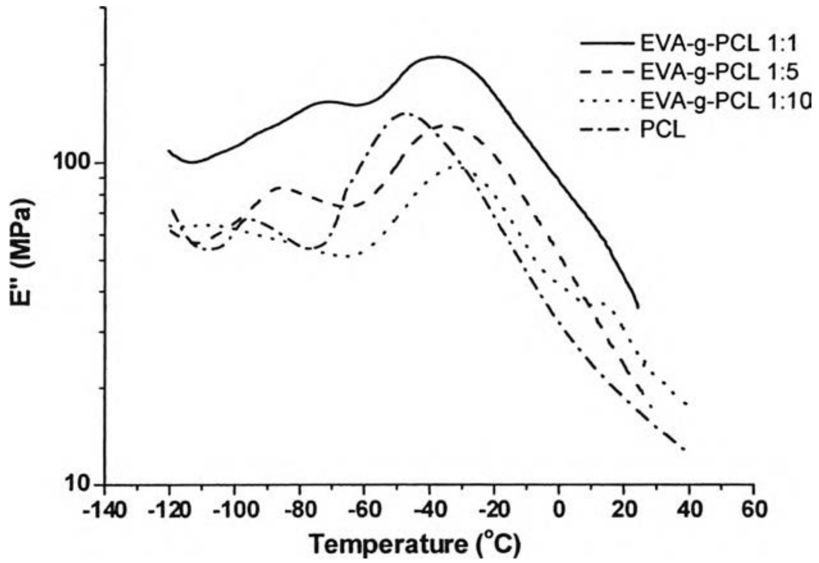
Sample	T_d onset (°C)			Weight loss (%)			Char residual (%)
	PCL	Acetate	Ethylene	PCL	Acetate	Ethylene	
EVA	-	341.8	448.3	-	20.2	78.0	1.8
Modified EVA	-	347.8	458.4	-	6.5	91.6	1.9
PCL	372.4	-	-	99.2	-	-	0.8
EVA-g-PCL (1:1)	331.6	-	464.9	54.6	-	40.3	5.1
EVA-g-PCL (1:5)	304.7	397.6	474.3	65.3	18.7	15.7	0.3
EVA-g-PCL (1:10)	313.1	399.0	473.6	61.9	24.6	11.7	1.8

6.4.6 Dynamic Mechanical Analysis

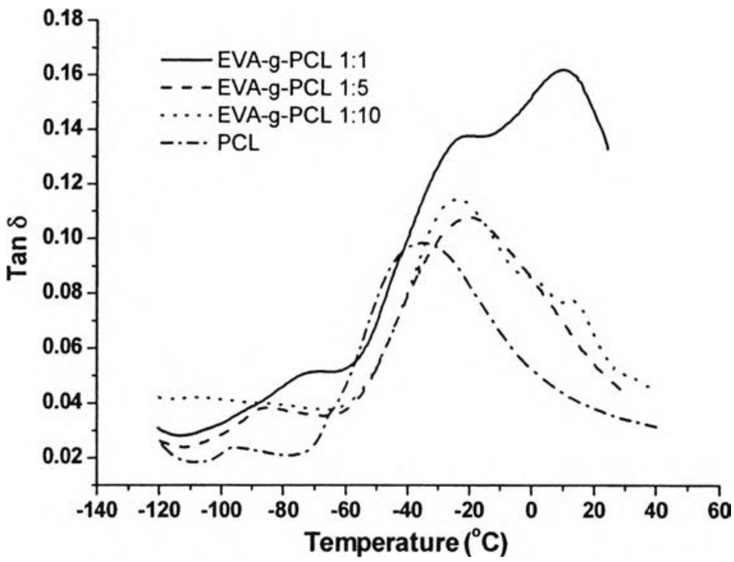
Each composition of crude graft copolymer was investigated for dynamic mechanical properties from temperature of -120 to 55°C. The results are shown in Figure 6.8 (a) storage modulus, (b) loss modulus, and (c) tan δ. These graft copolymer were compared to synthesized PCL with the same [ε-CL]/[$Sn(Oct)_2$] of 2000. At temperature from -120 to -60°C, the storage modulus of graft copolymer of higher PCL content shows higher modulus than that of lower PCL content but shows the opposite result at temperature of 5 to 25°C. The storage modulus at room temperature shows the highest value for pure PCL at 460 MPa and shows the lowest value for EVA-g-PCL, weight ratio 1:1 at 270 MPa. The glass-transition temperature observed at the maximum of tan δ peak corresponds to the compatibility of EVA-g-PCL. As results, each graft copolymer shows the shift of maximum tan δ peak from -34.5°C of pure PCL to higher position. EVA-g-PCL of 1:5 weight ratio exhibits the most compatibility compared to the others because it shows only one peak at -20.2°C



(a)



(b)

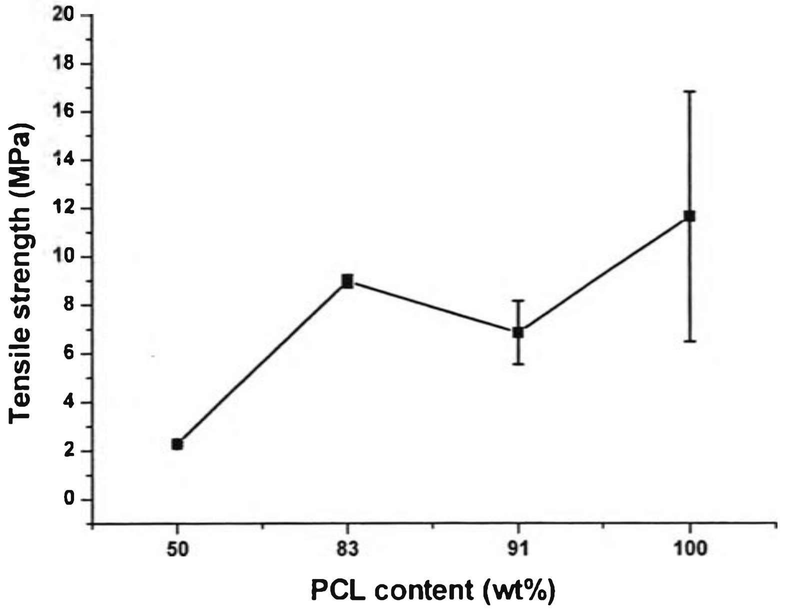


(c)

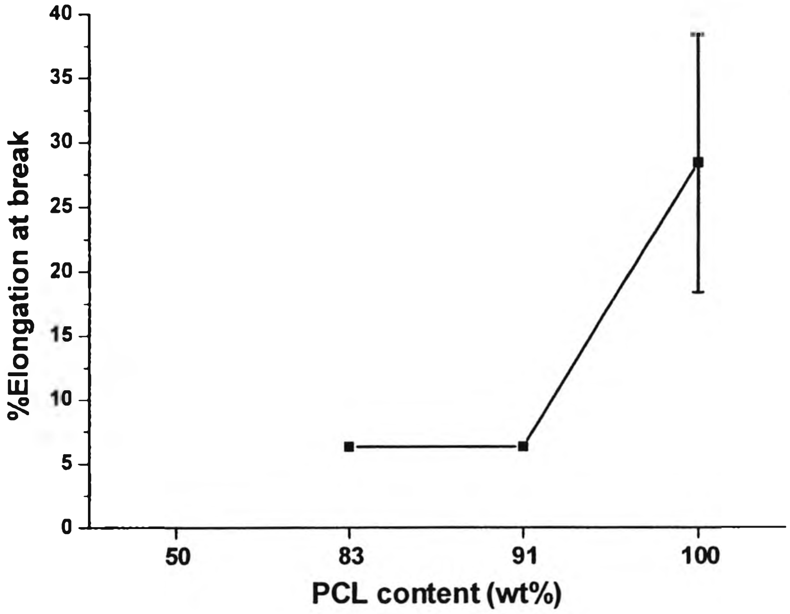
Figure 6.8 DMA results of EVA-g-PCL with various compositions (a) E′, (b) E″, and (c) tan δ as the function of temperature.

6.4.7 Mechanical Properties

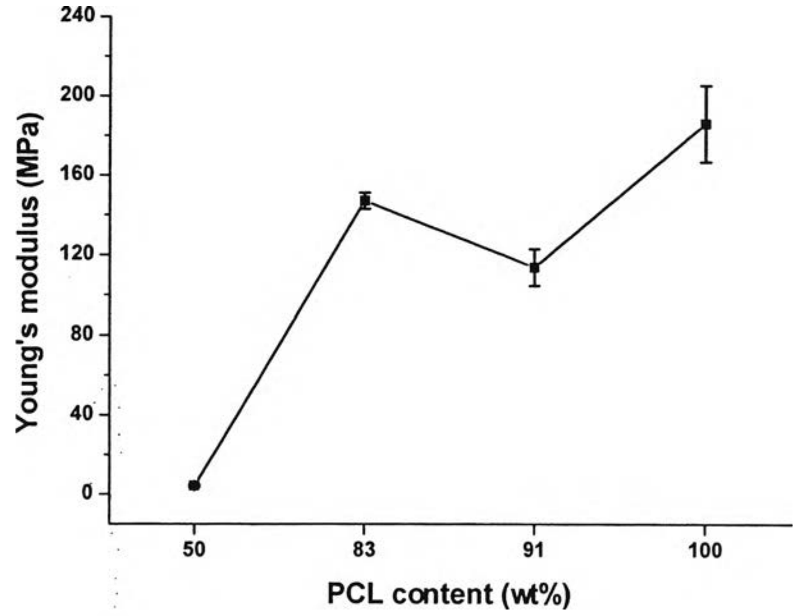
Figure 6.9 presents the results of tensile properties of crude graft copolymer. Tensile strength, %elongation at break, and young's modulus are shown in Figure 6.9 (a), (b), and (c), respectively. The observation of tensile strength cannot be done for EVA-g-PCL of 1:1 weight ratio so the tensile strength of EVA-g-PCL (1:1) is represented by the maximum strength at 500% elongation. The trend of tensile strength increases when PCL content increases. EVA-g-PCL of 1:1 weight ratio cannot be observed for %elongation at break as well. Young's modulus of graft copolymer with the lowest content of PCL shows very low modulus around 2 MPa. Young's modulus of graft copolymer drastically increases when PCL content increases from 1:1 to 1:5 (modified EVA:ε-CL), then remains the same for 1:5, 1:10 (modified EVA:ε-CL), and pure PCL.


Tensile strength (MPa)
20
18
16
14
12
10
8
6
4
2
0
50
83
91
100
PCL content (wt%)

(a)


%Elongation at break
40
35
30
25
20
15
10
5
0
50
83
91
100
PCL content (wt%)

(b)



(c)

Figure 6.9 Tensile properties of EVA-g-PCL with various compositions of ε-CL (a) tensile strength, (b) % elongation at break, and (c) Young's modulus.

Impact strength of crude graft copolymer was observed for the effect of PCL content. Impact strength of graft copolymer is shown in Figure 6.10. PCL content affects the impact strength of EVA-g-PCL, the addition of EVA can improve the impact strength compared to pure PCL by 115% and 15% increase of EVA-g-PCL at weight ratio 1:5 and 1:10, respectively. Modified EVA is the soft part added to PCL system, this soft part is the backbone of graft copolymer and behaves as the part for absorb energy, therefore impact strength increases. The observation of EVA-g-PCL at weight ratio 1:1 does not appear in this figure because it exhibits much high elastomeric properties so it cannot break for impact testing. These mechanical property results support that modified EVA can exhibit its elastomeric properties to graft copolymer.

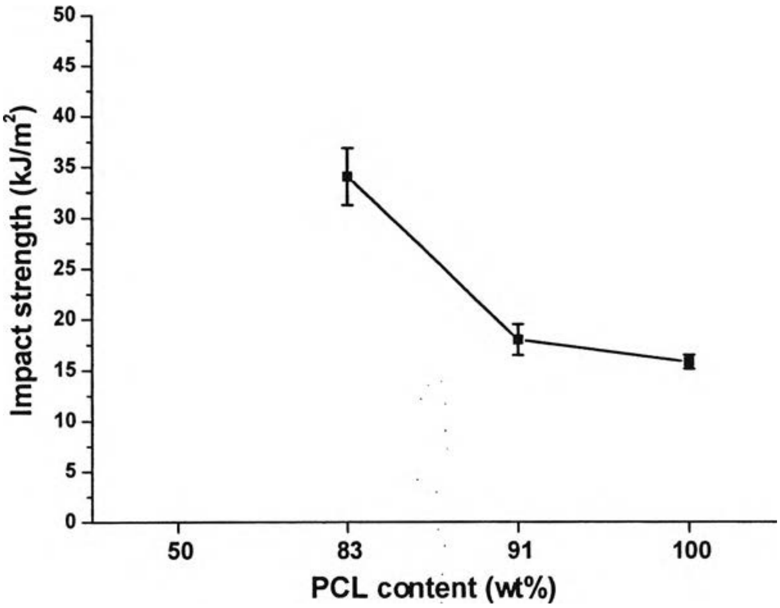
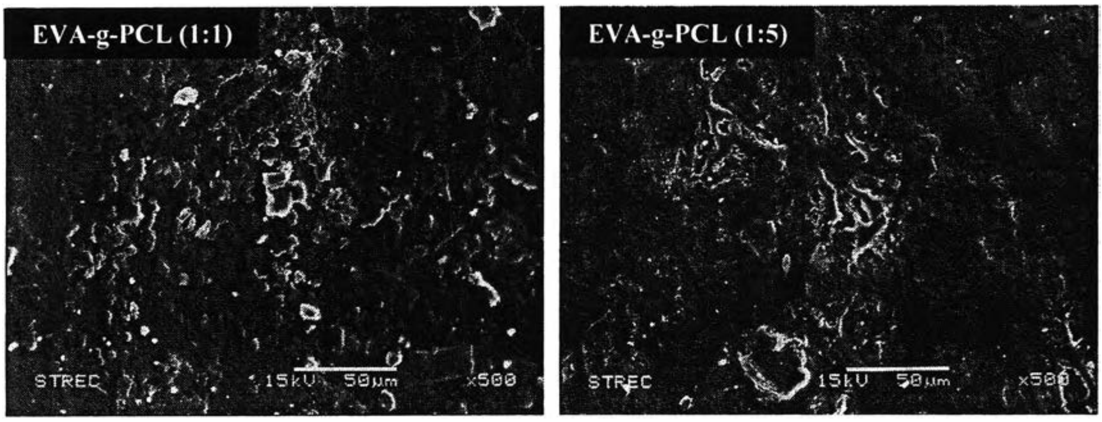


Figure 6.10 Impact strength of EVA-g-PCL with various compositions of ε-CL.

6.4.8 Morphological Characterization

SEM images for morphological study of graft copolymer are shown in Figure 6.11. Each specimen was observed after etching with tetrahydrofuran to dissolve homopolymer of PCL. The graft copolymer with higher PCL content shows smoother surface than the lower one. The addition of PCL smoothen the surface of graft copolymer.



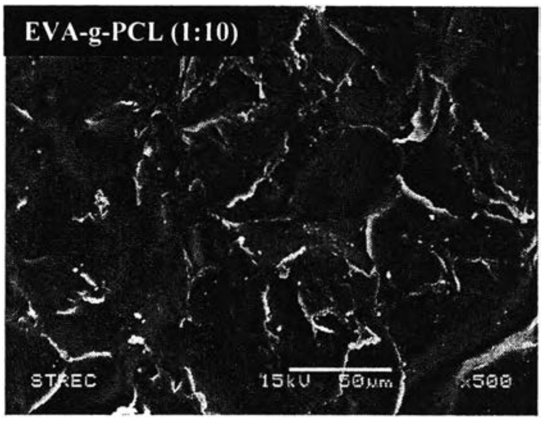


Figure 6.11 SEM images of fractured surface of EVA-g-PCL with various compositions of ε-CL after etching with tetrahydrofuran.

6.5 Conclusion

This is the first time of grafting between EVA and PCL, the closest system of graft copolymer is EVOH-g-PCL. Firstly, EVA must be modified through transesterification for replacing acetate group to hydroxyl group confirmed by the appearance of hydroxyl band in IR spectrum. EVA-g-PCL was also confirmed by FT-IR of the characteristic –OH peak of PCL at 3529 cm^{-1}. Modified EVA affected the crystal structure of PCL by the shift of 2θ position. DSC measurement showed the changes in both melting and crystallization temperature. Melting temperature of EVA-g-PCL shifted to lower temperature than pure PCL and modified EVA. The same result occurred for crystallization temperature at high PCL content as well. Thermal stability of PCL phase decreased after grafting of PCL on EVA backbone. Impact strength of PCL and EVA-g-PCL at 1:5 weight ratio showed the highest value by 115% increase from pure PCL. Dynamic mechanical properties showed the most compatibility of EVA-g-PCL at 1:5 weight ratio.

The addition of soft part could improve the impact strength of PCL which is an important property of mouth guard material. Mouth guard material should has high impact strength and high modulus at the same time. From the result, EVA-g-PCL at weight ratio 1:5 could reach that point because it showed high increase of impact strength from the pure PCL meanwhile the modulus was also close to the pure one.

6.6 Acknowledgement

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