



CHAPTER II LITERATURE REVIEW

2.1 Clay Minerals

Clay minerals, due to their unique layered structure, rich intercalation chemistry and availability at low cost, are promising nanoparticle reinforcements for polymers to manufacture low-cost, lightweight and high performance nanocomposites. The structure of commonly used clays is shown in Figure 2.1 as 2:1 layered or phyllosilicates which consist of nanometer thick layers (platelets) of aluminium octahedron sheet sandwiched in between two silicon tetrahedron sheets. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular Van Der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for

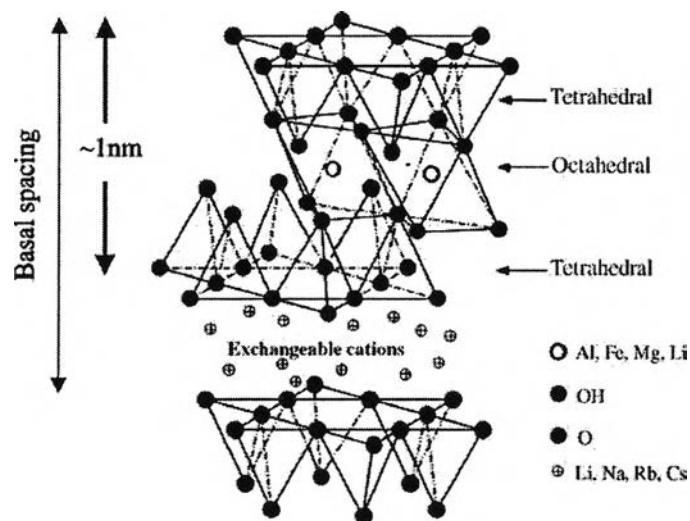


Figure 2.1 Structure of 2:1 phyllosilicates.

example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^{1+}) generates negative charges that are counterbalanced by alkali and alkaline earth cations such as Na^+ , Ca^{2+} inside the galleries. Clay is characterized by a moderate surface charge known as the

cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal. Two particular characteristics of clay that are generally considered for polymer/clay nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion of clay layered silicate in a particular polymer matrix depends on the interlayer cation.

The physical mixture of a polymer and clay may not form a nanocomposite. This situation is the same as polymer blends, and in most cases separation into discrete phases takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in polymer/clay nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique properties different from conventionally filled polymers. Commonly, clays contain hydrated Na^+ or K^+ ions which influence layered silicates to be miscible with the hydrophilic polymers. To render clays miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one, which are called organoclays, making the intercalation of many engineering polymers possible. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix.

2.2 Nanocomposite

Nanocomposite is nanomaterial that combines one or more separated components in order to obtain the best properties of each component (composite). In nanocomposite, nanoparticles (clay, metal, carbon nanotubes) act as fillers in a matrix, usually polymer matrix. In this research work, we focus on filler as clay minerals which have the layered silicates structure. However, the composite with another fillers such as wheat gluten, starch, etc. were also reviewed in literature research.

2.2.1 Types of Nanocomposites

In general, layered silicates have layer thickness on the order of 1 nm and a very high aspect ratio (e.g. 10–1000). A few weight percent of layered silicates that are properly dispersed throughout the polymer matrix thus create much higher surface area for polymer/filler interaction as compared to conventional composites. Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of polymer layered silicate nanocomposites are thermodynamically achievable. Each type of nanocomposites is shown in Figure 2.2

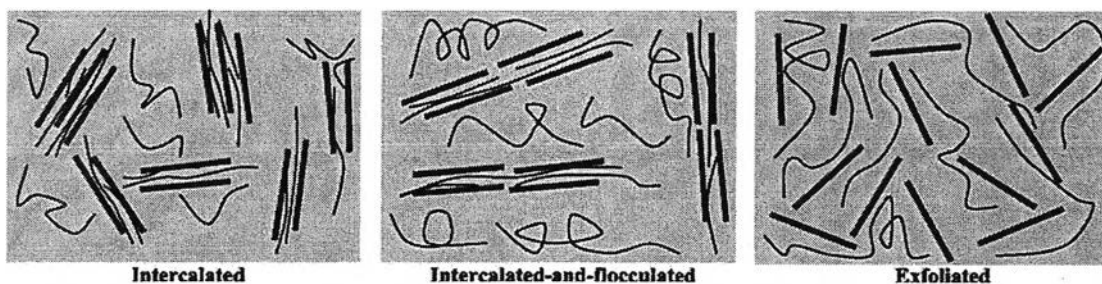


Figure 2.2 Types of nanocomposites.

a) *Intercalated nanocomposites*: in intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio.

Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.

b) *Flocculated nanocomposites*: conceptually this is same as intercalated nanocomposites. However, silicate layers are some times flocculated due to hydroxylated edge–edge interaction of the silicate layers.

c) *Exfoliated nanocomposites*: in an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

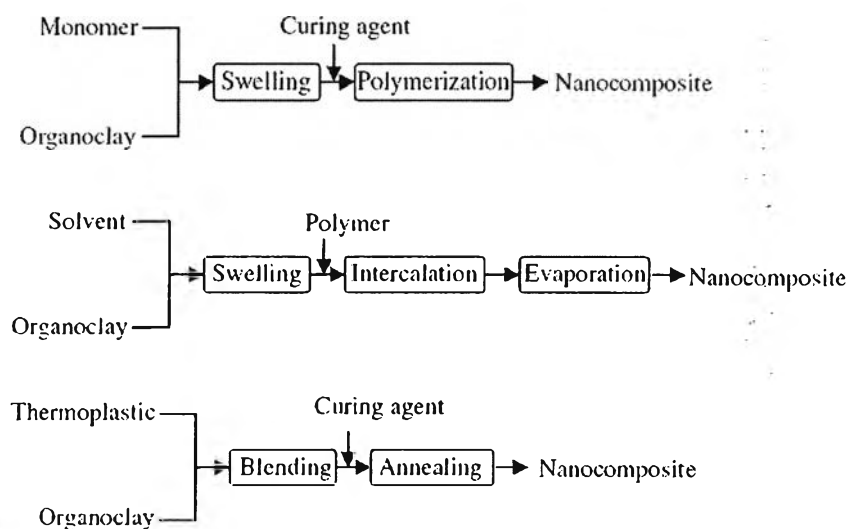


Figure 2.3 Flow chart of three processing techniques for clay-based polymer nanocomposites: in-situ polymerization (upper), solution exfoliation (middle) and melt intercalation (bottom).

2.2.2 Preparative Methods of Clay-based Polymer Nanocomposites

Figure 2.3 shows three processes of making clay-based polymer nanocomposites, including *in-situ* polymerization, solution exfoliation and melt intercalation. Each technique consists of several steps to achieve polymer nanocomposites and begins with organoclays or sometimes pristine clays. The different driving forces, advantages, and disadvantages of each process are summarized in Table 2.1. In the *in-situ* polymerization, monomers are intercalated

into layered clays and subsequently polymerized within the gallery via heat, radiation, pre-intercalated initiators or catalysts. In the solution exfoliation, layered clays are

Table 2.1 The comparison of three processing techniques for clay-based polymer nanocomposites: *in-situ* polymerization , solution exfoliation, and melt intercalation

Processing	<i>In-situ</i> Polymerization	Solution Exfoliation	Melt intercalation
Drive force	Interaction strength between monomer and clay surface; Enthalpic evolution during the interlayer polymerization.	Entropy gained by desorption of solvent, which compensates for the decrease in conformational entropy of intercalated polymers.	Enthalpic contribution of the polymer organoclay interactions.
Advantages	Suitable for low or non-soluble polymers; A conventional process for thermoset nanocomposites.	Prefer to water-soluble polymers.	Environmental benign approach; No solvent is required; Nanocomposites can be processed with conventional plastic extrusion and molding technology.
Disadvantages	Clay exfoliation depends on the extent of clay swelling and diffusion rate of monomers in the gallery; Oligomer may be formed upon incomplete polymerization.	Compatible polymer-clay solvent system is not always available; Use of large quantities of solvent; Co-intercalation may occur for solvent and polymer.	Slow penetration (transport) of polymer within the confined gallery.
Examples	nylon 6, epoxy, polyurethane, polystyrene, polyethyleneoxide, unsaturated polyesters, polyethylene terephthalate.	Epoxy, polyimide, polyethylene, polymethylmethacrylate	Nylon 6, polystyrene, polyethylene terephthalate.

exfoliated into single platelets using a solvent in which the polymer is soluble. The polymer is then mixed with the clay suspension and adsorbed onto the platelets. The solvent is finally eliminated from the clay polymer complex through evaporation. In the melt intercalation, layered clays are directly mixed with the polymer matrix in the molten state. The formation of polymer nanocomposites is driven by different forces depending on the technique used, and each technique has its advantages and disadvantages. The polymers studied so far cover almost the whole range of polymers, such as thermoplastics, thermoset plastics, elastomers, specific, and biodegradable polymers.

2.3 Transesterification

In organic chemistry, transesterification is the process of exchanging the alcohol group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base.

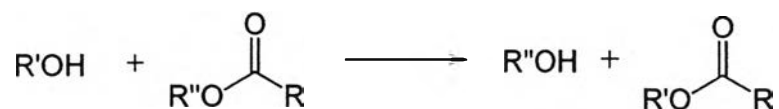


Figure 2.4 Transesterification reaction.

Acids can catalyze the reaction by donating a proton to the carbonyl group, thus making it more reactive, while bases can catalyze the reaction by removing a proton from the alcohol, thus making it more reactive.

2.4 Polycaprolactone (PCL)

Polycaprolactone is a biodegradable polyester with a low melting point around 60°C and a glass transition temperature of about -60°C. PCL is derived by chemical synthesis from crude oil. It can be prepared by ring-opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate. The mechanism of

stannous octoate is shown in Figure 2.6. Polycaprolactone has good water, oil, solvent and chlorine resistances.

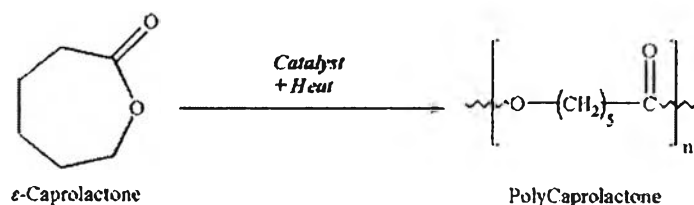


Figure 2.5 Ring-opening polymerization of ϵ -caprolactone.

This polymer is often used as an additive for resins to improve their processing characteristics and their end use properties (e.g.: impact resistance). Being compatible with a range of other materials, PCL can be mixed with starch to lower its cost and increase biodegradability or it can be added as a polymeric plasticizer to PVC.

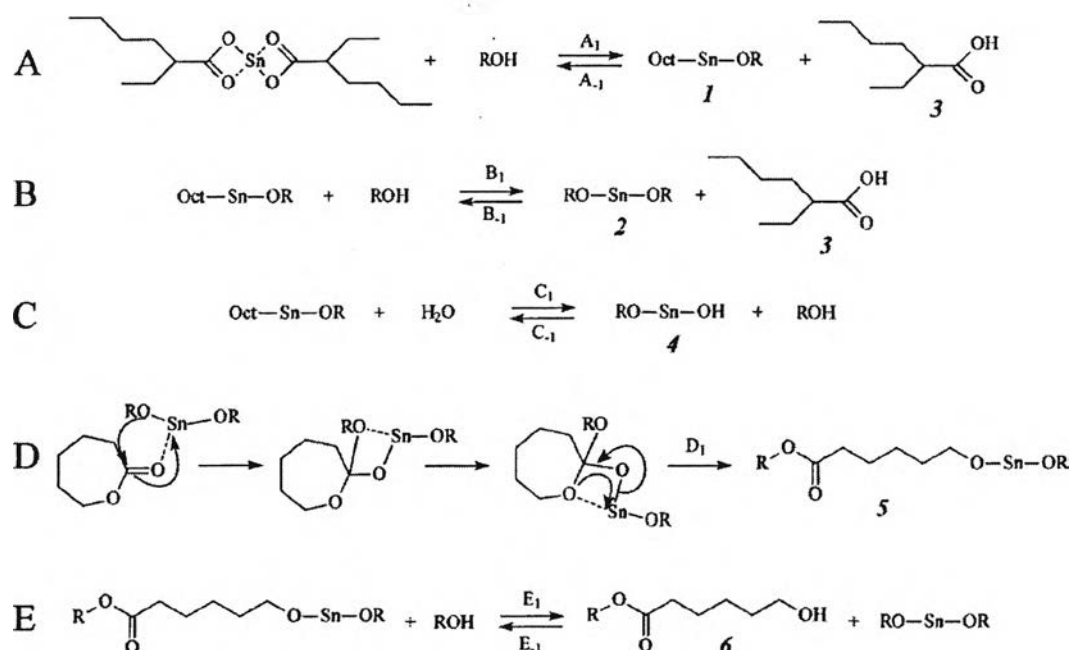


Figure 2.6 Mechanism of initiation in stannous octoate catalyzed polymerization of ϵ -caprolactone, including (A, B) formation of stannous alkoxide initiator, (C) deactivation of catalyst with reaction by water, (D) coordination/insertion of

monomer into the stannous alkoxide bond generating 1mer, and (E) chain transfer of active polymerizing center from 1mer to unreacted alcohol. (Storey, R.F. *et al.* 2002. *Macromolecules*. 35, 1504-1512).

2.5 Ethylene Vinyl Acetate (EVA)

Ethylene vinyl acetate is the copolymer of ethylene and vinyl acetate. The weight percent vinyl acetate usually varies from 10 to 40% with the remainder being ethylene. It is a polymer that approaches elastomeric materials in softness and flexibility, yet can be processed like other thermoplastics. The material has good clarity and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive and heat sealing properties and resistance to UV radiation. EVA has little or no odor and is competitive with rubber and vinyl products in many electrical applications.

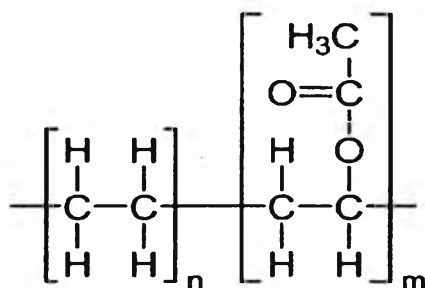


Figure 2.7 Chemical structure of EVA.

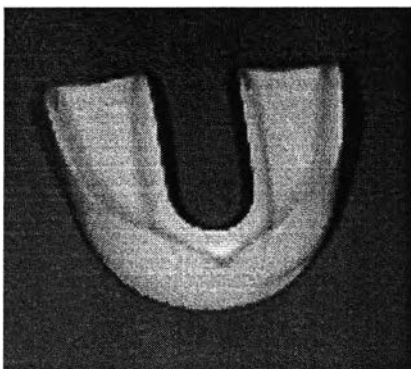
EVA foam is used as padding in equipment for various sports such as ski boots, hockey, boxing, and mixed martial arts. EVA is also used in biomedical engineering applications as a drug delivery device. While the polymer is not biodegradable within the body, it is quite inert and causes little or no reaction following implantation. Hot glue sticks are usually made from EVA, usually with additives like wax and resin. It is also used as a clinginess-enhancing additive in plastic wraps and typically used as a shock absorber in tennis shoes.

2.6 Sport Mouth Guards

Sports (athletic) mouth guards are plastic dental appliances 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). While all guards are made of plastic their specific design, composition, and method of fabrication vary. In general there are three types of sports mouthpieces: stock, boil and bite, and custom.

2.6.1 Stock Mouth Guards

The term “stock mouth guard” refers to preformed mouthpieces that are sold ready to be used without any additional customization by the wearer. This type of mouth guard is usually the cheapest type of guard, but the level of protection provided by stock guards is usually minimal. Stock mouth guards are only manufactured in just a few sizes (typically small, medium, and large). As a result for



many athletes these guards will be uncomfortable to wear and will not stay in place well. Also related to these same size limitations, stock mouth guards often will not cover over all of the back teeth as is needed for adequate protection.

To compensate for the poor retention of a stock mouth guard, an athlete will often clench their teeth together to hold the guard in place. This clenching activity can make it difficult for the player to speak and breathe, which in turn may provide a reason for them not to wear it. In some cases, an athlete may attempt to improve the functionality or comfort of their stock mouth guard by way of trimming it, which can serve to compromise the level of protection that the guard can provide.

2.6.2 Boil and Bite Mouth Guards

A “boil and bite” mouth guard refers to a type of guard that is made out of thermoplastic materials. The idea is that the athlete customizes the fit of the mouth guard by immersing it in hot water (until it becomes soft and pliable) and then placing it in their mouth and subsequently using their fingers, lips, tongue, cheeks, and biting pressure to seat and form the contours of the guard.

Boil and bite mouth guards are the most commonly used type. If choosing this type of mouth guard a size must be chosen that covers all of the wearer's front and back teeth. A criticism of this type of protector is that during the customization process the thickness of the plastic covering the chewing surface of the teeth can become thin, thus minimizing the amount of protection that the guard is capable of providing. Another common criticism aimed at boil and bite mouth guards is that they can be bulky. The retention of this type of mouth guard can be expected to be better than a stock guard but not as good as the fit of a custom mouth guard.

2.6.3 Custom Mouth Guards

Custom mouth guards are sports mouth protectors that are individually made for an athlete. A well-designed custom mouth guard is typically considered to be able to provide the greatest level of protection for an athlete as compared to either a stock or boil and bite guard. The design of a custom guard can be individualized not only for the athlete but in some cases also for the specific sport that will be played when it is being worn. The fit and comfort of a custom mouth guard can be expected to be excellent. The more comfortable make the athlete can wear it at all times. Additionally, the retention of a custom guard can be expected to be superior and therefore produce less interference with speech and breathing than other types of guards. While the cost of this type of appliance is more than a stock or boil and bite mouthpiece it should be considered money well spent.

2.7 The Characteristics of A Mouth Guard

2.7.1 The Mouth Guard should Fit Well and be Comfortable to Wear

Two of the most important characteristics that a mouth guard can possess are that it is comfortable to wear and stays in place well. If an athlete's guard is bulky, irritates their teeth or the soft tissues of their mouth, or does not have good retention then it is likely that they will not wear it, or at least not wear it all of the time. If a mouth guard is uncomfortable an athlete may try to adjust it by way of trimming off some of the guard's plastic. Any portion of a mouth guard that is trimmed away may compromise the level of protection that the guard provides.

Athletes are sometimes critical of wearing their sports mouth guards because they have trouble speaking or breathing when they wear them. It is quite possible that both of these troubles stem from the same problem, the fit of the mouth guard. If the guard does not have good retention then athlete will tend to hold it in place by way of clenching their teeth. It is this constant clenching action that makes it difficult for them to speak and breath.

2.7.2 Considerations associated with The Style and Shape of The Mouth Guard

Most sports mouthpieces are designed so they only cover over the athlete's upper teeth and jaw. The characteristics of a person's upper and lower jaws are quite different. The lower jaw is capable of a wide range of motion. This means that when a blow lands on the jaw or teeth some of the force of the blow will be buffered by the jaw's reactive motion. In contrast the upper jaw is fixed in position. A relatively greater portion of the force of the blow will have to be directly absorbed by the teeth and jaw bone. This difference in anatomy, the way the upper jaw is fixed in position, is one reason why a person's center two upper teeth are the most likely teeth to be damaged by an accident.

Some mouth guards are designed so they cover over both the upper and lower jaws. This design does provide a greater level of protection for the lower teeth and may possibly provide greater protection for the jaw joint. In some instances this type of mouthpiece can be relatively more uncomfortable to wear and therefore an athlete may not use it as consistently as a single arch guard. Clearly dual coverage mouth guards can be a good idea for those athletes who are undergoing orthodontic treatment (wear braces) and therefore require lip and cheek protection from their brackets and wires. The outline form of a mouth guard should include that it covers over all of the athlete's posterior (back) teeth (there is some debate regarding the necessity to cover over the wisdom teeth if they have erupted). Some studies have suggested that mouth guards that fail to cover over a significant number of the posterior teeth can place the athlete's lower jaw at greater risk of fracture.

2.7.3 Thickness, Resiliency, and Stiffness Considerations for Mouth Guards

Clearly different sporting activities have differing potential for placing their participants at risk of experiencing a traumatic blow. It is easy to imagine that a

football player would be expected to have a greater likelihood of experiencing tooth or mouth trauma than a tennis player. Along this same line of thought, it is customary that the design (primarily thickness considerations) of a sports guard should be based on the type of sport that the wearer will be participating in.

Athletes that participate in sports that do not entail a high degree of physical contact may achieve satisfactory protection from a mouth guard that is on the order of 1/16th of an inch (2 mm) or so in thickness. Heavier contact sports (such as football) would necessitate the design of a thicker mouth guard, more along the lines of 1/8th of an inch (4 mm) or more. A thicker guard yet would be required for those athletes participating the heaviest of contact sports such as boxing.

The resiliency of the plastic chosen for a mouth guard needs to be of some consideration. The plastic's sponginess can be expected to help to absorb a portion of the force delivered by a traumatic blow. Equally important if a mouth guard is not somewhat flexible it may be quite irritating to the soft tissues of the mouth when it is worn. The rigidity of a guard may have more to do with the level of protection that it can provide than the guard's spongy resilience. The stiffness of a sports mouthpiece will allow it to help distribute a delivered blow over a larger surface area, thus buffering the amount of direct force any one tooth or mouth area is subjected to.

2.8 Literature Research

2.8.1 Polycaprolactone

Polycaprolactone has been studied for many years. In 1989, polycaprolactone modeling and molding compositions was studied by *Sieverding, L.D.* 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. However, high molecular weight polycaprolactone had been determined to develop certain deficiencies for this application when it was repeatedly worked in the melt. This work was concerned with blending into a high molecular weight polycaprolactone a sufficient amount of a "skin detackifier" such that the polymer can be remelted and handled by hand in the melt condition without sticking to hands. The

skin detackifiers useful in the practice of this work were the class of salts and amides. The most desirable of these amides contained fatty acid which is an unsaturated fatty acid such as oleic acid and ricinoleic acid or saturated fatty acid containing 8 to about 14 carbon atoms. Because of added cost associated with the addition of the detackifier, it was preferred to employ the minimum amount needed to effect the desired amount of detackification of the high molecular weight polycaprolactone during use and retain the polycaprolactone's excellent paintability. He found that about 0.5 to about 2.5 wt% of the detackifier will generally provide the desired results.

In 1991, dental impression process using polycaprolactone molding composition was studied by *Oxman, J.D. et al.* They prepared polycaprolactone molding composition by blending high molecular weight (MW~40,000) and low molecular weight (MW~500-10,000) polycaprolactone at various compositions. The blends had lower viscosity and higher modulus than a composition containing only high molecular weight polycaprolactone. In this work, dimension stability, compression set, strain in compression, and inlay accuracy were investigated. As results, the viscosity decreased when the amount of low molecular weight polycaprolactone increased; and % shrinkage, % compression set, and % strain in compression were around 0.60-0.90, 0.80-1.10, and 0.30-0.80, respectively. Rectangular 2.5×13×33 mm torsion bars were casted from the molding composition of 85% high molecular weight (40,000) and 15% low molecular weight (10,000), then evaluated for storage and loss moduli using a rheometric dynamic analyzer operated at 1.4% maximum strain and 10 radian/second strain rate. The data showed that the composition had a sharp melting point at temperatures that would be acceptable in the mouth. At body temperature (about 38°C), the molding composition exhibited solidity, usefully high modulus, and desirably low plasticity.

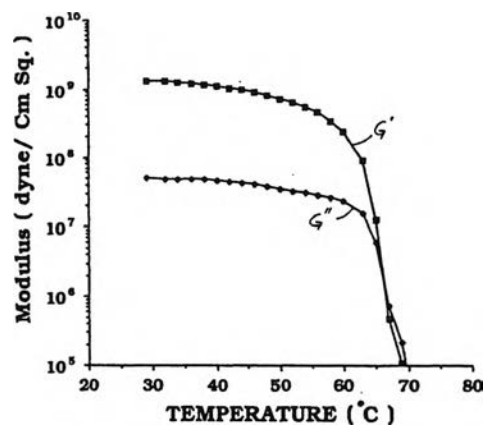


Figure 2.8 A plot of the modulus measurements between 32°C and 70°C.

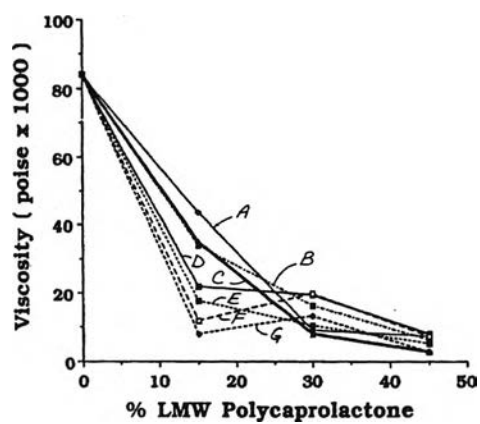


Figure 2.9 The effect of low molecular weight contents on the viscosity.

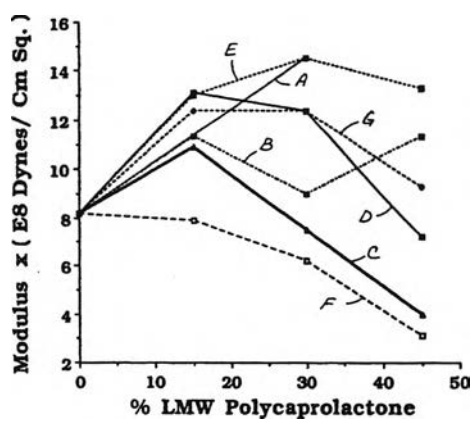


Figure 2.10 The effect of low molecular weight contents on the modulus.

Curves A to G connect the data points for blends containing the “TONE” (Union Carbide Corp.) low molecular weight polycaprolactones “0260” (MW~3000), “0230” (MW~1250), “0200” (MW~530), “P-300” (MW~10000), “0240” (MW~2000), “0305” (MW~540), and “2240” (MW~2000), respectively.

In 1996, *Grosvenor, M.P. et al.* studied the effect of molecular weight on the rheological and tensile properties of polycaprolactone. They used different molecular weight fractions of polycaprolactone which were produced by catalytic degradation of polycaprolactone having $M_w = 49,500$. As a result of the preparation method, fractions of polycaprolactone were obtained having molecular weight in the range 16,900 to 35,500 with polydispersities between 1.7 and 1.9. The viscosity of polycaprolactone increased when molecular weight increased and tensile strength of polycaprolactone film 50 μm also increased when molecular weight increased. Because of higher tensile strength of high molecular weight polycaprolactone, it was proper to use high molecular weight for making mouth guard.

2.8.2 The Addition of Rigid Part

Polycaprolactone was mixed with some additives or blend with other polymers to improve some properties such as biodegradability, mechanical properties, etc. Some mixed materials or composites or blends had good properties for making boil and bite mouth guards. In 1998, *John, J. et al.* studied the processing of biodegradable blends of wheat gluten and modified polycaprolactone. Different compositions of wheat gluten (65% and 75%) and polycaprolactone were melt blended in a twin screw extruder. Polycaprolactone was modified to incorporate a functional group that could interact with the functional groups on the protein. Maleic anhydride was grafted to the polycaprolactone backbone using dicumyl peroxide as the initiator. The grafting reaction was accomplished in an extruder. Results indicate that a small amount of anhydride modified polycaprolactone in the blend improved the physical properties of these blends over those of simple mixtures of wheat gluten and polycaprolactone. The processing parameters (pressure, torque and energy) of the blends were significantly increased by the addition of 2.5% by weight of anhydride modified polycaprolactone. Similarly, the properties were also enhanced by the addition of modified polycaprolactone.

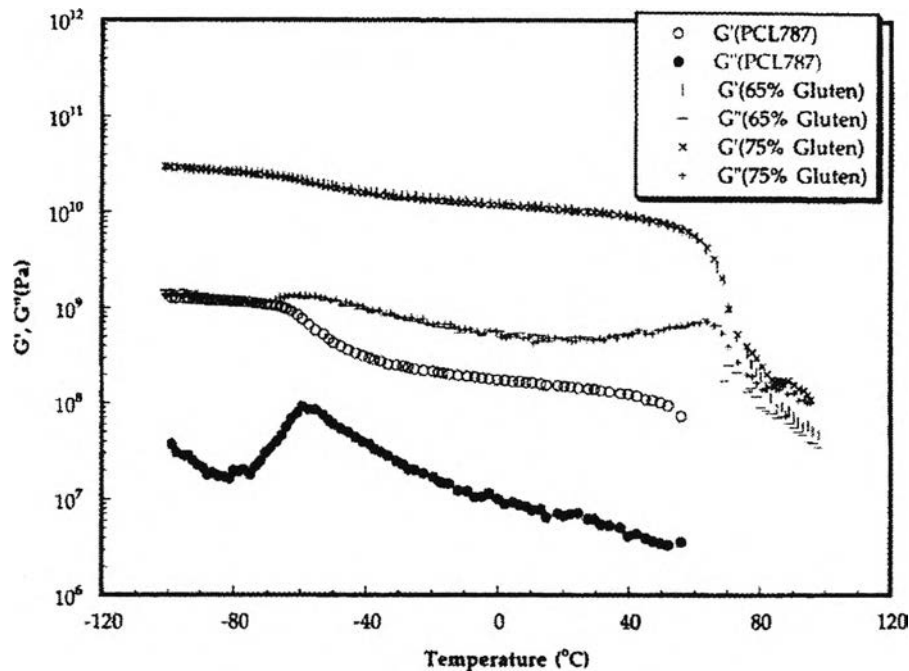


Figure 2.11 Dynamic mechanical analysis of PCL-787 and blends of PCL/PCL-MA/Gluten.

The viscosity of the blends containing modified polycaprolactone was significantly higher than that of blends containing simple mixtures. Since polycaprolactone has a low melting temperature, the loss of material when used at temperatures near or above its melting point is a possibility. However, the 65% gluten blend, when immersed at temperatures as high as 75°C for 15 min, did not indicate any loss in weight. At higher gluten content a small amount of material was lost when immersed in water at temperatures above 65°C. In Figure 2.11, dynamic mechanical analysis indicates that the modulus of blends containing a compatibiliser is higher than those in which the compatibiliser is absent. Similarly, the modulus is higher for the compatibilised blends than those of pure polycaprolactone. Morphology of the blends indicated better mixing in an extruder than in a batch mixer. Also, when a small amount of modified PCL was added, a finer phase morphology was observed.

Starch or thermoplastic starch is one of the choices for mixing with polycaprolactone. *Averous, L. et al.* studied properties of thermoplastic blends, starch-

polycaprolactone in 2000. Different compositions of wheat thermoplastic starch (TPS) and polycaprolactone were melt blended by extrusion and infected. A large range of blends was analysed with different glycerol (plasticizer): starch contents ratios (0.14:0.54) and various PCL concentrations (up to 40 wt.%). The amylose and amylopectin contents of wheat starch were 25 and 75%, respectively. Residual protein content was less than 1%. Figure 2.12 shows the modulus of the blend of 75% starch/glycerol (65/35) with 25% polycaprolactone around 0.8-1.0 MPa at 60-80°C and 20-30 MPa at 25-35°C. When the starch matrix has a glassy behavior, blending with polycaprolactone results in a decrease of the material's modulus but the impact resistance is improved. On the other hand, when the starch has a rubbery behaviour, polycaprolactone increases the modulus of the materials. The dimensional stability was improved significantly, whatever the starch formulation and with a level of polycaprolactone incorporation as low as 10 wt.%. The hydrophobicity of the blends was much more important than the one of starch.

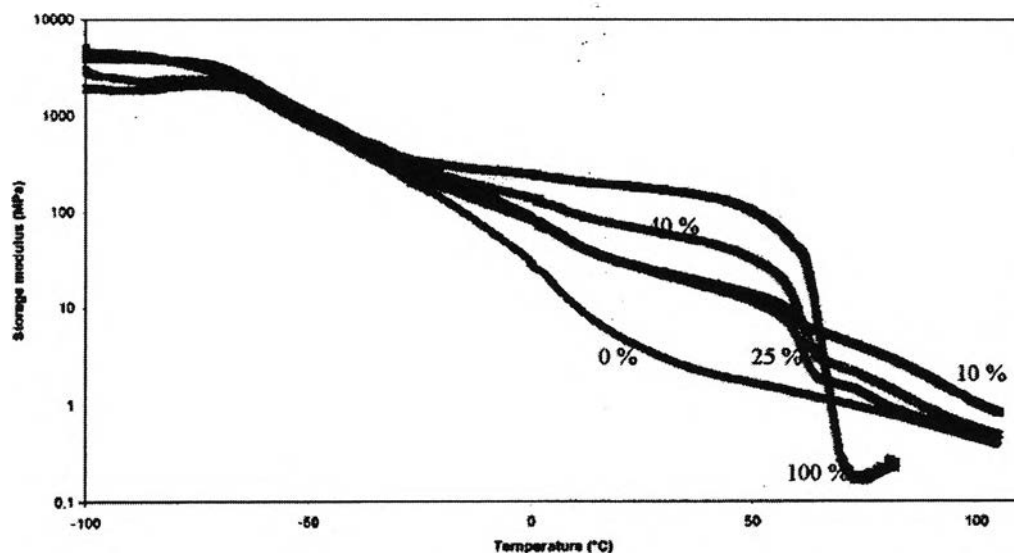


Figure 2.12 Storage modulus curves (DMTA) for S65G35-based blends (0, 10, 25, 40, 100 wt.% of PCL).

The blend of starch and polycaprolactone was still studied by *Matzinos, P. et al.* in 2002, they studied about processing and characterization. The native corn-starch from Greece containing 30 wt% amylose and 70 wt% amylopectin was used in

their work. At the composition 10-50% starch/water (87/13) blend with polycaprolactone could provided modulus up to 250-350 MPa at room temperature. The properties of polycaprolactone/plasticized starch blends processed by extrusion, injection molding and film blowing methods, were investigated. Blending plasticized starch with PCL increased the modulus but decreased the other mechanical properties for both injection molded specimens and films.

In 2003, *Lee, S.H. et al.* studied mechanical and thermal flow properties of wood flour-biodegradable polymer composites. Wood flour, polycaprolactone (PCL) and polybutylenesuccinate butylenecarbonate (PBSC) composites were prepared by knead processing. PCL-*graft*-maleic anhydride (PCL-g-MA) was used as a compatibilizer. The effects of a compatibilizer on the tensile and thermal flow properties of the composites were investigated. They found that the addition of PCL-g-MA improved the mechanical properties, water resistance, and dimensional stability of both WF-PCL and WF-PBSC composites. With the addition of 5% PCL-g-MA, they obtained tensile strength values of 27 MPa for WF-PCL composite and 28 MPa for WF-PBSC composites and Young's modulus values of 1011 MPa for WF-PCL composite and 1007 MPa for WF-PBSC composites. These values are considered to be comparable to those of other WF-polyester composites. Thermal flow temperature and melt viscosity of the composites were increased with the addition of PCL-g-MA. Improvement of mechanical properties and increase of thermal properties may be due to the improvement of surface adhesion by the chemical or physical reaction between the acid anhydride groups of PCL-g-MA and the OH-groups of WF.

Generally, the impression or mouth guard materials should not absorb any amount of water, therefore some additives would be neglected. The last composite that many researchers had been studied was the composite with clay or layered silicate. 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.

In 2002, polycaprolactone/clay nanocomposites prepared by melt intercalation: mechanical, thermal, and rheological properties were studied by *Lepoittevin, B. et al.* Nanocomposites of polycaprolactone were prepared by melt blending at 130°C using a conventional two-roll mill with natural Na⁺ montmorillonite, montmorillonite organo-modified by dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium and modified by methyl bis(2-hydroxyethyl) (hydrogenated tallowalkyl) ammonium. Mechanical and thermal properties were studied as a function of the filler content by tensile testing, Izod impact testing, thermogravimetric analysis and differential scanning calorimetry. The rheological behavior at 80°C was also analysed in relation to the structure and content of the layered silicate.

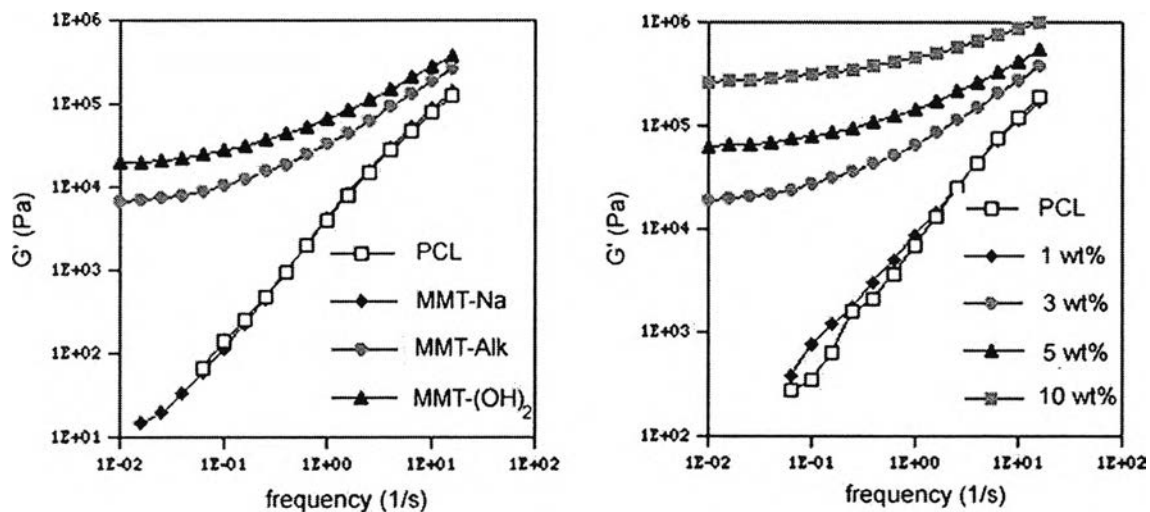


Figure 2.13 Storage (G') moduli for unfilled PCL and PCL modified by 3 wt% of MMT-Na, MMT-Alk, MMT-(OH)₂ at 80°C and PCL nanocomposites containing 1, 3, 5, and 10 wt% of MMT-(OH)₂ at 80°C.

In 2002, *Pantoustier, N. et al.* studied biodegradable polyester layered silicate nanocomposites based on polycaprolactone. Nanocomposites based on biodegradable polycaprolactone and layered silicates (montmorillonite, MMT) were

prepared either by melt intercalation with polycaprolactone or by *in-situ* ring-opening polymerization of ϵ -caprolactone as promoted by the so-called coordination-insertion mechanism. Both non-modified clays (Na^+ -MMT) and silicates modified by various alkylammonium cations were studied. Mechanical and thermal properties were examined by tensile testing and thermogravimetric analysis. The melt intercalation is a solvent-free approach involving mixing of the layered silicate with molten polycaprolactone. Depending on the type of the modifying agent, the stiffness of the polycaprolactone nanocomposites could be significantly improved compared to neat polycaprolactone, even at a filler content as low as 3 wt% of inorganic layered silicate as shown in Figure 2.15. By *in-situ* polymerization, nanocomposites are prepared by polymerization of ϵ -caprolactone in the presence of layered silicates and by initiation of polymerization with tin derivatives ($\text{Sn}(\text{Oct})_2$, $\text{Bu}_2\text{Sn}(\text{OMe})_2$) or by thermal activation. Exfoliated structures have been produced by *in-situ* polymerization in the presence of MMT surface-modified with ammonium cations bearing hydroxyl groups. polycaprolactone/clay nanocomposites displayed higher thermal temperature degradation than the corresponding unfilled polymer. Hybrid polyester nanocomposites generated through the covalent grafting of polyester chains onto the filler surface exhibited higher thermal stability than nanocomposites filled with non-functional clays.

Polymer-layered silicate nanocomposites based on polycaprolactone was studied by *Kiersnowski, A. et al.* in 2004. They prepared PCL nanocomposites based on montmorillonite modified with hexadecyltrimethylammonium bromide (M-HTAB) by the *in-situ* polymerization technique. They had successfully polymerized ϵ -caprolactone in the presence of synthetic montmorillonite modified with hexadecyltrimethylammonium bromide without any additional catalyst. As a result, nano-structured PCL/M-HTAB systems were obtained. It was found that the molecular weight of PCL decreased with an increase in silicate content in the system. It was found that M-HTAB strongly affects the crystallization process of PCL in PCL/M-HTAB systems. A small amount of M-HTAB in the composite accelerates crystallization process. On the other hand, higher loadings of silicate in the system induce a decrease in crystallinity degree and make the crystallization process slower.

Two techniques of nanocomposite preparation, casting and intensive were compared by *Luduena, L. 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, 10°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.

2.8.3 The Addition of Soft Part

The other way to modify PCL in this research is the addition of soft part. The addition of soft part was not the blend with soft polymer but it was the structure modifying of PCL. The graft copolymer is the method chosen in this research because some research works showed the interesting properties of graft copolymer that may appropriate for the mouth guard materials.

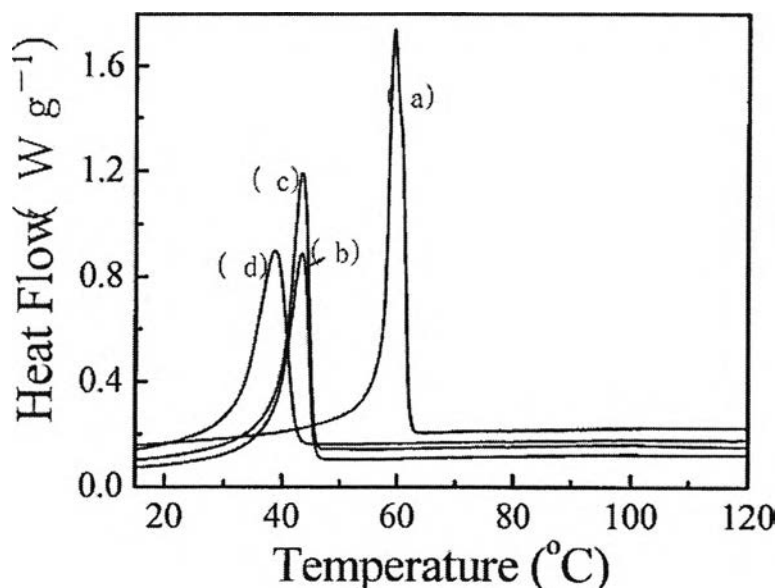


Figure 2.14 DSC curve of a linear PCL (a) and EVOH-g-PCLs: 3 (b), 2 (c), and 1 (d) in table 2.2.

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 (Figure 2.14). 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 PCL by grafting method. The system of PCL graft copolymer with another materials have been widely studied by basic principle of the initiating group to start the ring-opening polymerization.

Table 2.2 The graft copolymerization of ϵ -caprolactone at 120°C

No.	Ethylene Content EVOH mol%	MI ^e of EVOH g 10 min ⁻¹	Sn(Oct) ₂ g	M _n ^a × 10 ⁴	D M _w /M _n	Conversion CL %	[η] dL g ⁻¹	T _m °C	ΔH_m J g ⁻¹
1	44	3.5	0.020	12.3	2.30	58.9	0.48	38.2	49.8
2	32	1.3 ^c	0.020	14.7	2.20	77.6	0.61	41.9	58.2
3	27	3.9	0.020	16.9	2.13	77.9	0.66	43.7	47.6
4 ^d	27	3.9	0	8.3	3.48	40.0	0.41	–	–

^aFor all the polymerizations, Monomer/EVOH (g/g) = 10.3. ^bGPC in THF calibrated with PS standards. ^c190°C/2160 g. The condition of the others is 210°C, ASTM D 1238. ^dThe reaction time is 30 h. The reaction time of the others is 20 h. ^e melting indices.

The initiating group that is generally used for the ring-opening polymerization is hydroxyl group. Polysaccharide or starch is one of many materials using as the backbone of graft copolymer with PCL (Dubois, P. et al. 1999 and Chen, L. et al. 2005). Nevertheless, materials from nature such as polysaccharide or starch seemed to affect the degradability of PCL. To avoid this problem, the polymer like ethylene vinyl alcohol such as polyvinyl alcohol, poly(vinyl alcohol-co-vinyl acetate (Becquart, F. et al. 2007) are better choice for this system. In order to use as mouth guard materials, the impact strength should be concern. 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. Nevertheless, the problem of EVA for using as the backbone of graft copolymer with ϵ -caprolactone is the absence of hydroxyl group or other group to initiate the ring-opening polymerization. Acetate group cannot be the initiator for opening lactone ring. The solution for this problem is to replace acetate group by 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.

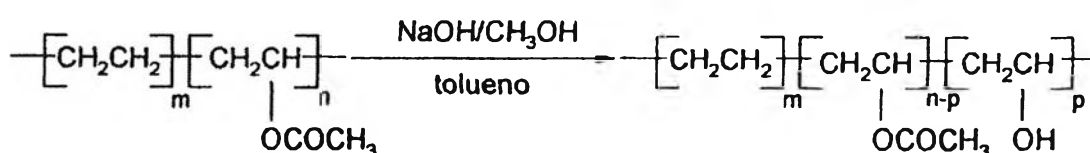


Figure 2.15 Transesterification of EVA (Garcia, F.G. *et al.* 2002. *European Polymer Journal*. 38, 759-769).

The addition of rigid part and soft part are two expected methods in this research for improving the mechanical properties of PCL. However, structure, thermal, mechanical, and dynamic mechanical properties were investigated as well.