



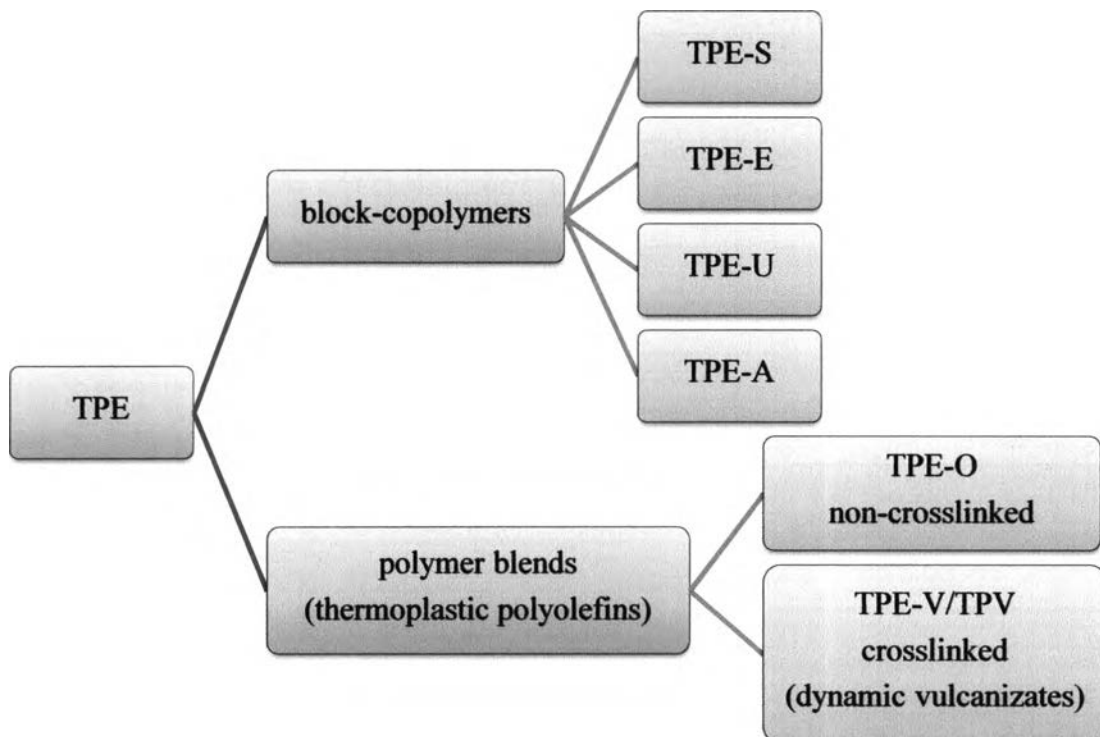
## CHAPTER II LITERATURE REVIEW

### 2.1 Thermoplastic Elastomer

Thermoplastic elastomer (TPE) is a plastic which have a physical mix of two or more polymers to provide a particular material that has all properties of them. It is usually a combination of rubber and thermoplastic which consists of both thermoplastic and elastomeric properties.

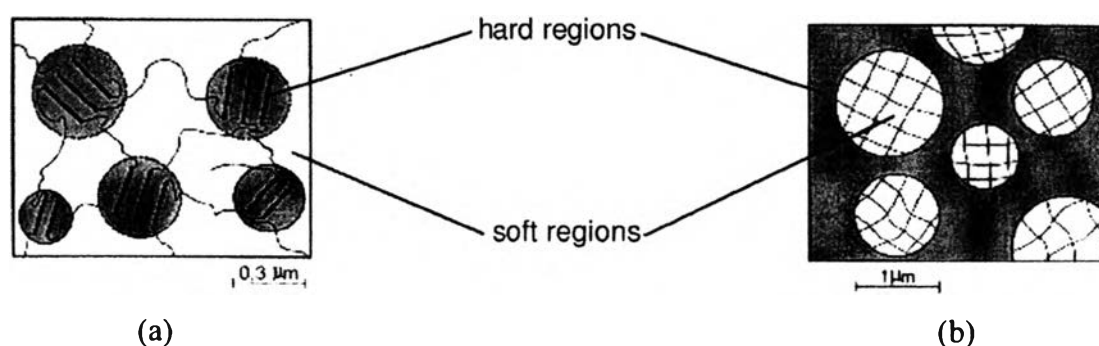
#### 2.1.1 Classification of TPE

There are six types of thermoplastic elastomer by economically considering. They are under the two main categories, multi-block copolymers and blend. The TPE classification chart is shown in Figure 2.1.



**Figure 2.1** Classification of TPE.

The first category is block copolymers which consist of an elastomeric block and a hard block. The four types of a block copolymers category are styrene-block copolymer (TPE-S), polyester-block copolymers (TPE-E), polyurethane/elastomer block copolymers (TPE-U), and polyamide/elastomer block copolymers (TPE-A). Another category is polymer blends which are polyethylene/poly( $\alpha$ -olefin) block copolymers. The two types of TPE in this category are thermoplastic polyolefins with a non-crosslinked rubber phase (TPE-O) and thermoplastic polyolefins with a cross-linked rubber phase (TPE-V or TPV). Partially and fully crosslinked TPV are widely use in an automotive industry because their properties, low hardness and high using temperature until over 100 °C, which involves a dynamic vulcanization process (Scharnowski, 2005). The schematic structures of the two categories of TPE are shown in Figure 2.2.

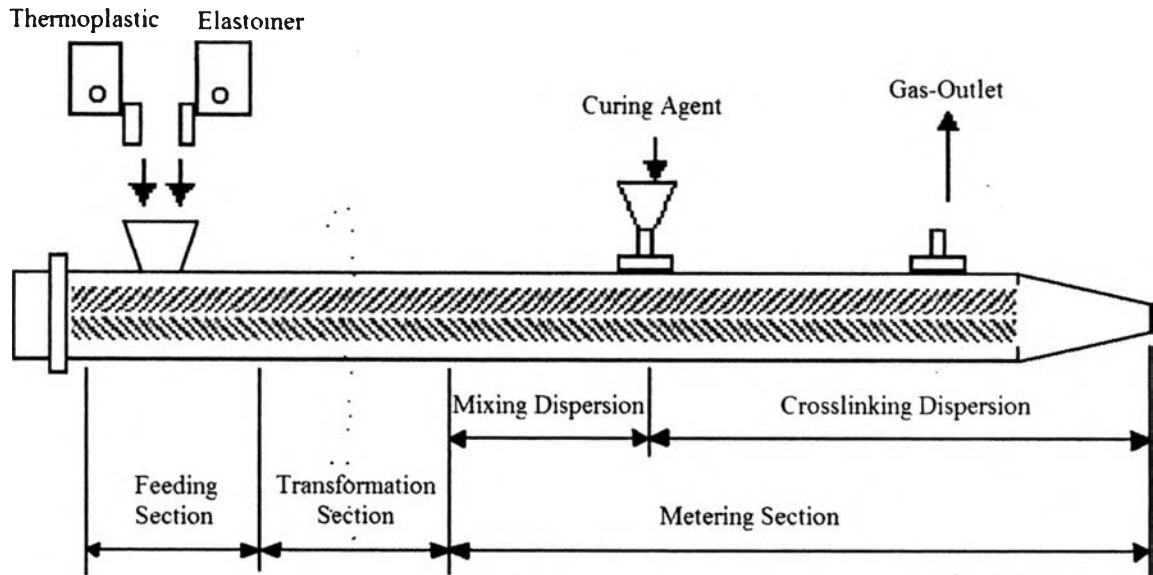


**Figure 2.2** Schematic structures of TPE: (a) block copolymers, and (b) polymer blends, (Scharnowski, 2005).

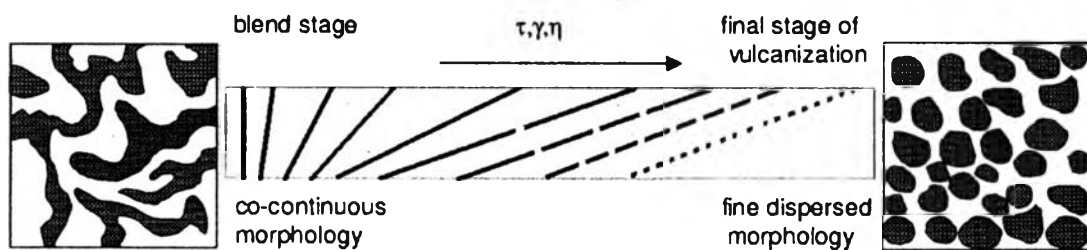
### 2.1.2 Dynamic Vulcanization

Dynamic vulcanization is the best method to produce TPV that sometimes referred to dynamic vulcanizate (DV) or thermoplastic vulcanizate (TPV). It is the process of vulcanizing an elastomer phase during its melt mixing with a molten plastic (Holden *et al.*, 2004). Generally, a melt mixing process can be done by banbury mixers, mixing extruders, and twin-screw mixers, but twin-screw extruders are commercially used. In an extruder, the dynamic vulcanization is done by melt-blending of a thermoplastic matrix phase and a rubber phase first. After a well-mixed

blend form, the crosslinking is occurred by means of a curing agent (vulcanizing agent) which is added into the extruder. The vulcanization then occurs while mixing continuous. The schematic of extruder profile is shown in Figure 2.3.



**Figure 2.3** Schematic of extruder profile for dynamic vulcanization (Scharnowski, 2005).



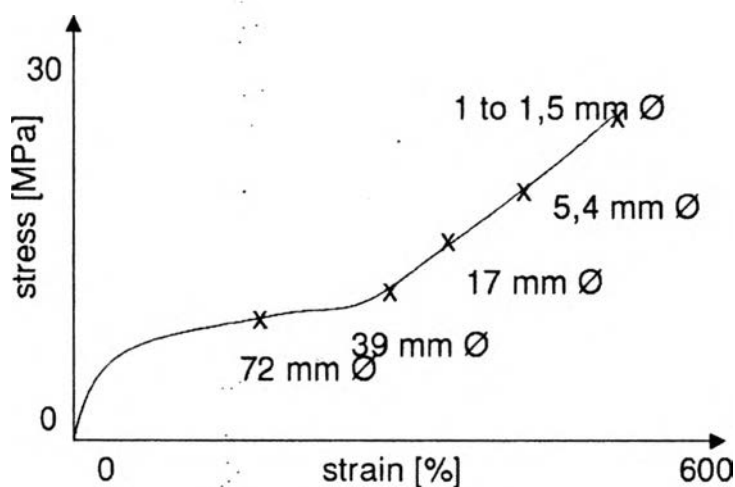
**Figure 2.4** Schematic of morphology development of dynamic vulcanizates during the crosslinking (Scharnowski, 2005).

During the crosslinking, a rubber phase viscosity is increased while a thermoplastic phase viscosity stays the same. Abdou-Sabet *et al.* (1996) indicated; If the rubber phase has a high crosslink density, the rubber phase will deform under shear stress with ripping apart. On the other hand, the poor crosslink density let the

rubber phase undergo large deformation and remains co-continuous phase as see in Figure 2.4. In 2005, Scharnowski collected the optimum crosslink density and found that it should be  $10$  to  $20 \times 10^{-5} \text{ mol/cm}^3$ .

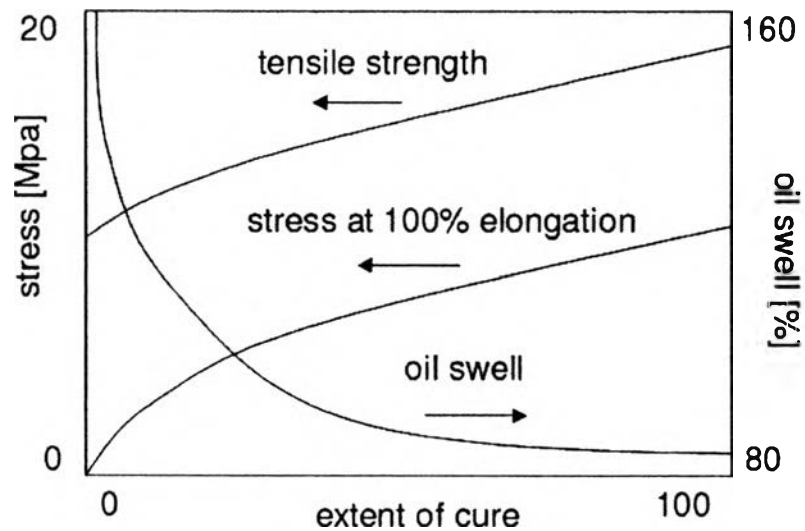
### 2.1.3 TPV Properties

One of purposes to dynamic vulcanize is to produce compositions which can improve properties of both materials. If the elastomer particles of a blend are small enough and fully vulcanized, the properties of TPE-V are improved greatly (Abdou-Sabet *et al.*, 1996) as a stress-strain curve showed in Figure 2.5.



**Figure 2.5** Abdou-Sabet *et al.*, (1996) result indicates the effect of rubber particle size on stress-strain properties of TPV (Scharnowski, 2005).

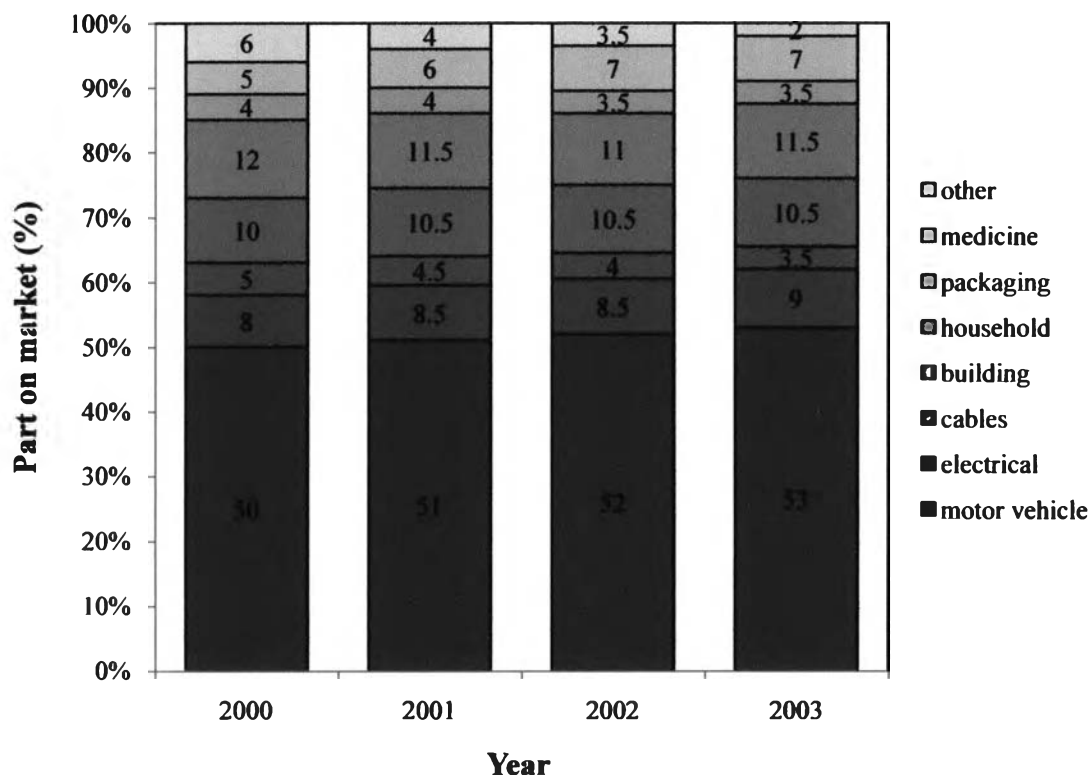
The properties of the TPV that are improved include the improved ultimate mechanical properties, Greater hot oil resistance and other fluids, improved high-temperature utility, reduced permanent set, improved fatigue resistance, greater stability of phase morphology in the melt, and more reliable thermoplastic fabricability. Some improved properties of TPV are shown in Figure 2.6.



**Figure 2.6** Abdou-Sabet *et al.*, (1996) result indicate the effect of curing on mechanical properties and oil swell of TPV (Scharnowski, 2005).

#### 2.1.4 Applications of TPV

The beginning of the use of TPV is to substitute elastomer in existing application. But now a days, it is opening to many application fields. The mainly use TPV is in automotive industry since it has been prepared to improve oil resistance, hot stability as well as to reduce compression set. Another reason is because a manufacturing method, TPV can be produced in general manufacturing methods like thermoplastic such as extrusion molding, injection molding, compression molding, blow molding, thermoforming, and heat welding. But the most important manufacturing methods are extrusion molding and injection molding which can produce parts in one step and also fast joints that easy to de-montage like 2-component-injection molding (Jürdens, 2002). The automotive products commonly made by TPV are suspension bushings for automotive performance applications due to it has a resistance to deformation greater than regular rubber bushings. For other products, TPV can be use as an electrical cable jacket or mostly inner insulation in portable cord. Major application fields of TPV and their development over the years are shown in Figure 2.7.

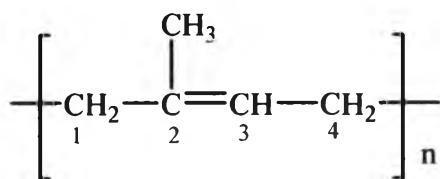


**Figure 2.7** Divisions of application fields for TPV in Germany through the years 2000-2003 (Jürdens, 2002).

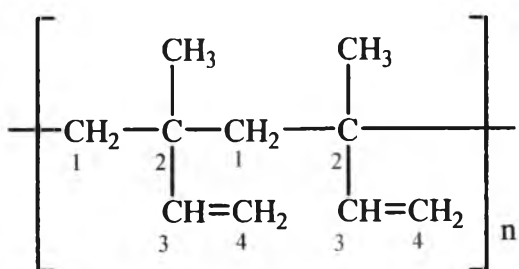
## 2.2 Natural Rubber (NR)

Natural rubber (NR) is an elastomeric polymer obtained from rubber trees. The most natural rubbers come from the *Hevea brasiliensis* rubber tree because this species provides the most latex and properties more than other species.

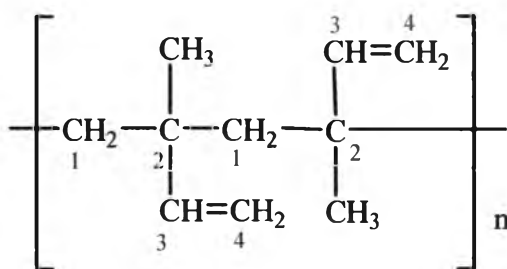
NR has the chemical name as cis-1,4-polyisoprene because polyisoprene has 6 possible isomers and the cis-1,4-isomer is the main structure of rubber received from *Hevea brasiliensis* rubber trees (It gives 97% cis-1,4-isomer of all isomers). The empirical formula of NR and polyisoprene are  $(C_5H_8)_n$ . The chemical structure of NR and the possible isomers of polyisoprene are shown in Figure 2.8.



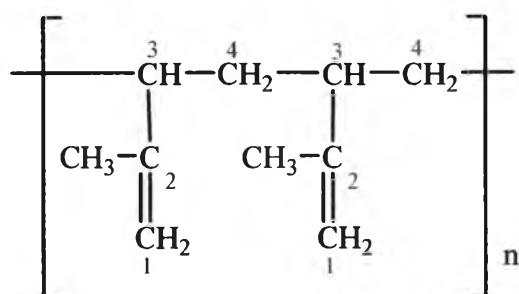
Polyisoprene



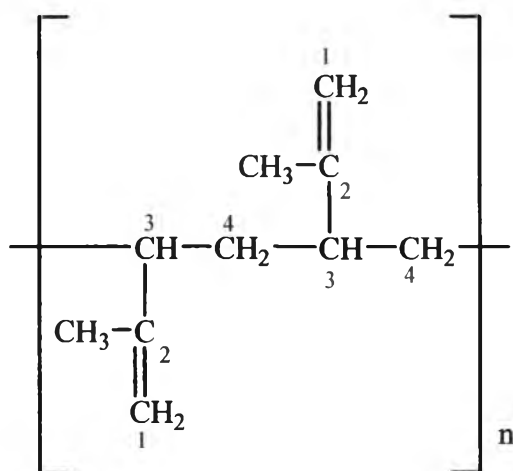
1,2-isomer isotactic



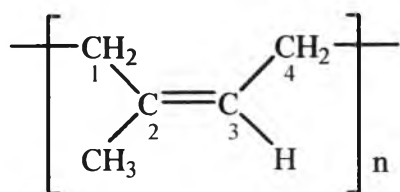
1,2-isomer syndiotactic



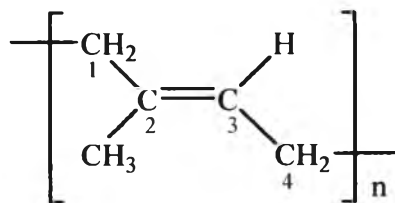
3,4-isomer isotactic



3,4-isomer syndiotactic



cis-1,4-isomer (NR structure)



trans-1,4-isomer

**Figure 2.8** Chemical structures of polyisoprene, NR and polyisoprene isomers.

### 2.2.1 Physical Properties of NR

The physical properties of NR are depend on seasons, weathers, soil, species of rubber trees, age of rubber trees, a length of tapping, a frequency of tapping, a suitable time for tapping, and other factors. The physical properties of NR can be change a little bit because it has some substances that are not a rubber molecule.

Because of having an unsaturated bond in a molecule of NR, it is easy to react with sulfur in vulcanization process. An electron on a methyl group can delocalize to a double bond in a molecule and let NR vulcanizes more faster when compared to other rubbers which do not have any methyl group. But in the same principle, it is very easy to oxidize with oxygen and ozone by the acceleration of metal (such as manganese, iron, copper), heat, light, internal stress from the folding and bending of molecules. It will crack easily that causes a very fast degradation of NR. The amount of ozone 100 ppm can destroy NR in 2 minutes.

NR has a very low oil resistance. It is only hydrocarbon with non-polar molecule which cannot withstand non-polar solvents such as naphtha, toluene, gasoline, oil, carbon disulfide. It is broken very fast when dipped in some chemicals such as nitric acid, sulfuric acid, chromic acid, hydrogen peroxide, and sodium hypochlorite. But it is durable in water, diluted acid, base, and salt.

A service temperature is about -70 to 70 °C. If the temperature is decreased below -70 °C, NR becomes harden and oxidized when the temperature is increased over 70 °C. The glass transition temperature is -72 °C. This let NR can be used at a very lower temperature than another synthetic rubber except silicone rubber and butadiene rubber. The softening point is about 120 °C.

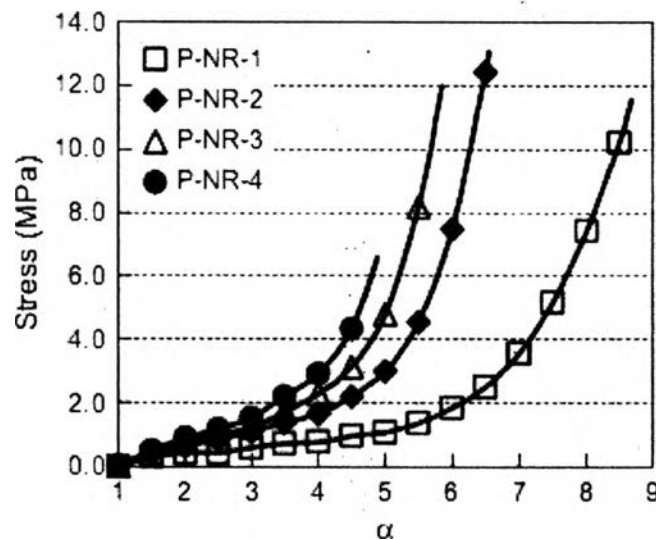
NR can be crystallized when decrease to a temperature under 10 °C. The flexible is decreased and its color will be changed to opaque. The density will be changed from 0.92 to 0.95. If NR has a tidy and nice order structure. The crystallization can be easy to occur by stretching. This makes it has:

- High gum strength (about 4000 psi) without reinforcing filler, so it can use as a low cost filler to reduce a production cost.
- High tear strength, also hot tear strength, which easy to tear off a complex mold.



- High green strength. A green rubber can be stretched to 800-1000%, which can use to make green rubber components for assembly before a vulcanization. For examples, rubber pipe components, tyre components.
- Good tack.
- Moderate wear resistance.

For a vulcanized NR, a more stretching vulcanized NR makes a tensile strength get higher. Ikeda *et al.* (2007) indicated, a higher elongation ratio makes a higher stress as shown in Figure 2.9. Here,  $\alpha$  is defined as  $\alpha = \frac{l}{l_0}$ , in which  $l_0$  is the initial length and  $l$  is the length after deformation.



**Figure 2.9** The stress-strain curves of peroxide-crosslinked NR samples (Ikeda *et al.*, 2007).

From the chemical structure, the single bonds between carbon and carbon make molecules move easily. This causes the softness and the flexible of NR and including very high resilience and low hysteresis. It is not store energy and heat.

For another property, it is a good insulator. Its density is around 0.915-0.930 kg/m<sup>3</sup>. The refractive index is about 1.5215-1.5238 at 20 °C.

However, gum cannot be directly used for applications. It needs to put some additives and fillers in (green compound) and vulcanizes (vulcanized rubber). There are several reasons to describe that gum is not suitable for uses.

First, gum has a viscoelastic property. It behaves both characteristics, plastic and elastic. It will deform when receives forces. When the forces are released, it will come back to the original shape if it deforms under the elastic region. If the forces are higher to the plastic region, it will deform permanently or may come back to the original shape but not 100% which results in property changes. Second, gum has a thermoplastic property. At low temperatures, it would be stiff. But it becomes soft and flows at elevated temperature. This allows using in limited temperatures. Third, gum has low strength, low resistance to pressure and friction forces. Fourth, gum can dissolve in many solvent. It is a big molecule with molecular weight about 30,000-300,000 g/mol. These molecules are fixed together by a low force such as Van de waals force. Thus, the molecules can separate out easily in non-polar solvent or substances that have a solubility parameter close to it.

### 2.2.2 Vulcanization System

Due to the characteristic of gum, an important thing in rubber production is vulcanization. Vulcanization or curing is a process that makes crosslink networks in the molecules of rubber. A vulcanized rubber or cured rubber will be changed in properties. These are:

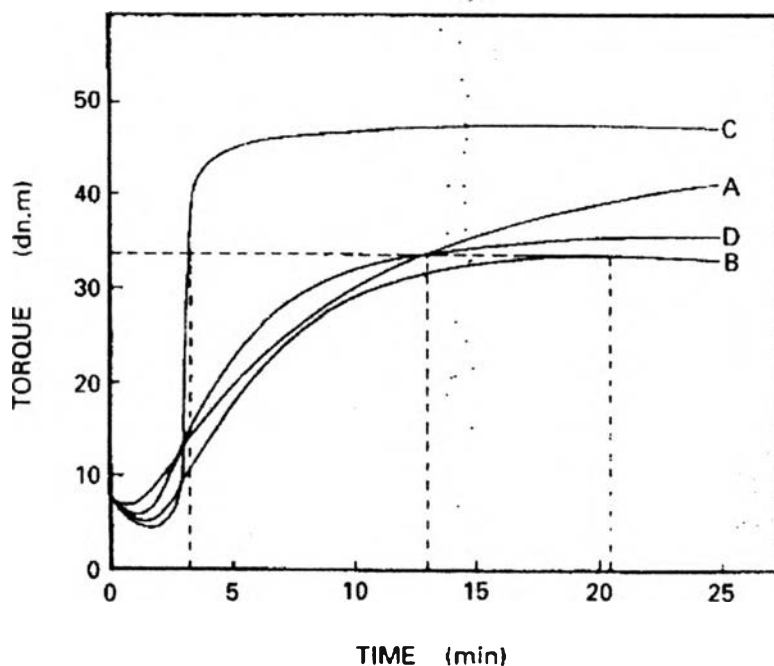
- Change a thermoplastic to thermosetting property.
- Change a viscoelastic to elastic property.
- Change a soluble in solvent to non-soluble.

Therefore, vulcanization is the process to improve properties of NR as mentioned before.

There are 2 types of chemicals that put in the rubber, additives and fillers. Additives are the chemical substances that add into the rubber to allow the vulcanization. Vulcanizing agents are used to make the crosslink rubber; accelerators are used to reduce time to vulcanization; and activators are used to increase the efficiency of accelerators. But fillers are the substances that fill into the rubber for specific purposes. For examples, carbon black is used to reinforce, calcium carbonate to reduce cost, softener to help compounding, processing aids (or plasticizers) to help in

processing, antioxidants and antiozonants to prevent oxidation, age-resistors to prevent degradation from weathers, blowing agents to make foams or sponges, flame retardants to prevent burning, and colorants to make color products.

After putting additives and fillers into the rubber, this rubber is called a “green compound” or “green rubber”. Next is the time for vulcanization. Green rubber is kept in a specific heat and pressure for a specific time to occur a chemical reaction which gives the crosslink in the rubber. The rubber that passes the vulcanization process is called a “vulcanized rubber” or “cured compound”.



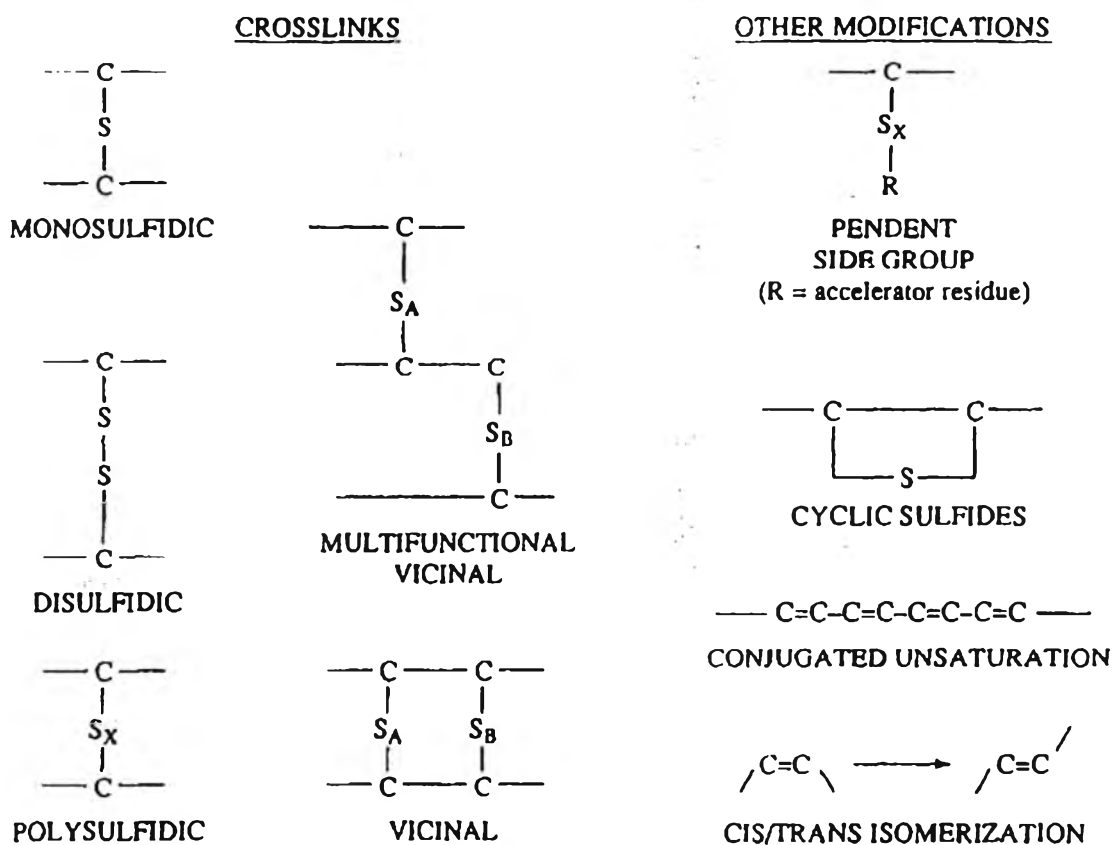
**Figure 2.10** Rheographs of themixes indicating the curing of NR to a common torque of 33.8 dNm. (A) Dicumyl peroxide, (B) CV, (C) EV, and (D) mixed. (Unnikrishnan *et al.*, 1997).

There are many systems to vulcanize rubber. These are conventional system (CV system), efficient vulcanizing system (EV system), semi-efficient vulcanizing system (semi-EV system), peroxide system, and urethane system. Each vulcanization system needs different additives and gives different vulcanization time as

shows in Figure 2.10. In this study, the vulcanization system involving sulfur (CV and EV system) and peroxide system are concentrated.

### 2.2.2.1 Sulfur Systems (CV and EV Systems)

The sulfur system is the system that use sulfur as a vulcanizing agent. The difference between CV system and EV system is the accelerator to sulfur ratio (Acc:S ratio). The different Acc:S ratios cause the different crosslink structures which are shown in Figure 2.11.



**Figure 2.11** The crosslink structures of natural rubber by sulfur vulcanizing agent (Akiba *et al.*, 1997).

The CV system has a low Acc:S ratio. It means that this system use low amount of accelerator and high amount of sulfur. The crosslink structure received are low monosulfidic and disulfidic crosslinks but high polysulfidic crosslinks. The high total crosslinks occur very fast after starting the vulcanization and

greatly decrease after 40 minutes. The properties of vulcanized rubber from sulfur system are high strength, high temperature stability is very poor, high %compression set, and good flexible life.

In additions, the system having accelerator combination shows higher yield stress values than systems having a single accelerator in NR latex vulcanized by both CV and EV system (Varkey *et al.*, 1996).

The EV system has a very high Acc:S ratio. That is the use of high accelerator amount and very low sulfur amount. It provides very low polysulfidic and disulfidic crosslinks but very high monosulfidic crosslinks. The total crosslinks occur slower and the amount of total crosslinks is lower than the sulfur system, but the amount of total crosslinks is quite stable or a little decrease. The properties of vulcanized rubber from EV cure are lower strength, high temperature stability is very good, low %compression set, and poor flexible life.

There are several features of EV system. It uses a small amount of sulfur but high amount of accelerator or may use a sulfur donor compound. Each crosslink contains only one or two sulfur atoms. The vulcanized rubber resists to a reversion but has quite low mechanical properties than CV system. Akiba *et al.* (1997) indicated in Table 2.1 that the resulted vulcanizates efficiently utilize sulfur to form networks in which the crosslinks are mainly monosulfidic, which exhibits a low degree of main-chain modifications. The use of EV systems in natural rubber reduces or eliminates reversion, except at very high curing temperatures. Thus, the resulting vulcanizates exhibits a high resistance to thermal and oxidative aging.

**Table 2.1** Structures of vulcanized rubber and properties of different curing systems (Akiba *et al.*, 1997)

	CV system	EV system
Poly- and disulfidic crosslinks (%)	95	20
Monosulfidic crosslinks (%)	5	80
Cyclic sulfide concentration	high	low
Low-temperature crystallization resistance	high	low
Heat-ageing resistance	low	high
Reversion resistance	low	high
Compression set, 22 h at 70°C (%)	30	10

#### 2.2.2.2 Peroxide System

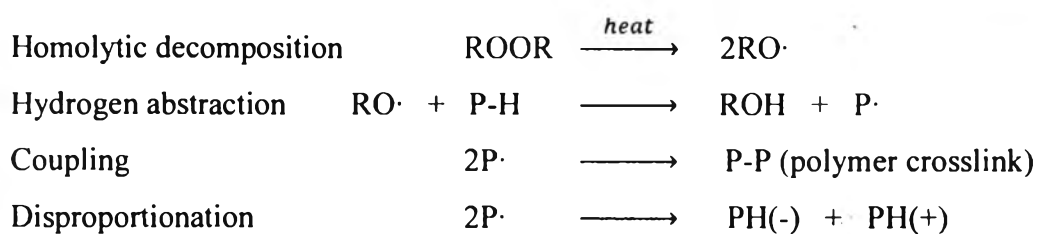
This vulcanization system uses peroxides as a vulcanizing agent instead of sulfur. The highly often used peroxides are dicumylperoxide and bis-(*t*-butylperoxy isopropylbenzene). They have different half-life at different temperatures as shown in Table 2.2. Peroxide has a fast scorching and slow cure time and the cure time is 6 times of its half-life. A half-life will decrease at elevated temperature. In general, a curing temperature of peroxide is in between 160-190 °C. It is needed to consider a curing temperature and half-life together.

**Table 2.2** Half-life of peroxides

Peroxides	Half-life (min)	
	160 °C	180 °C
Dicumylperoxide	5.5	0.8
bis-( <i>t</i> -butylperoxy isopropylbenzene)	12	2
2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane	7.7	1.1

Peroxide is not used too much. It is only about 2.5-3 phr. If it has high content, a rubber will decrease in modulus and elongation. Tensile strength will both increase and decrease.

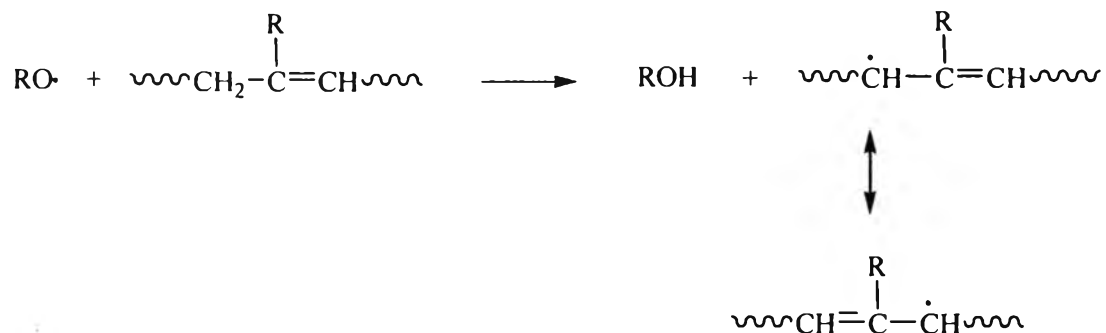
Akiba *et al.* (1997) were described a peroxide crosslinking mechanism as shown in Figure 2.12. The crosslinking reaction starts from the homolytic decomposition involving of peroxide to produce alkoxy radicals, then peroxide radicals will abstract hydrogen atom of a polymer chain (rubber) and make it into a polymer radical. From the studies, they are indicated that the hydrocarbon radicals (polymer radicals) can occur in two ways. These are coupling reaction and disproportionation reaction. But the hydrocarbon radicals predominantly undergo coupling reaction rather than disproportionation.



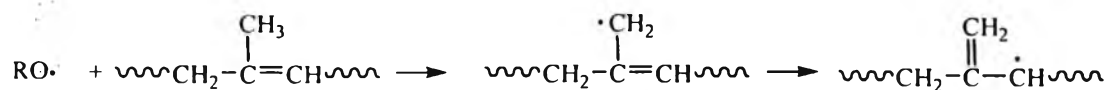
**Figure 2.12** The crosslinking reaction of the peroxide vulcanization system.

The coupling reaction forms crosslinks between polymer chains. For polydiene elastomers, experimental evidence indicates that the primary radical formed by peroxide decomposition abstracts a hydrogen atom from a carbon alpha to the double bond. But in natural rubber, the methyl group is also reactive towards hydrogen-atom abstraction, as shown in Figure 2.13.

## Polydiene

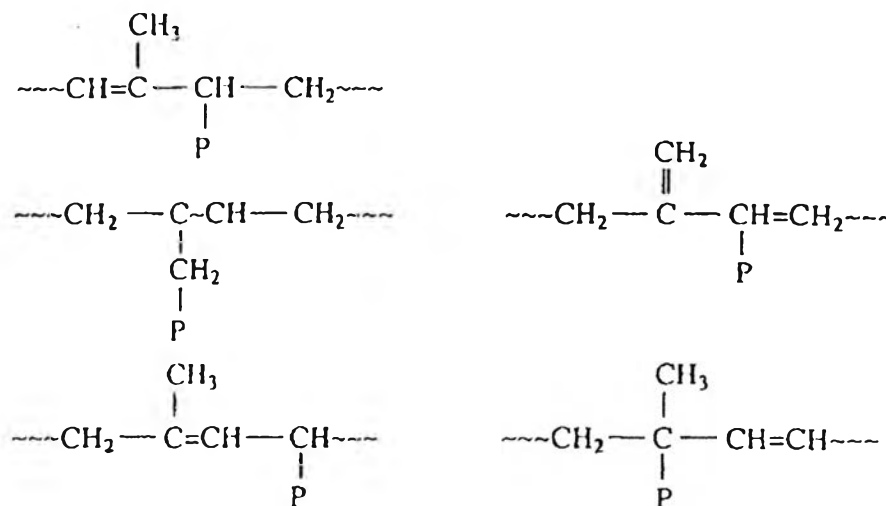


## Natural Rubber



**Figure 2.13** The radical formation of polydiene and NR.

Therefore, the possible structures present in peroxide crosslink natural rubber are shown in Figure 2.14.



**Figure 2.14.** The possible crosslink structures present in peroxide crosslinked natural rubber (P = Polymer chain) (Akiba *et al.*, 1997).



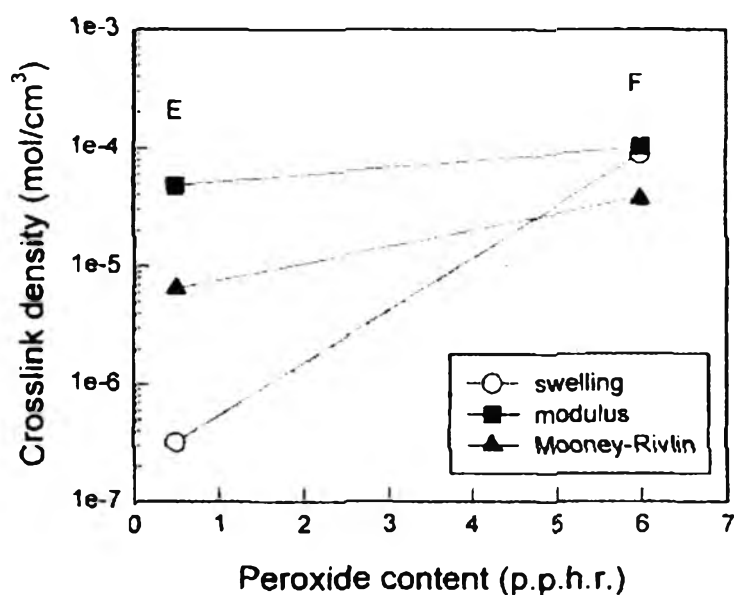
And the relative crosslinking efficiencies of some rubbers when cured with dicumyl peroxide (DCP) are shown in Table 2.3.

**Table 2.3** Relative crosslinking efficiencies of various rubbers with DCP (Akiba *et al.* 1997)

Rubbers	Crosslinking efficiencies
SBR	12.5
BR	10.5
NR	1.0
NBR	1.0
CR	0.5
RE	1.0
IIR	0

There are some important warnings in using peroxides. First, they are dangerous chemicals and need to keep and use with the best safety conditions. Peroxides are easy to degrade in a hot air. It needs to keep it cold below 37 °C and keep it away from heat generators, the UV light, spark, and flame. Also it should be kept far from oxidants and reducers, avoided an attack and kept it in an originally container to prevent a contamination. Second, it has to be very careful in selecting chemicals. Peroxides are more sensitive than sulfur. They react with other chemicals as side reactions and do not vulcanize rubber. For examples, acidic carbon blacks will decrease a cure rate, some plasticizers bring a peroxide react to hydrogen such as aromatic oils, some antioxidants and antiozonants react with peroxide too. Third, a close system condition is preferred for curing or vulcanization. Because the oxygen gas in an open condition will oxidize with peroxide radicals to become hydroperoxides, peroxide decomposition, and reduce crosslinking cause a rubber degradation. And for the last, some peroxides give bad smell during a vulcanization process. It may be toxic for human.

Rubbers vulcanized by sulfur are well known in good mechanical and thermal properties than peroxides. Because, the use of sulfur provides crosslink networks contain high proportions of polysulfidic crosslinks, while peroxides give carbon-carbon crosslink type which sulfur crosslinks are stronger than carbon crosslinks.



**Figure 2.15** The plot between crosslink density and peroxide content in NR shows modulus values, stress-strain values, and swelling values (Hagen *et al.*, 1996).

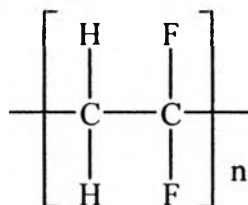
As seen in Figure 2.15, it is indicated that the peroxide system can increase modulus by increasing the peroxide content. At low peroxide contents, the crosslink density gives the lowest values, whereas the crosslink density increases at the higher peroxide content to a value slightly lower than the modulus value (Hagen *et al.*, 1996). In 1997, Unnikrishnan *et al.* indicated that the NR crosslinked by using dicumyl peroxide showed the lowest equilibrium uptake value in all penetrants compared to the other systems. This is due to the difference in crosslink types and the difference in crosslink densities. The NR with peroxide cure system has the lowest interaction with the penetrants compared to other systems.

Nevertheless, the peroxide system has many good advantages. Peroxides can crosslink both saturated and unsaturated rubbers such as silicone

rubber (Q), ethylene-propylene rubber (EPM). The peroxide system does not need accelerators and activators. A vulcanized rubber has the highest thermal resistance, the lowest %compression set, and can bend at low temperature without fracture. Products from this system have white color, not opaque, and the color does not fade in UV light, which can use in high color products.

### 2.3 Poly(vinylidene fluoride) (PVDF)

Poly-1,1-difluoroethene or poly(vinylidene fluoride) (PVDF) is a thermo plastic materials in the fluoropolymer family. It can be synthesized from the gaseous vinylidene (VDF) monomer by a free radical polymerization using 2 processes, emulsion polymerization process and suspension polymerization process. Suspension polymers are available as free-flowing powder or in pellet form for extrusion or injection molding (Drobny *et al.*, 1999).

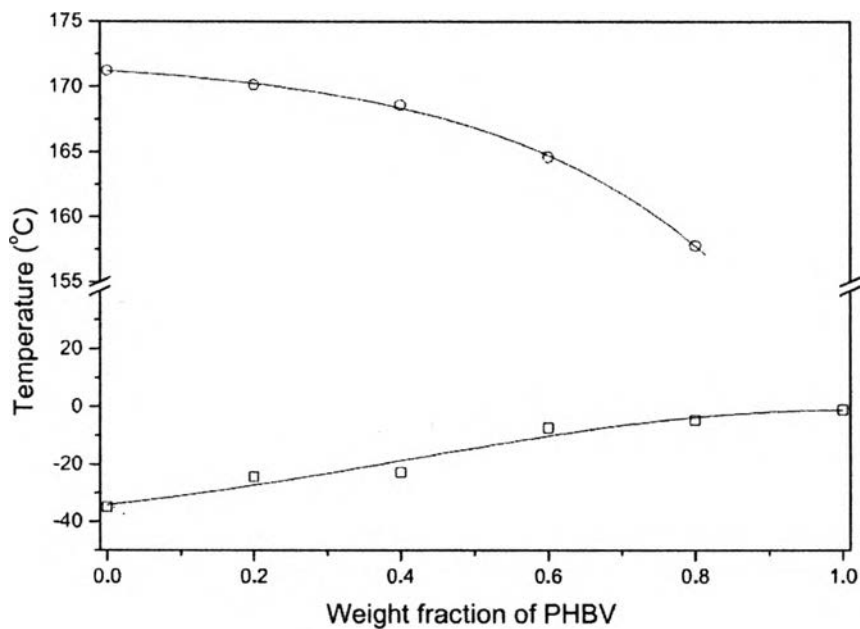


**Figure 2.16** The chemical structure of PVDF.

#### 2.3.1 Properties of PVDF

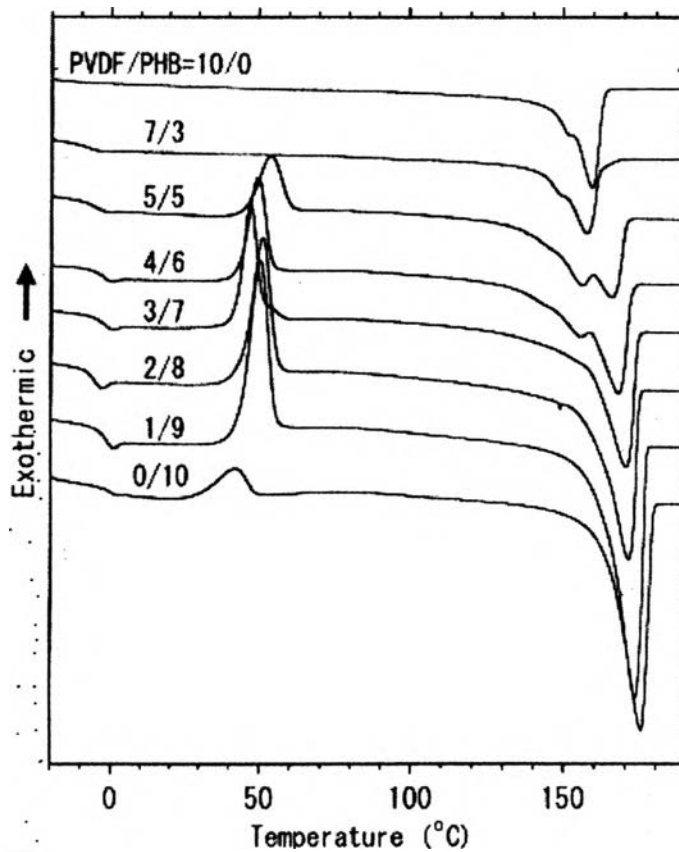
The PVDF a high purity polymer with special properties. It appears whitish or translucent solid which is both strong and tough. But in a form of thin section such as films, filament, and tube, it becomes transparent and flexible. It has a low density of 1.78 and non-soluble in water. It has high thermal stability and high temperature capabilities. It has a low melting point is around 177 °C which is easy for melt processes and also is able to weld. It has a continuous use temperature up to 150 °C and has an excellent aging resistance.

The blending ability of PVDF with another polymer has several carried out. Qiu *et al.* (2004) found, PVDF can be miscible with PHBV based on their result of single composition dependent  $T_g$  over the composition range and  $T_m$  of PVDF decreased with increased PHBV as shown in Figure 2.17.



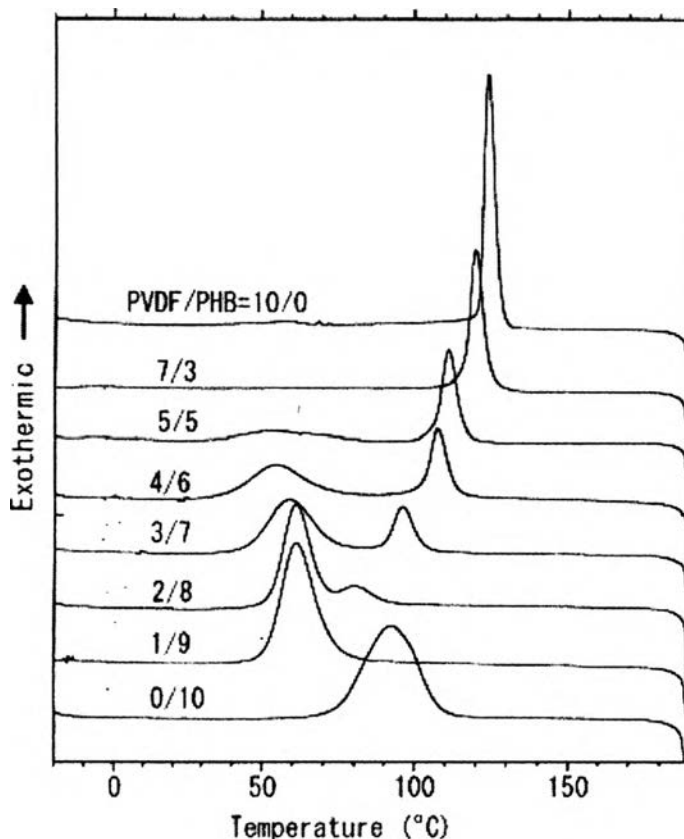
**Figure 2.17** Variation of the  $T_g$  of PVDF/PHBV blends (□) and the  $T_m$  of PVDF (○) as a function of the PHBV composition (Qiu *et al.*, 2004).

Later, Kaito (2006) had studied the crystal of polymers in PVDF/PHB miscible blends. He found that PHB and PVDF/PHB blends with a weight ratio of 1/9-5/5 crystallized during heating process at the temperature around 40-60 °C as shown in Figure 2.18. But the PHB crystallization was restricted for the blends when the PVDF content was higher.



**Figure 2.18** DSC curves of melt-quenched samples of PVDF, PHB, and PVDF/PHB blends during the heating process at 10 K/min (Kaito, 2006).

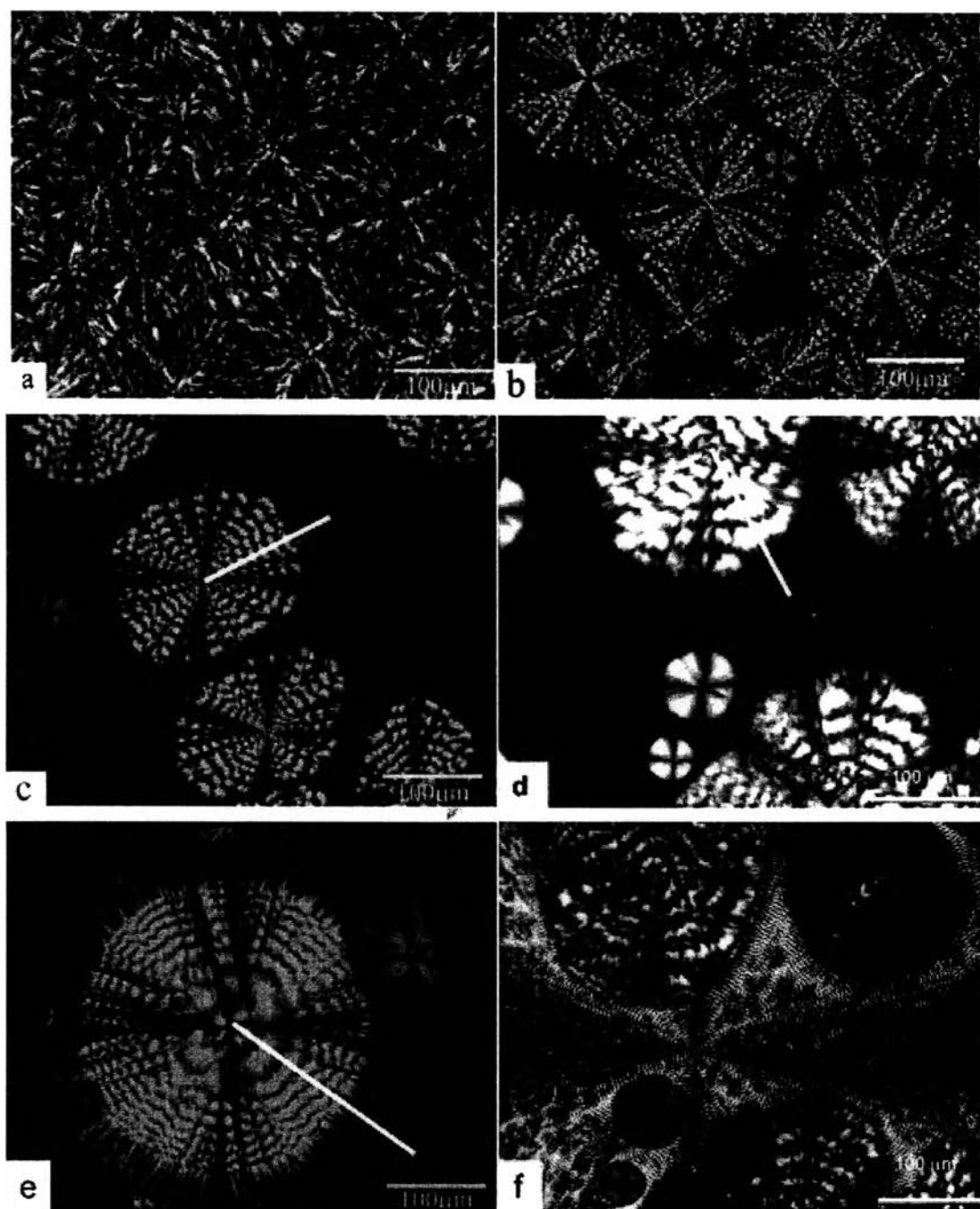
During the cooling process from the molten state, PVDF, PHB and PVDF/PHB blends of 2/8-5/5 are crystallized by melt-crystallized process. But the crystallization were restricted for the minor component. The crystallization during the cooling process is shown in Figure 2.19.



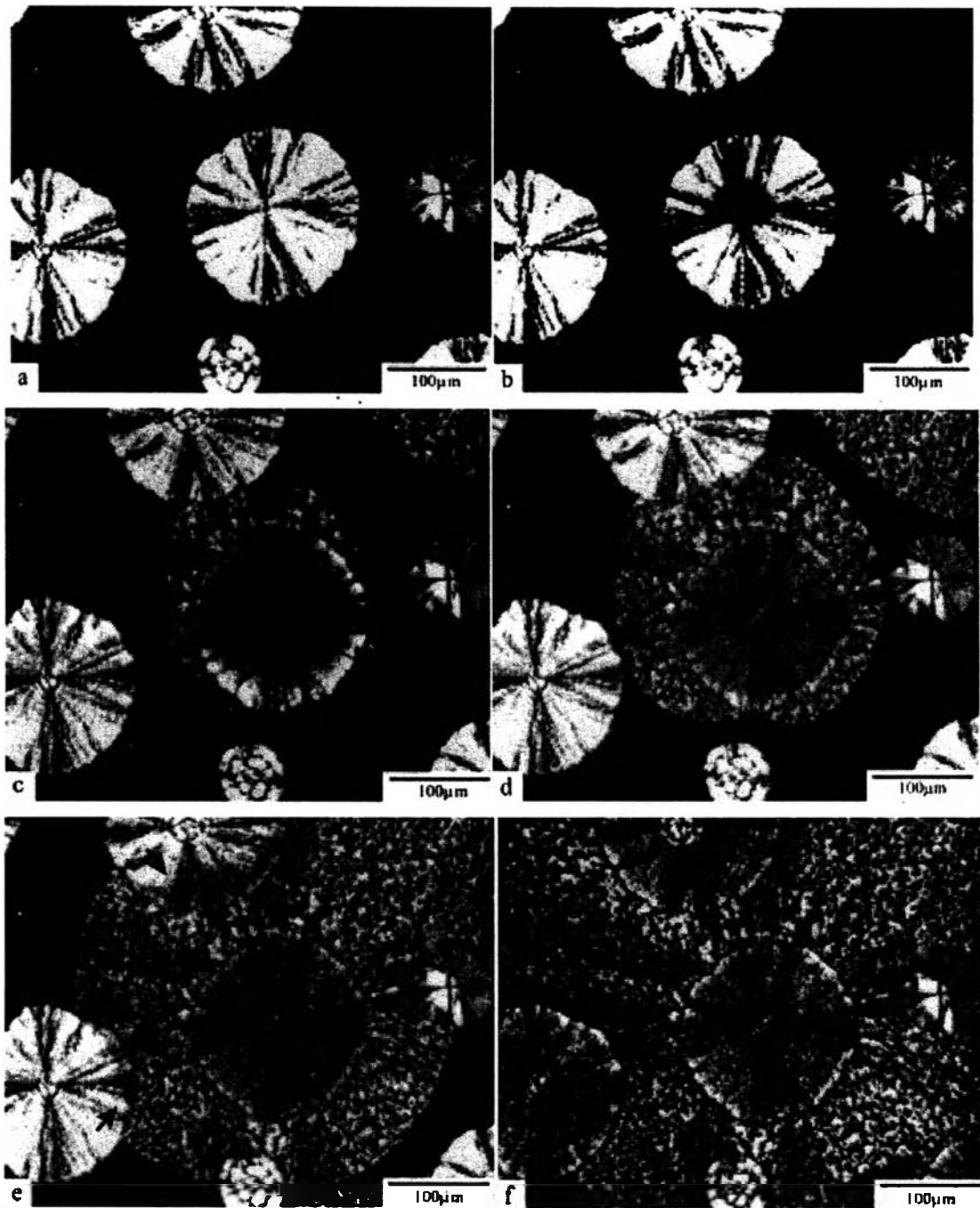
**Figure 2.19** DSC thermogram of PVDF, PHB, and PVDF/PHB blends during the cooling process from the molten state at 10 K/min (Kaito, 2006).

Recently, the interpenetrating and interlocking spherulitic crystallization was found in the PVDF/PHB blend (Liu *et al.*, 2007). The interpenetrating crystallization will occur where spherulites of the one component intrude in those of the other. But the interlocking spherulitic crystallization is occur in which one component nucleates its spherulites in the internal of those of the other and grows then—depending on the nucleation density—by incorporation of a large number of the latter.

These two phenomena are found in the PVDF/PHB blend = 40/60 (wt/wt) crystallization. The interpenetrating crystallization occurred by the first crystallization of PVDF at high temperature around 140-158 °C as shown in the Figure 2.20.



**Figure 2.20** Spherulitic morphologies of PVDF in 40/60 (wt/wt) PVDF/PHB blends crystallized isothermally at various crystallization temperatures of PVDF: (a) 140 °C, (b) 145 °C, (c) and (d) 150 °C, (e) 158 °C, and (f) as (d) but additional PHB crystallized at the crystallization of PHB = 60 °C (Liu *et al.*, 2007).



**Figure 2.21** (a) spherulitic morphology of PVDF crystallized at the temperature = 148 °C in a blend PVDF/PHB = 40/60.(wt/wt). (b)-(f) PHB spherulite nucleated inside a PVDF spherulite and grown radially at 60 °C for: (b) 3 min, (c) 15 min, (d) 21 min, (e) 30 min, and (f) crystallized completely. (Liu *et al.*, 2007).



The PVDF spherulites grew in a certain time and then stopped, due to the impoverishment of the rest melt in PVDF and the morphology became stable. Then PHB crystallized after the temperature was cooled down to the crystallization temperature of PHB at 60 °C. PHB crystallized from the melt that surrounding of PVDF spherulites and became larger. Their growth fronts were contacted PVDF spherulites and further grow penetrated pass into the growth front of dendritic spherulites of PVDF.

Figure 2.21 shows the interlocking spherulitic crystallization. It was occurred by the first crystallization of PVDF at the temperature of 148 °C, then PHB follow crystallized when the temperature was cooled down to 60 °C like the interpenetrating crystallization. But in crystallization of PHB, PHB spherulites were nucleated inside the PVDF spherulites and grew radially. They also had the interpenetration, if the larger growth front of PHB spherulites come to the growth front of other PVDF spherulites and crystallized within, as see the arrows in Figure 2.21 (e). This decelerates upon interpenetration and becomes curved inward. For the same reason, the PHB spherulites showed an inward curvature after leaving the nucleating PVDF spherulites.

For other properties of PVDF, it is a highly non-reactive fluoropolymer. It has an excellent chemical resistance. It can resistant to solvents, acids, bases, and heat. It stables to sunlight and other sources of ultraviolet radiation. It is also resistant to weathering and fungi. It has excellent mechanical properties. It has a high tensile properties, impact strengths, and abrasion resistance. It is an excellent polymer in resistance to creep and fatigue. When PVDF is under load, it is rigid and resistant to creep under mechanical stress and load. PVDF appears high dielectric strength, generate low smoke when fire burning. It is easy for many processes such as extrusion, injection, compression, blow molding solution processes. It is a physiologically harmless polymer and approved for contact with food products.

### 2.3.2 Applications of PVDF

PVDF has low cost compare to other fluoropolymers and general applications are involve its properties. It is used in high purity application like membranes such as high purity water flirtation, waste water treatment, and gas separation. It can be used in chemical process industry such as pipes and fittings, pump, valves.

It is used in high purity fluid transportation and Plumbing. Due to the excellence in mechanical properties, it can use in off shore oil industry like multilayer structures for oil and gas. It can be use in other application involve high temperature applications and high pressure applications. For wire and cables industries, it can make an insulator for premium wire and jacketing for communication cables in USA. PVDF can be used in other applications such as semiconductor, medical, solar glazing, nuclear waste processing and defense industries like lithium ion batteries.

The superior properties PVDF let it to be used in automotive applications. It exhibits high chemical and abrasion resistance, excellent thermal stability, unaffected by UV radiation, and resist to creep under mechanical stress and load. It can be used for molded parts, for extruded profiles, or as protective coatings. Its strength, durability and versatility make it suitable for automobile wiring harnesses, fuel lines and fuel line coatings, decals and decorative films, coatings, electrochromic applications and plastic optical fibers (POF) (Arkema Inc., 2005).

#### *2.3.2.1 Wiring Harnesses*

Due to the excellent properties of PVDF offer it for wire coatings. It can be extruded as primary insulation or used as a protective cover. The excellent chemical resistance and high melting point make it well suited for applications under the hood. PVDF insulated wire is commonly crosslinked by electron-beam radiation to further increase its toughness, cut-through resistance and continuous-service use temperature. If it has specific formulas and processes, the crosslinked polymer makes light-weight, flame-retardant wire insulation that offers a temperature rating of approximately 175 °C, does not melt and is resistant to most solvents, fuels, lubricants and other hydrocarbon fluids.

#### *2.3.2.2 Decorative Films*

PVDF films for automotive accessories provide an attractive, corrosion-resistant alternative to paint. There are many parts that PVDF film used on, such as rocker panels, roofing strips, tail lamp housings, body side moldings, front and rear bumpers, mirror housings and pillars. It can apply to many polymers such as PVC, PC, TPO, and ABS. It also can be supplied with a heat-activated adhesive for bonding to polyolefins. PVDF films are available in virtually any color, including solid, metallic, pearlescent, chrome and brushed aluminum.

### *2.3.2.3 Fuel Lines*

It is very good for fuel lines because PVDF can resist gasoline, road salt, oils, lubricants, brake fluid, transmission fluid, windshield washer fluid, coolants, and battery acid. The tubing is a multilayer construction consisting of five layers. It provides a barrier layer in low-permeation automotive fuel lines. In addition to being easily processed on conventional co-extrusion equipment, this innovative fuel line construction exhibits excellent cold temperature impact strength (-40°C), chemical resistance and dimensional stability. It is also compatible with a wide range of fuel-alcohol blends and is available in a conductive version. It can be used as a protective coating over carbon steel, fuel and brake fluid lines, and under-chassis applications. It can be applied in very thin layers and maintains durability and corrosion resistance. It can also be applied as a liquid coating, as a powder coating, or by cross-head extrusion.

### *2.3.2.4 Functional Powder Coating*

Based on the resistance to oils and many fluids, a corrosion resistance, and non-effective with UV light, it is suitable for exterior and interior applications. It may be used to coat carbon steel parts as a low-cost alternative to stainless steel. This powder coating is durable and may be applied in very thick coatings up to 100 mm.

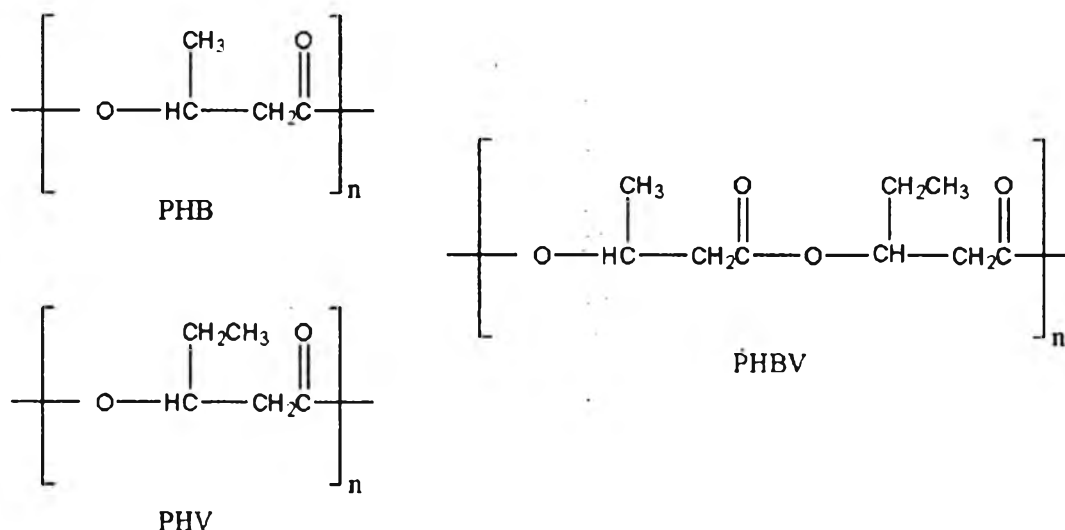
### *2.3.2.5 Electrochromic Technology*

From this technology, PVDF can be used to control the transmission of visible and UV light through automotive windows. Windows will darken or lighten to control the amount of light permitted inside a vehicle. This because the electrical property of PVDF. This PVDF is also used in lithium ion batteries which can be used in hybrid electric vehicles (HEV).

## **2.4 Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)**

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or PHBV is a kind of biodegradable polymer belonging to the aliphatic polyesters class. It is a natural-based polymer derived from cornstarch with 100 % biodegradability. PHBV is a copolymer of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV) which made from bac-

terial fermentation process with variety of feedstock. The chemical structures of PHB, PHV, and PHBV are indicated in Figure 2.22. It has high biological compatibility and can be digested by bacteria also utterly decompose to carbon dioxide, water and biomass in soil or under composting condition.



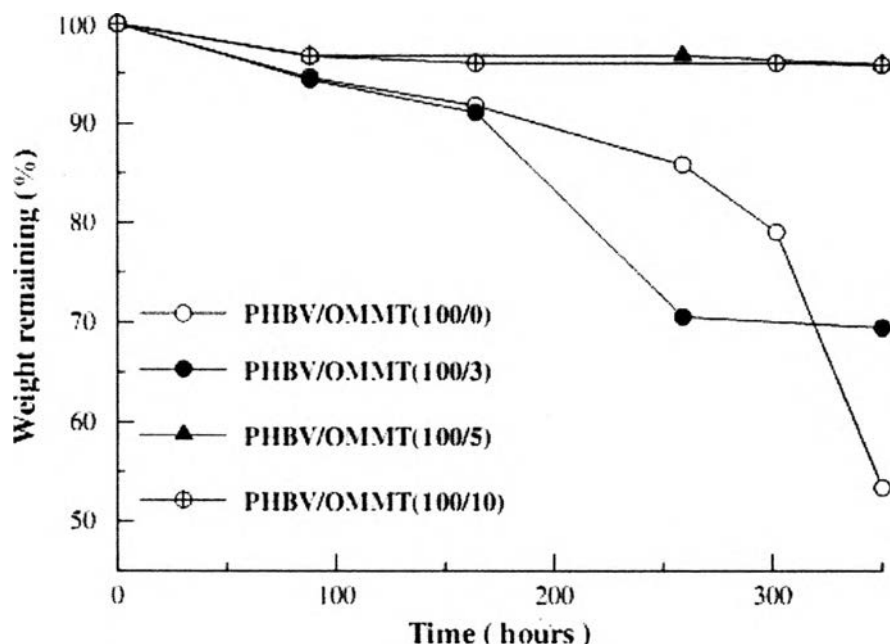
**Figure 2.22** The chemical structures of PHB, PHV, and PHBV.

#### 2.4.1 Properties of PHBV

The mechanical properties and the degradation rate of PHBV depend on the ratio of PHB and PHV in the PHBV copolymer. PHB homopolymer is very stiff and brittle, but the introducing of PHV to PHB polymer backbone makes it become tougher, more ductile and flexible because PHBV reduces the crystallinity and leads to the more process ability and improve mechanical properties. It can withstand the temperature up to 140 °C.

In 2005, Wang *et al.* studied on characteristics and biodegradation properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organophilic montmorillonite (PHBV/OMMT) nanocomposite. They can extend the degradation time of PHBV by adding OMMT indicated from the very high percent weight remaining of the composite at the time over 300 hr as shown in Figure 2.23 and the increasing of

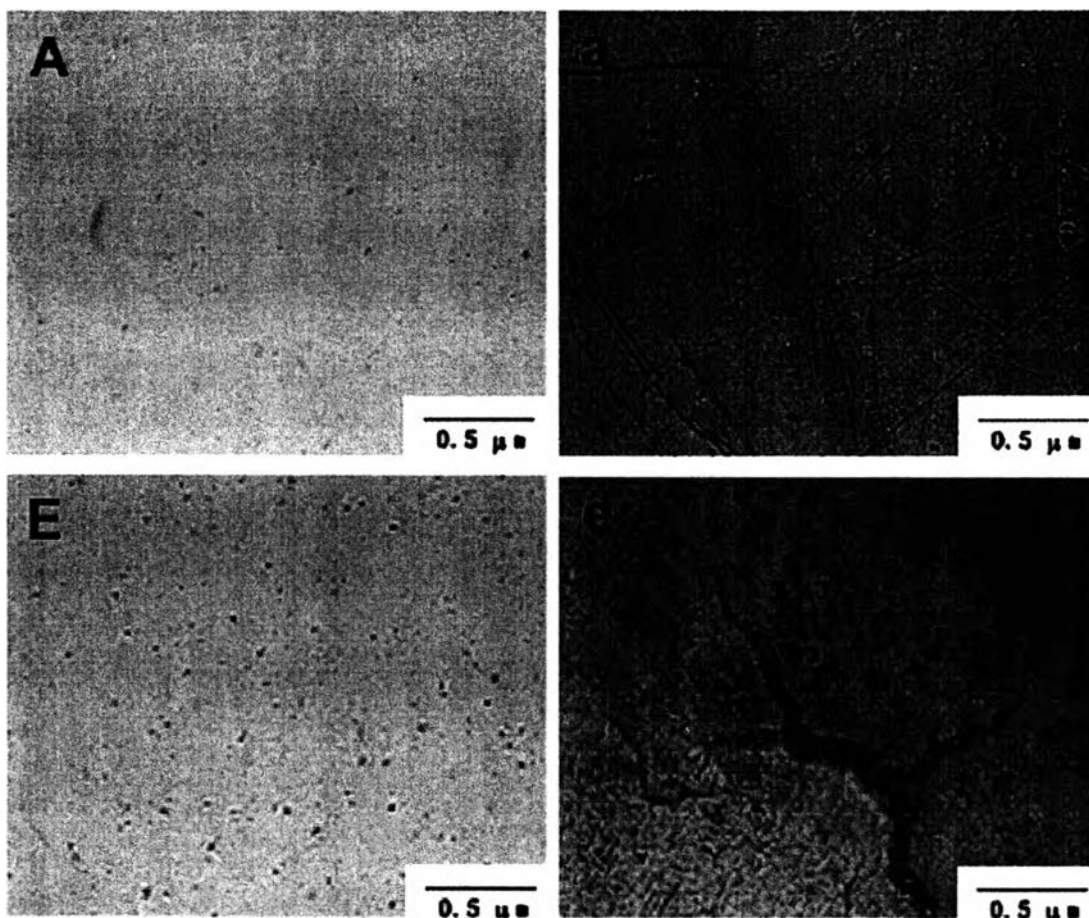
degradation time and the percent weight remaining can be controlled by increasing the amount of OMMT in the nanocomposite.



**Figure 2.23** The weight remaining of PHBV and PHBV/OMMT nanocomposites in soil suspension (Wang *et al.*, 2005).

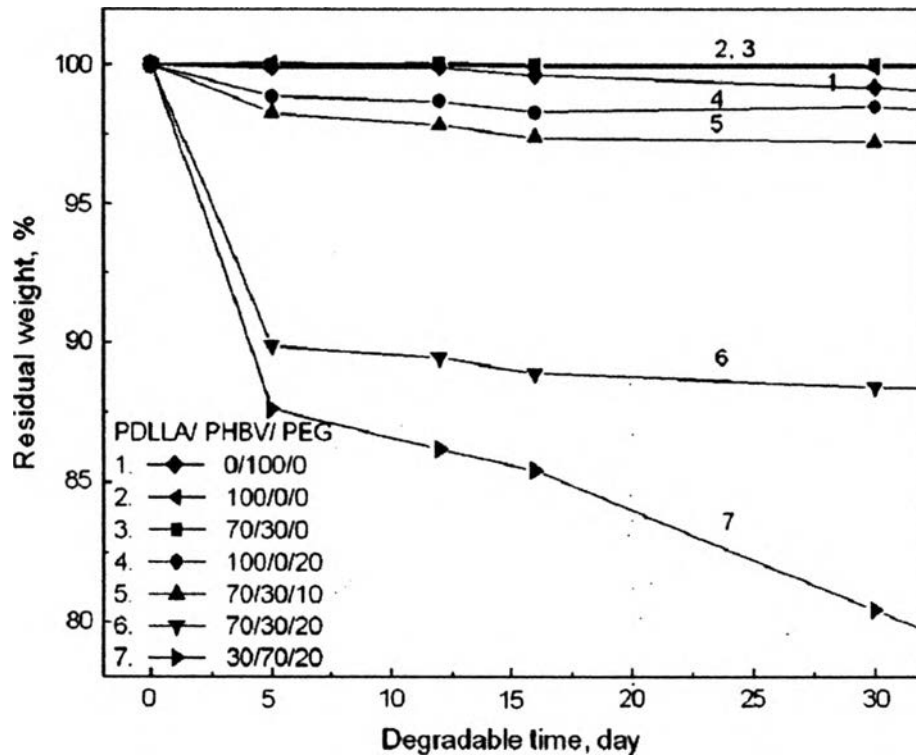
In 2008, Wang *et al.* demonstrated, the addition of PEG can dramatically increase the degradation rate of poly(D,L-lactide) (PDLLA) and the blends of PDLLA/ PHBV in a soil at room temperature as shown their degradation result in Figure 2.25 and the appearance of sample surface after degradation from optical microscope is shown in Figure 2.24.

From the result in Figure 2.25, the neat PHBV (curve 1) degraded a little bit faster than neat PDLLA (curve 2). The increasing of PEG in the PDLLA/PHBV blend composition of 70/30 (curve 5 and 6) provides the higher rate of degradation than the blend with no PEG added (curve 3), because the hydrophobic of PDLLA and PHBV themselves. PHBV also enhances the degradation rate of the blend, the degradation rate increases with increasing PHBV content as shown in curve 4, 6, and 7 which refer to 0, 30, and 70% PHBV content.



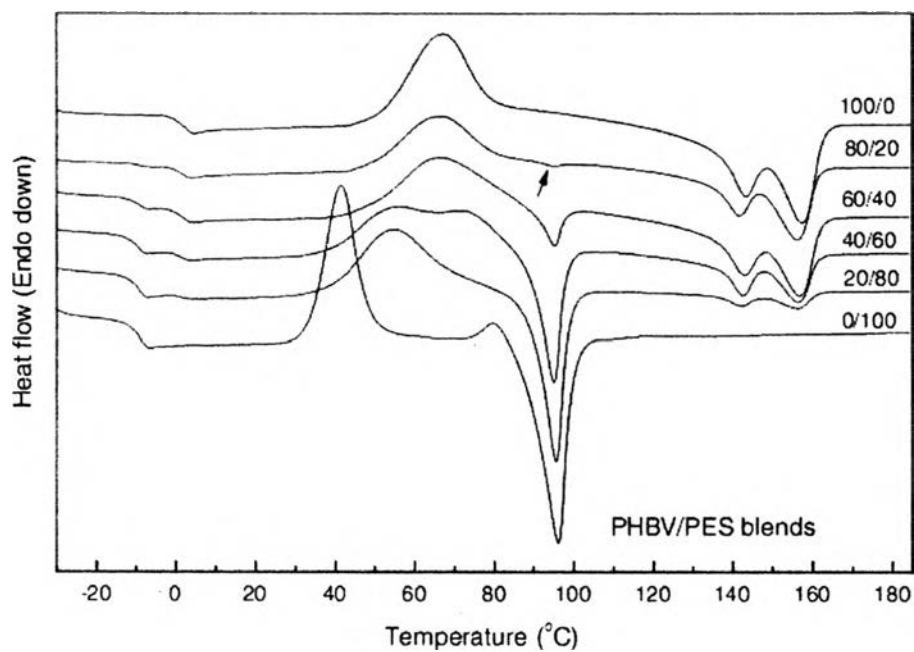
**Figure 2.24** The appearances of sample surface before and after (30 days) of the environmental degradation test by optical microscopy (A) PDLLA (before), (a) PDLLA (after); and (E) PDLLA/PHBV/PEG (70/30/20) (before), (e) PDLLA/PHBV/PEG (70/30/20) (after) (Wang *et al.*, 2008).

Both PHBV and PDLLA were undergone hydrolysis reaction and the linear chains were broken down at the ester bond in their structures and finally resulted in molecular weight and mass lost.

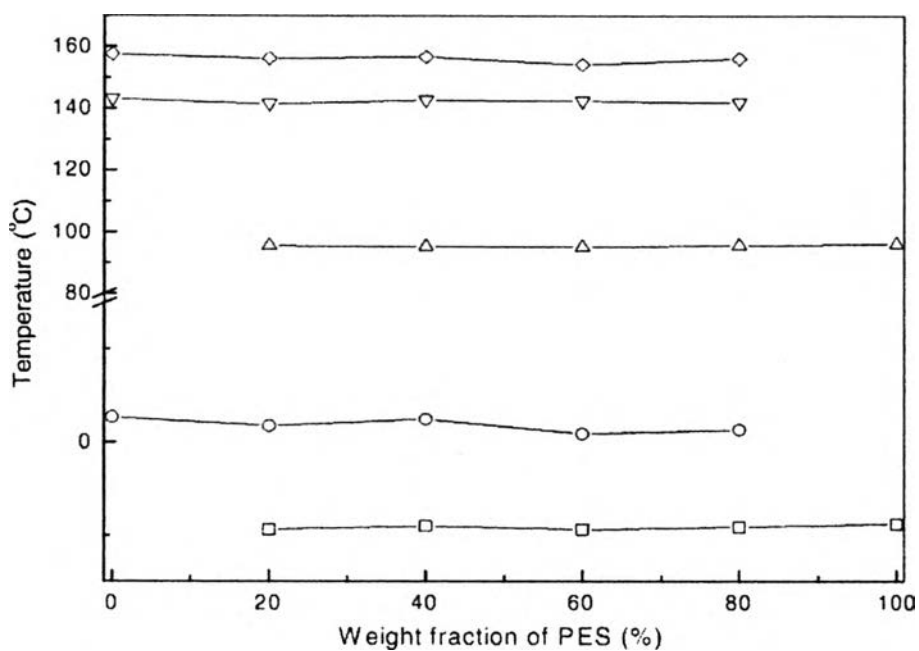


**Figure 2.25** The weight-loss curves of PDLLA/PHBV/PEG blends (Wang *et al.*, 2008).

In the same year 2008, PHBV can be improved the mechanical properties without decrease the degradable efficiency by blending with poly(ethylene succinate) (PES) which is a biodegradable polyester. This proved by Miao *et al.* They found that PES was immiscible with PHBV because the two composition independent glass transition temperatures and the biphasic melt were occurred as indicated in DSC thermograms are shown in Figure 2.26 and 2.27. The improvement in mechanical properties of the blend is also shown in Figure 2.28.

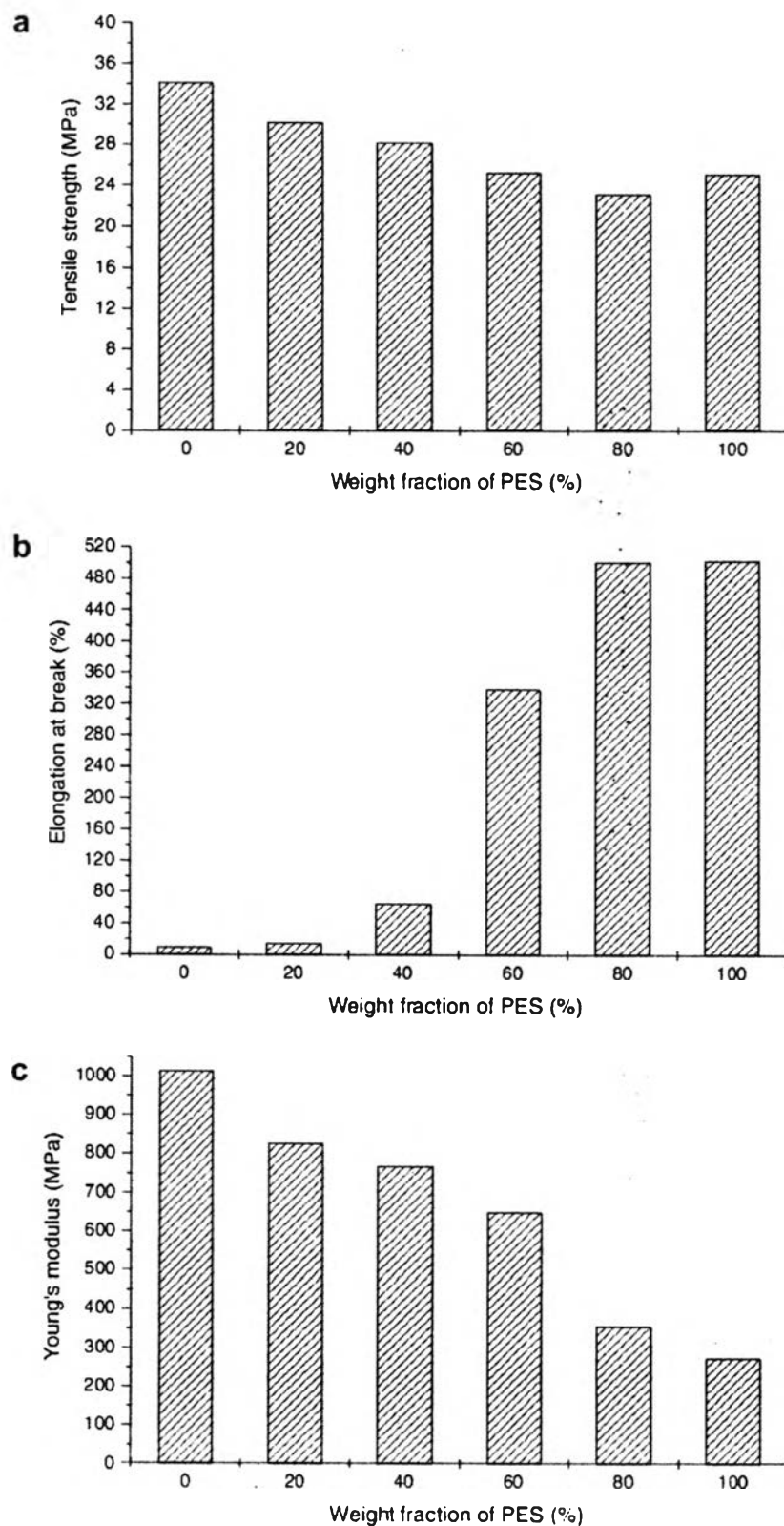


**Figure 2.26** The DSC traces of PHBV/PES blends after melt-quenching at a heating rate of 20 °C/min (Miao *et al.*, 2008).



**Figure 2.27** The summary of the results of  $T_g$  and  $T_m$  of PHBV/PES blends after melt-quenching at a heating rate of 20 °C/min; □, ○:  $T_g$ s of PES and PHBV, respectively; △:  $T_m$  of PES; ▽, ◇:  $T_m$ s of PHBV, respectively (Miao *et al.*, 2008).





**Figure 2.28** The Mechanical properties of PHBV/PES blends: (a) tensile strength, (b) elongation at break and (c) Young's modulus (Miao *et al.*, 2008).

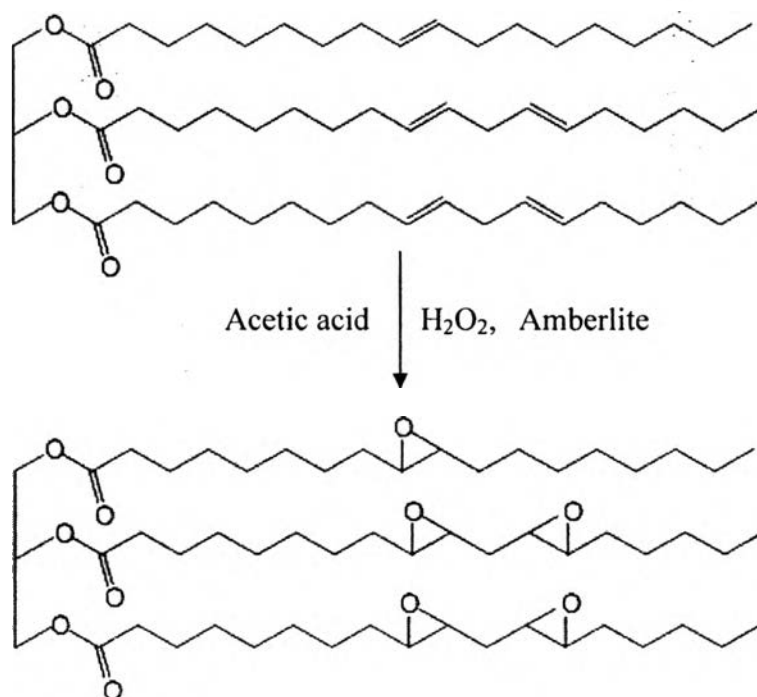
Miao *et al.*, 2008 also found that the PES can improve the percent elongation at break while maintain the high tensile strength and Young's modulus in PHBV-rich phase. This improvement and the 100% biodegradable still remain are expected to the practical applications of PHBV in some field that are great importance.

#### 2.4.2 Applications of PHBV

PHBV is currently in many commercial uses. There is a wide range of application such as bio-additive and bio-colorant which are additive and color concentrate for Biodegradable Polymers. It can use as biodegradable tableware, bio-packaging and also bath room accessories. It is used for blow molded shampoo bottle in the US, Germany, and Japan even used to make razor handles (Narayan, R., 1994).

#### 2.5 Epoxidized Soybean Oil (ESO)

Epoxidized soybean oil (ESO) is synthesized from the oxidation reaction of triglycerides and the free fatty acid as a schematic shown in Figure 2.29.

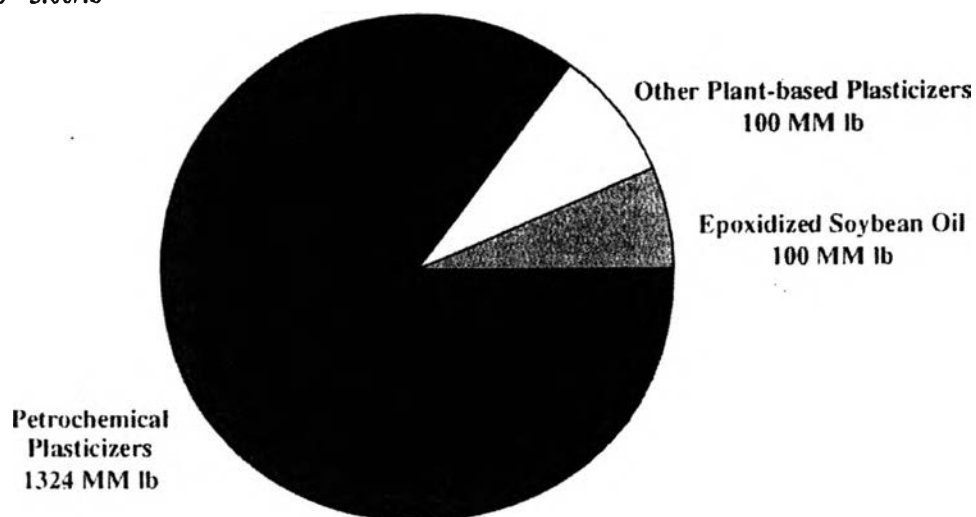


**Figure 2.29** The schematic of ESO synthesis (Park *et al.*, 2004).

### 2.5.1 Applications of ESO

The applications of ESO are found in the higher value-added products such as composites, epoxy based thermoset materials, and as plasticizers. It is found that ESO had been used as plasticizers for different plastic resin almost one hundred million pounds per year. But it is very small when compared to 1.324 billion pounds in petrochemical plasticizer that found in plastic area (Narayan, R., 1994) that can be shown in Figure 2.30.

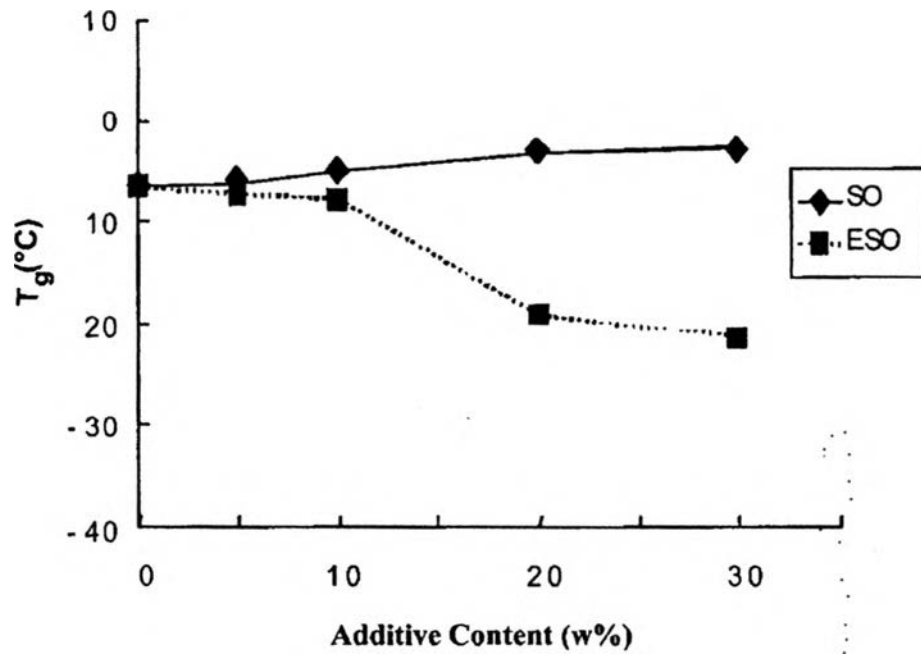
**TOTAL: 1.6 billion pounds**  
**Price: \$0.50 - 3.00/lb**



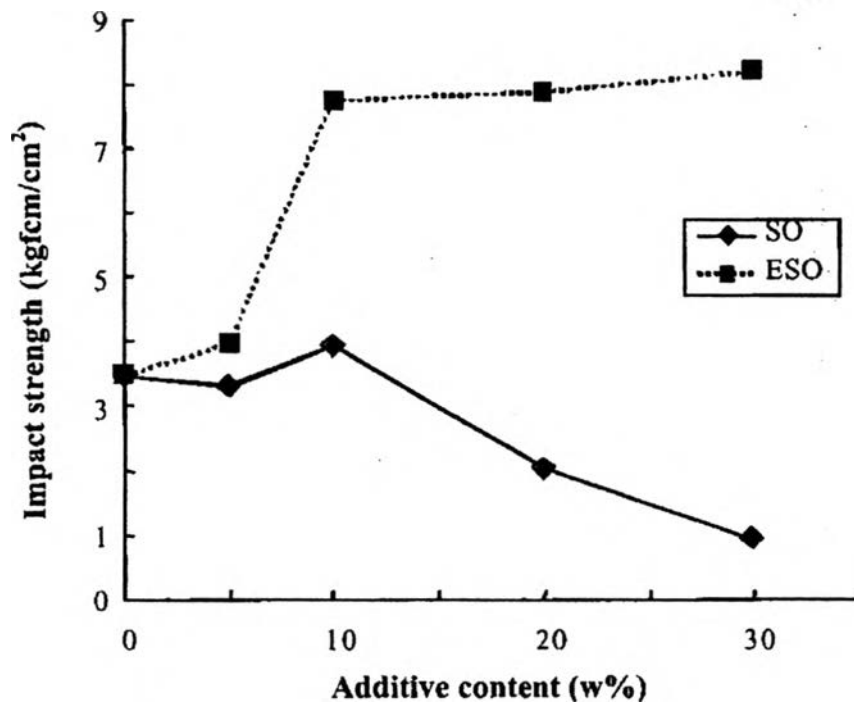
**Figure 2.30** The plasticizer production from plant oils and petrochemical feedstocks in the U.S., millions of pounds per year (Narayan, R., 1994).

Mostly, ESO was used to plasticized poly(vinyl chloride) (PVC) because it can give thermal stability to materials in addition to plasticization. Nowadays, it can be use to improve properties for many kinds of materials.

In 2003, Choi *et al.* demonstrated, ESO ac as plasticizer of PHB. It can be miscible to PHB due to the and improve the mobility of PHB molecular chains in amorphous phase exhibited in the decreasing of  $T_g$  in Figure 2.31 and the increasing of impact strength in Figure 2.32.

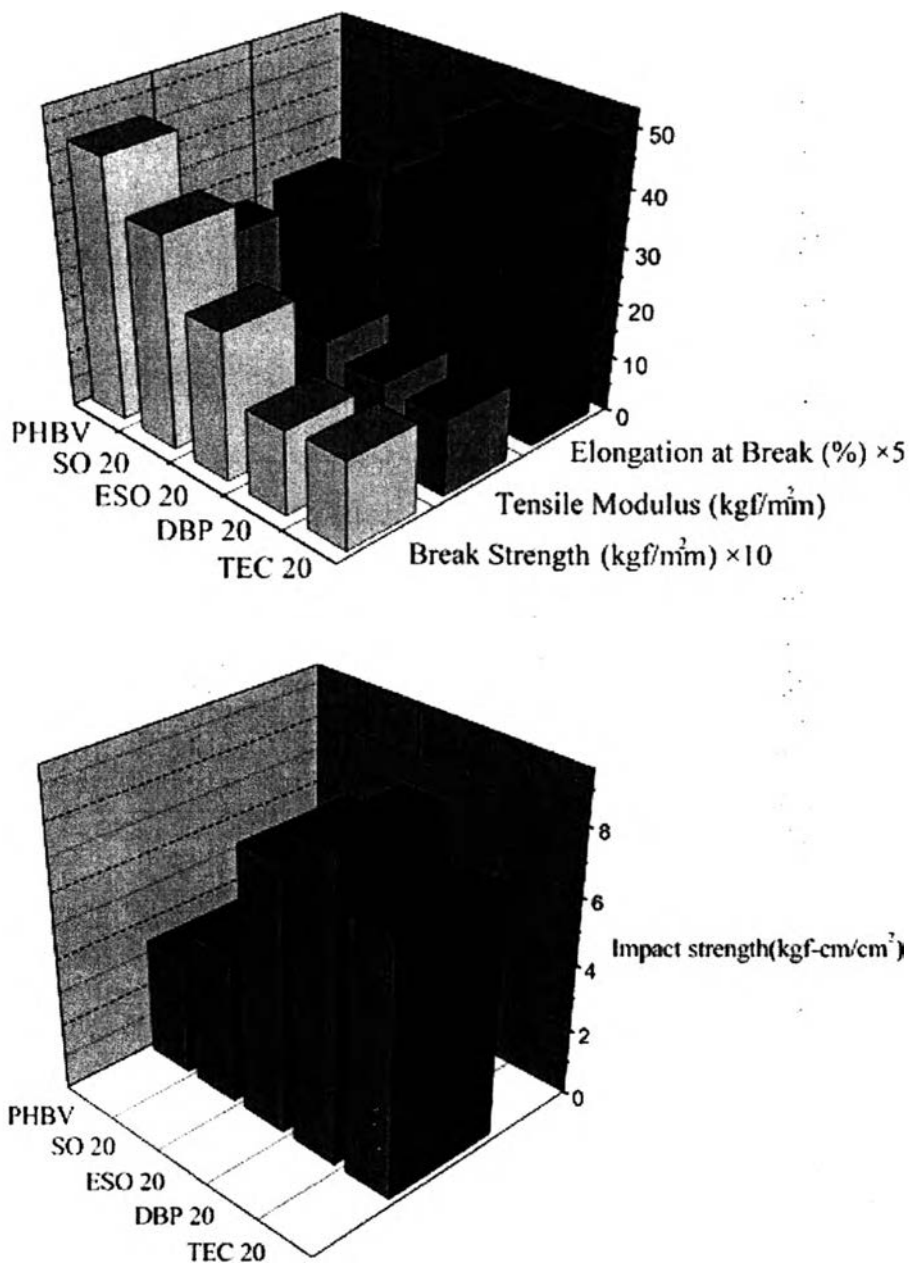


**Figure 2.31** The  $T_g$ s of PHBV blend as a function of additive (SO and ESO) content (Choi *et al.*, 2003).

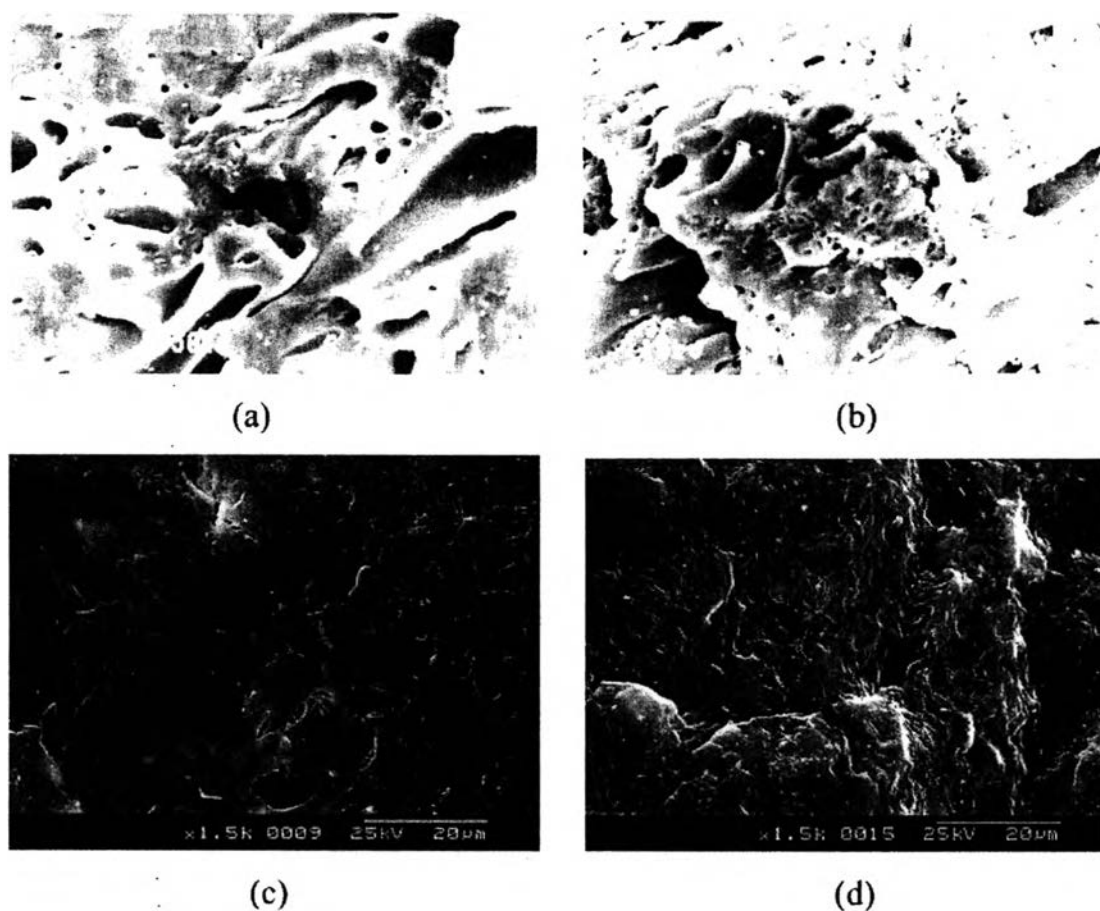


**Figure 2.32** The impact strength of PHBV blend as a function of additive (SO and ESO) content (Choi *et al.*, 2003).

Next year later, their study was also found that ESO can be plasticized and compatibilized PHBV but not much more than other plasticizers such as dibutyl phthalate (DBP) and triethyl citrate (TEC) as indicated in the results shows in Figure 2.33-2.34.



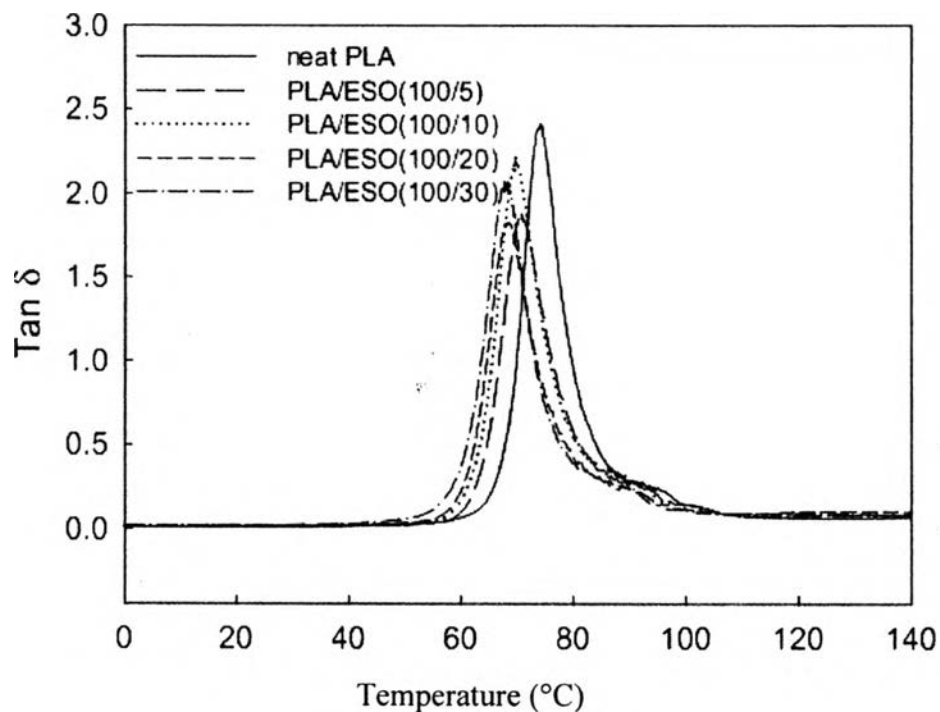
**Figure 2.33** The mechanical properties of PHBV/plasticizer blends (Choi *et al.*, 2004).



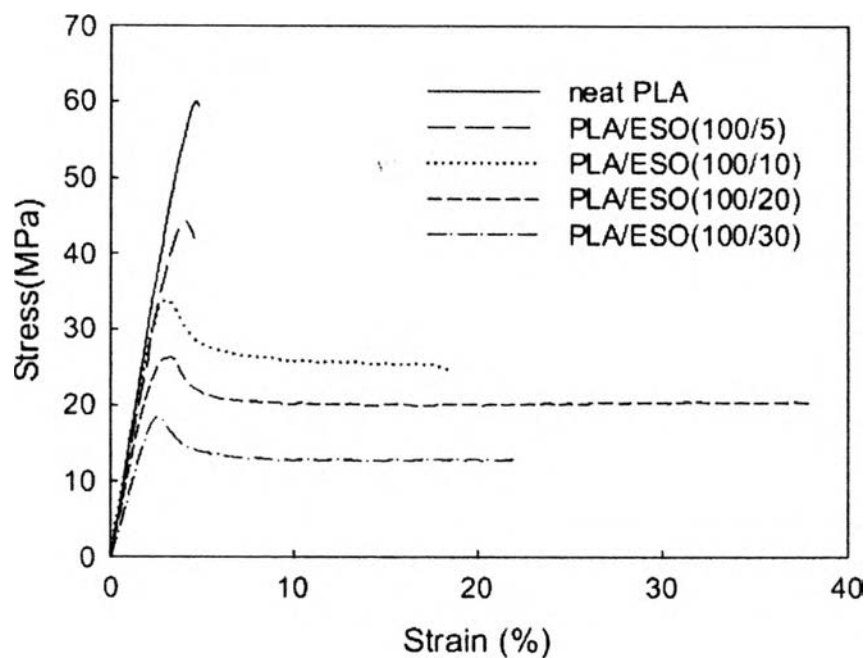
**Figure 2.34** The Scanning electron micrographs of PHBV/plasticizer blends: (a) SO, (b) ESO, (c) TEC, and (d) DBP (Choi *et al.*, 2004).

ESO can reduce tensile strength and modulus of PHBV but improved elongation at break and impact strength. It exhibits a large microdomain on PHBV than those of TEC and DBP.

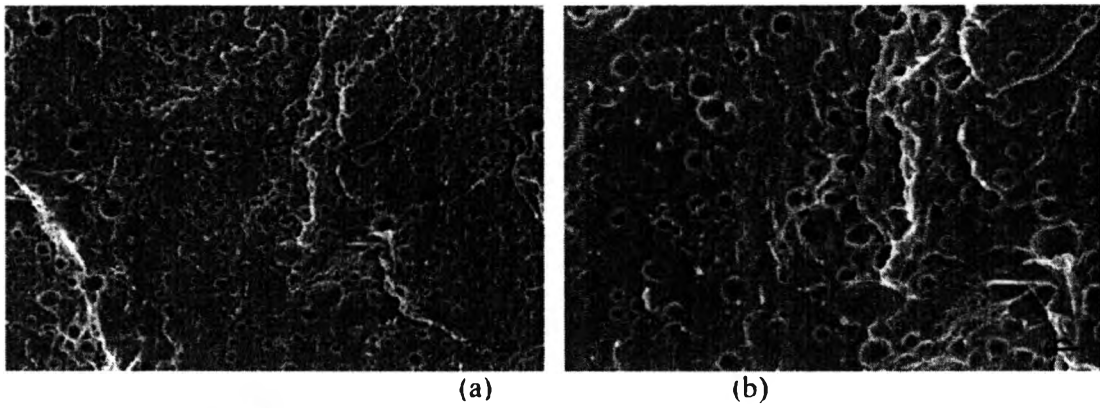
Recently in 2009, Ali *et al.* indicated that ESO improved flexibility of PLA by melt blending. The DMA result in Figure 2.35 shows the  $T_g$ s from  $\tan \delta$  peak were shift to lower temperature with increasing ESO content implied the partially miscible of ESO in PLA. The stress-strain curve in Figure 2.36 exhibits the flexibility improvement of PLA by introducing ESO. The SEM micrograph in Figure 2.37 indicates the larger domain of ESO with the increasing ESO content refer to the increasing flexibility.



**Figure 2.35** The  $\tan \delta$  of neat PLA and PLA/ESO blends as a function of temperature (Ali *et al.*, 2009).



**Figure 2.36** The stress-strain curves of neat PLA and PLA/ESO blends (Ali *et al.*, 2009).



**Figure 2.37** The SEM micrographs of fracture surfaces of PLA/ESO blends: (a) 100/10 (b) 100/20 (Ali *et al.*, 2009).