



CHAPTER II LITERATURE REVIEW

2.1 Thermoplastic Elastomer (TPE)

Thermoplastic elastomer (TPE) is a class of copolymers or a physical mixtures of two or more polymers to provide a particular material that have each properties of them. Commonly TPE is a combination between rubber and thermoplastic which consist of both thermoplastic and elastomeric properties.

❖ Classification of TPE

There are six types of thermoplastic elastomer which divided by economical consideration. There are two main categories, multi-block copolymers and polymer blends. The TPE classification chart is shown in Figure 2.1.

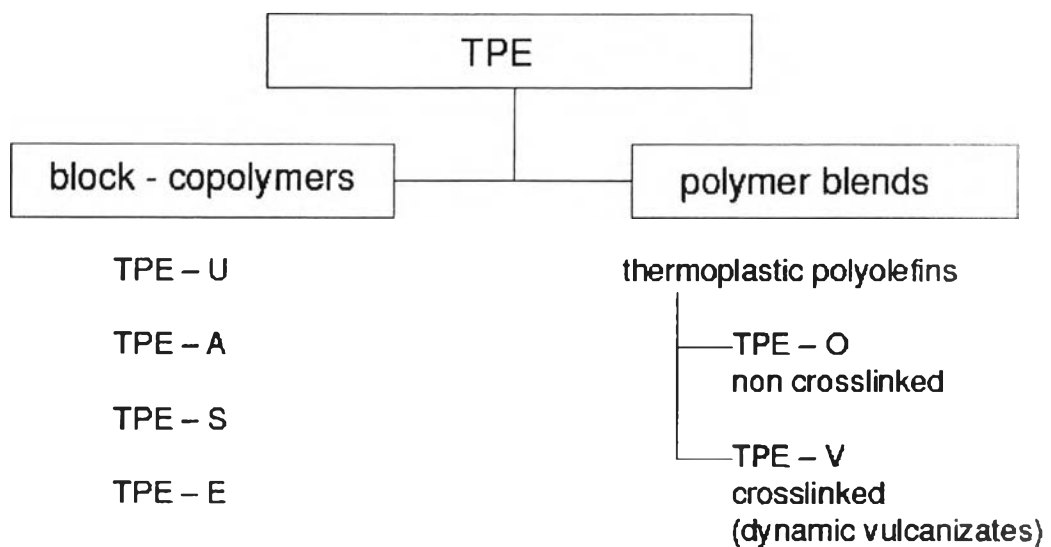


Figure 2.1 Classification of TPE (Scharnowski, 2005).

The first category is block copolymers which consist of an elastomeric block and a hard block. The block copolymers were separated into 4 types which are polyurethane/elastomer block copolymers (TPE-U), polyamide/elastomer block copolymers (TPE-A), styrene-block copolymer (TPE-S) and polyester-block

copolymers (TPE-E). The second category is polymer blends which are polyethylene/poly(α -olefin) block copolymers. These TPE blends can be divided into 2 types which are a non-crosslinked rubber phase (TPE-O) and thermoplastic polyolefins with a crosslinked rubber phase (TPE-V or TPV). Partially and fully crosslinked TPE-Vs are widely use in an automotive industry because their properties, low hardness and high using temperature until over 100 °C, and this TPE-V type involves a dynamic vulcanization (Scharnowski, 2005). The schematic structures of the two categories of TPE are shown in Figure 2.2.

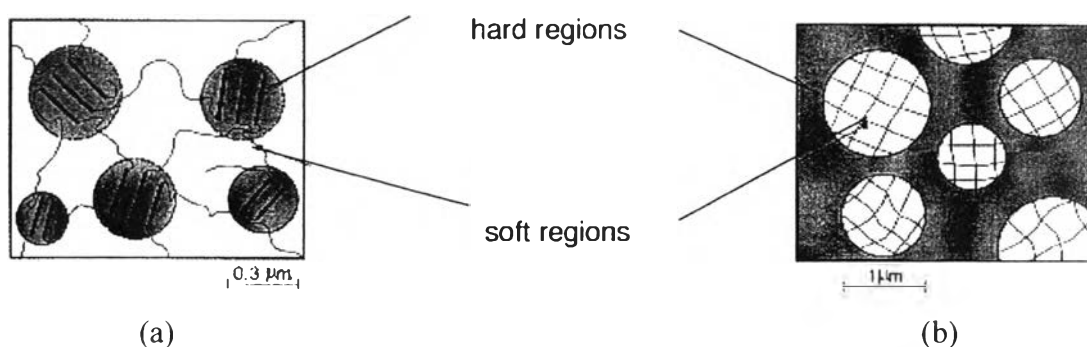


Figure 2.2 Schematic structures of TPE, (a) block copolymers and (b) polymer blends, (Scharnowski, 2005).

❖ Dynamic Vulcanization

TPE-V is produced by dynamic vulcanization that sometimes referred to dynamic vulcanizate (DV). Dynamic vulcanization is the best method to produce TPE-V. It is the process of vulcanizing an elastomer phase during its melt mixing with a molten plastic phase (Holden *et al.*, 2004). Generally, these melt mixing process can be done by banbury mixers, mixing extruders, and twin-screw extruders, but twin-screw extruders are commercial one and commonly used. In an extruder, the dynamic vulcanization is done by melt-blending of a thermoplastic matrix phase and a rubber phase first. After well-mixed blends were formed, the crosslinking are generated by means of curing agent or vulcanizing agent which is one of the ingredient added together into the extruder at a second opening. The vulcanization

will occur while mixing proceed continuously. The schematic of extruder profile is shown in Figure 2.3.

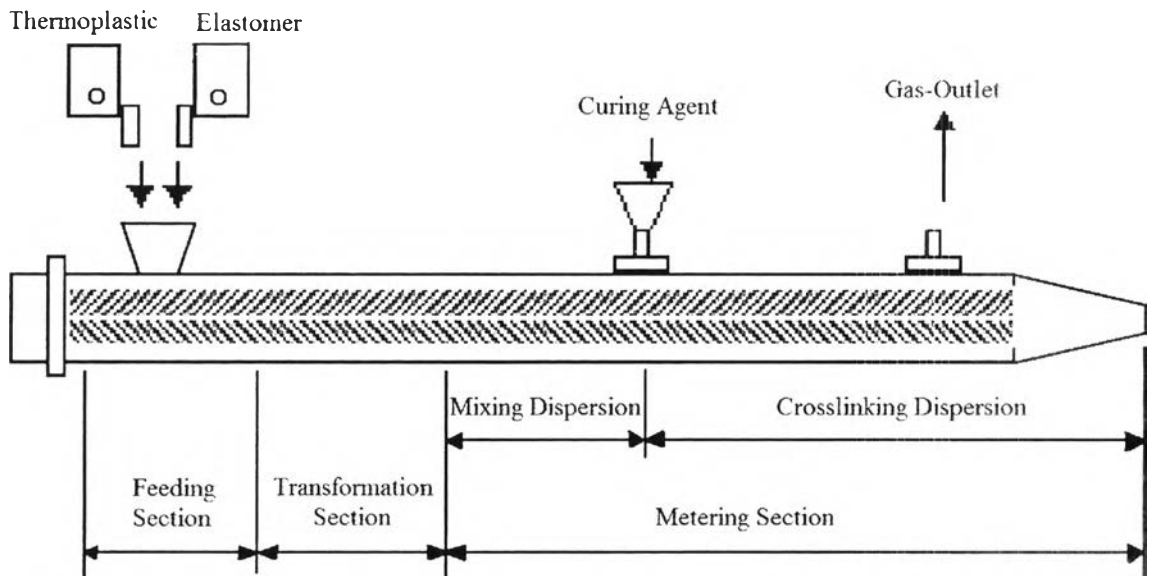


Figure 2.3 Schematic of extruder profile for dynamic vulcanization (Scharnowski, 2005).

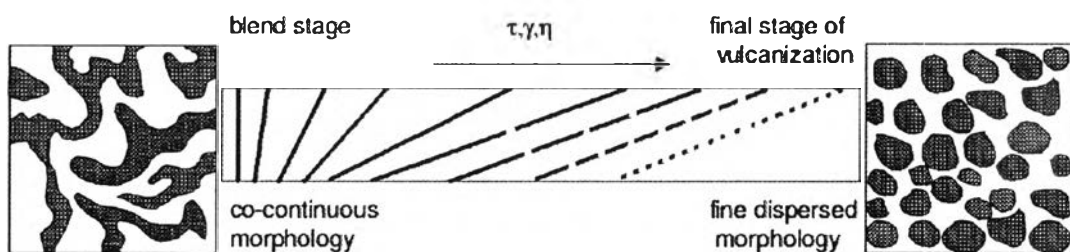


Figure 2.4 Schematic of morphology development of dynamic vulcanizates during the crosslinking (Scharnowski, 2005).

During the crosslinking process, a rubber phase viscosity is increase 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 10^{-5} mol/cm³.

❖ TPE Properties

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

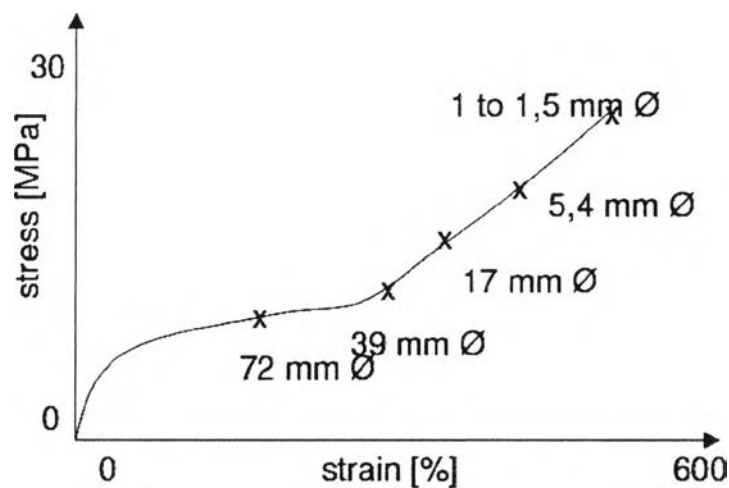


Figure 2.5 Abdou-Sabet *et al.*, (1996) result indicate the effect of rubber particle size on stress-strain properties of TPE-V (Scharnowski, 2005).

The improved properties of the TPE-V are the ultimate mechanical properties, greater hot oil resistance and other fluids, better high-temperature utility, reduced permanent set, improved fatigue resistance, greater stability of phase morphology in the melt state, and more reliable and able to fabricate thermoplastic. It can be shown some improved properties of TPE-V in Figure 2.6.

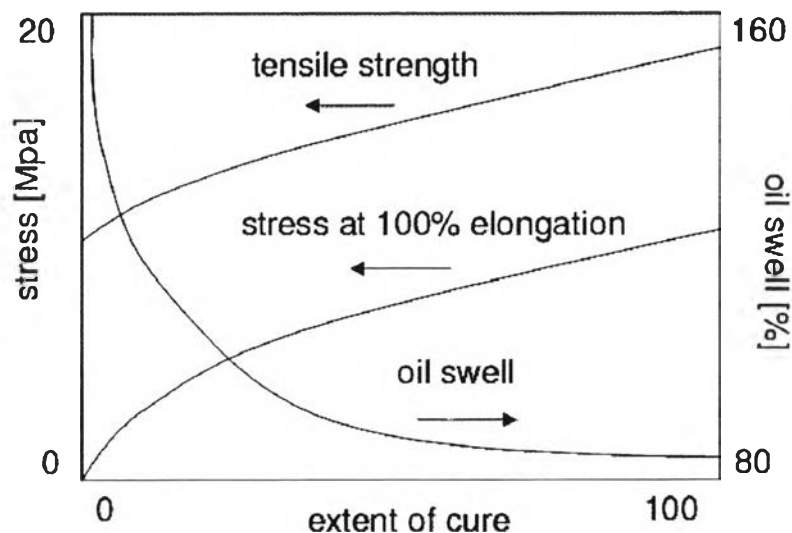


Figure 2.6 Abdou-Sabet *et al.*, (1996) result indicate the effect of curing on mechanical properties and oil swell of TPE-V (Scharnowski, 2005).

❖ Literature Review Regarding to TPE

A. Mousa *et al.* (2000) found, the melt rheological behavior of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) thermoplastic elastomers (TPEs) was studied with a special reference to the effect of dynamic vulcanization, apparent shear rate and temperature using a twin screw capillary rheometer. PVC/ENR TPEs were compounded with a twin screw extruder. At a particular temperature it was found that the apparent viscosity decreased with increased in apparent shear rate following a pseudoplastic behavior, thus indicating that the dynamically vulcanized TPEs are processible as thermoplastics.

The elastic phenomena were investigated by calculating the die swell which was found to be affected by the apparent shear rate and processing temperature. The extrudate surfaces at different apparent shear rates were studied by means of optical microscopy. The photomicrographs of the uncured and cured with 1 phr sulfur PVC/ENR TPEs extrudates obtained at 10, 40 and 80 rpm at 150°C are shown in Figure 2.7 and 2.8, respectively.

It was observed that as apparent shear rate increases the extrudate surface exhibits a higher degree of deformation, the extent of which is also dependent on the sulfur concentration.

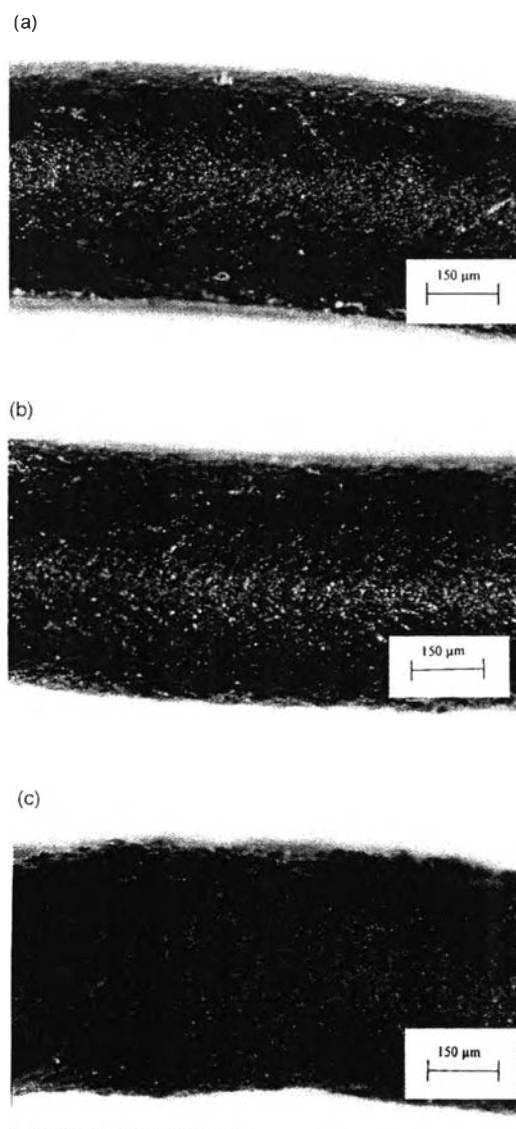


Figure 2.7 Photomicrographs of the uncured PVC/ENR TPEs extrudates obtained at (a) 10 rpm, (b) 40 rpm, (c) 80 rpm at 150°C (A. Mousa *et al.*, 2000).

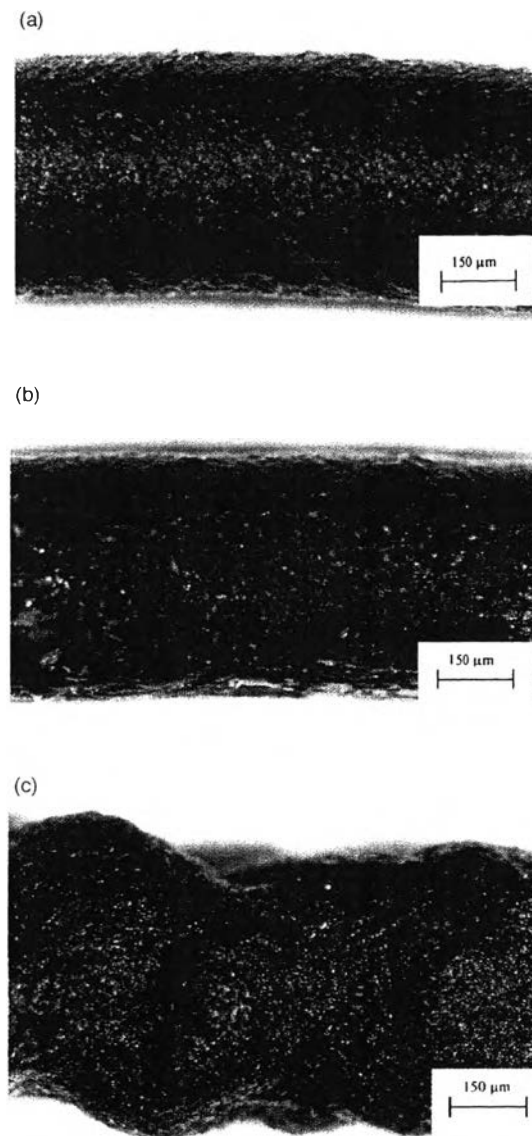


Figure 2.8 Photomicrographs of the cured (1 phr sulfur) PVC/ENR TPEs extrudates obtained at (a) 10 rpm, (b) 40 rpm, (c) 80 rpm at 150°C (A. Mousa *et al.*, 2000).

❖ Applications of TPE

The beginning of the use of TPE-V is to substitute elastomer in existing application. They are used where conventional elastomers cannot provide the range of physical properties needed in the product. These materials find large application in the automotive sector and in household appliances sector thus the scientists have been done to innovate oil resistance, hot stability as well as compression set reducing in elastomer field.

Another reason is a manufacturing method. TPE-V can be done in general manufacturing method 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. They have production parts in only one step and also fast joints that easy to de-montage like 2-component-injection molding (Jürdens, 2002). The automotive products commonly made by TPE-V are suspension bushing for automotive performance applications due to it has a resistance to deformation greater than regular rubber bushings. For other products, TPE-V can use as an electrical cable jacket or mostly inner insulation in portable cord.

TPE materials have the potential to be recyclable since they can be molded, extruded and reused like plastics, but they have typical elastic properties of rubbers which are not recyclable owing to their thermosetting characteristics. TPE -also require little or no compounding, with no need to add reinforcing agents, stabilizers or cure systems. Hence, batch-to-batch variations in weighting and metering components are absent, leading to improved consistency in both raw materials and fabricated articles. TPEs can be easily colored by most types of dyes. Besides that, it consumes less energy and closer and more economical control of product quality is possible.

2.2 Peroxide Vulcanization System

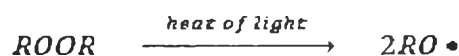
This vulcanization system uses peroxides as a vulcanizing agent. The highly often use peroxides are Dicumylperoxide and bis-(t-butylperoxy isopropylbenzene). They have different half-life at different temperatures as show in Table 2.1 Peroxide has a fast scorching and slow cure time and the cure time that used 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 need to consider a curing temperature and half-life together.

Table 2.1 The half-life of peroxides (Akiba *et al.*, 1997)

Peroxides	Half-life (min)	
	160 °C	180 °C
Dicumylperoxide	8.7	1.3
bis-(t-butylperoxy isopropylbenzene)	12	2

Normally peroxide isn't used too much. It usually use only about 2.5-3 phr. If it has high content, a rubber will decrease in modulus and elongation value. Tensile strength may both increase and decrease.

Akiba *et al.* (1997) were described a peroxide crosslinking mechanism as followed. The crosslinking reaction start from the homolytic decomposition involving of peroxide to produce alkoxy radicals as shown in Figure 2.9.

**Figure 2.9** The homolytic decomposition of peroxide.

Then peroxide radicals will abstracted by hydrogen atom of polymer chain (rubber) as Figure 2.10.

**Figure 2.10** Hydrogen abstraction.

From the studies with model compounds, they are indicated that the hydrocarbon radicals (polymer radicals) can occur in two ways as shown in Figure 2.11. These are coupling reaction and disproportionation reaction. But the hydrocarbon radicals predominantly undergo coupling rather than disproportionation.

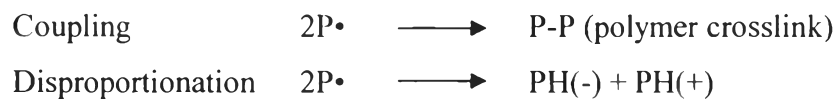


Figure 2.11 Coupling and disproportionation of the hydrocarbon radicals (polymer radicals).

The coupling reaction forms crosslinking 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, as shown in Figure 2.12.

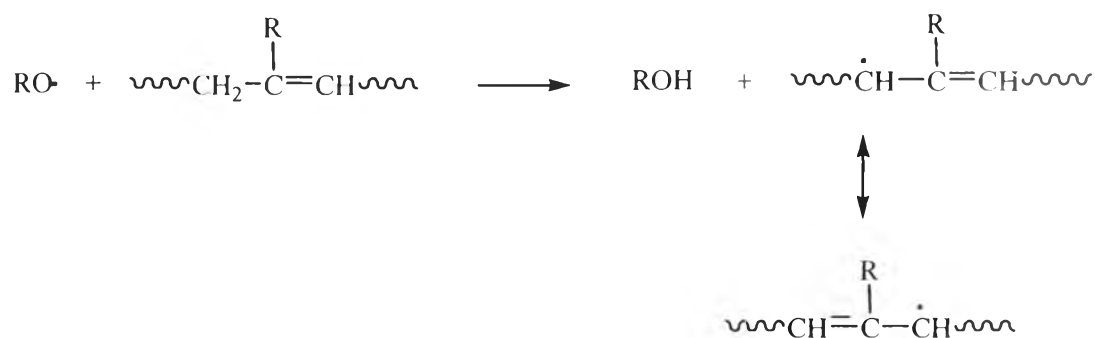


Figure 2.12 The polymer chains crosslink together by coupling reaction.

In natural rubber, the methyl group is also reactive towards hydrogen-atom abstraction. That is shown in Figure 2.13.

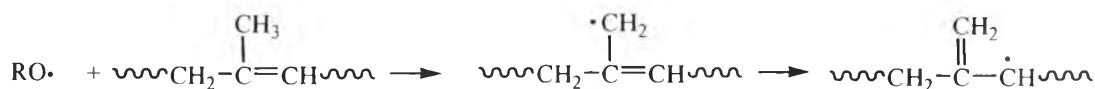


Figure 2.13. Hydrogen abstraction in natural rubber.

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

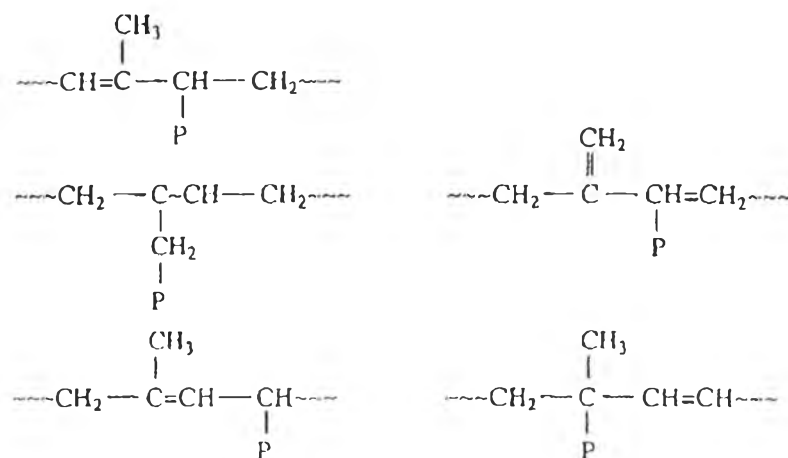


Figure 2.14 The possible crosslink structures present in peroxide crosslinked natural rubber (P = Polymer chain) (Akiba *et al.*, 1997).

There are some important warnings in using peroxides. First, they are dangerous chemicals and need to be kept and be used with the best safety conditions. Peroxides are easy to degrade in a hot air. It needs to be kept it in cold condition below 37 °C. Keep it away from heat generators, the UV light, spark, and flame. Also keep it far from oxidants and reducers. Avoid an attack and keep 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 contribute to react with other chemicals, occurring 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 because of 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.

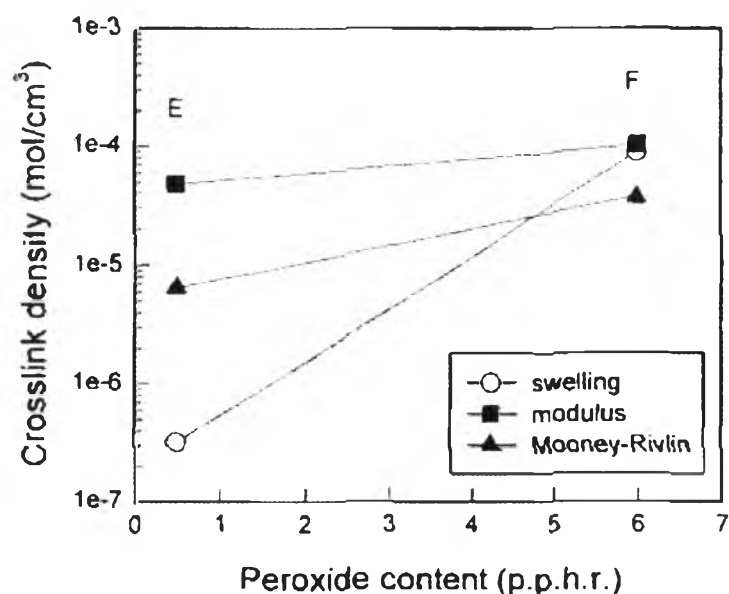


Figure 2.15 The plot between crosslink density and peroxide content in NR shows modulus values, stress-strain values, and swelling values (Hagen *et al.*, 1996).

As seen in Figure 2.15, it is indicated that the peroxide system can increase in 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, the NR crosslinked by using dicumyl peroxide showed the lowest equilibrium uptake value in all penetrants compared to the other systems. It is because of the difference in the 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.

❖ **Literature Review Regarding to Peroxide Vulcanization System**

Yamoun C. (2010) studied, the blending of fluoroelastomer (FKM), natural rubber (NR) and high-density polyethylene (HDPE) by dynamic vulcanization using peroxide (DBPH, DCP) as a curing agent were prepared. HDPE was melt-mixed with NR and FKM at different compositions (HDPE/FKM/NR i.e. 30/60/10, 30/55/15, 30/50/20 and 30/35/35 %wt) using an internal mixer at 150 °C and 50 rpm rotor speed. Table of blends formations is shown in Table 2.2.

Table 2.2 Blends formations (Yamoun C., 2010)

HDPE/FKM/NR blend (%wt)	Code		
	Without	DCP	DBPH
30/60/10	WI10	DC10	DB10
30/55/15	WI15	DC15	DB15
30/50/20	WI20	DC20	DB20
30/35/35	WI35	DC35	DB35

The mechanical properties and oil swelling resistances of these blends were analyzed according to ISO 37 (Type 1) and ASTM D471, respectively. The results of mechanical properties and swelling index of blend composition are shown in Table 2.3 and 2.4.

Table 2.3 Mechanical properties of the HDPE/FKM/NR blends
(Yamoun C., 2010)

Sample	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)
WI10	5.05	66.08	91.38
WI15	5.83	103.11	87.98
WI20	5.56	106.64	87.14
WI35	4.31	147.94	74.82
DC10	5.02	14.13	89.24
DC15	5.66	34.79	87.54
DC20	5.42	47.73	83.72
DC35	4.29	75.31	71.14
DB10	11.51	174.35	89.68
DB15	10.07	210.16	89.60
DB20	10.12	209.41	87.81
DB35	8.32	175.48	80.11

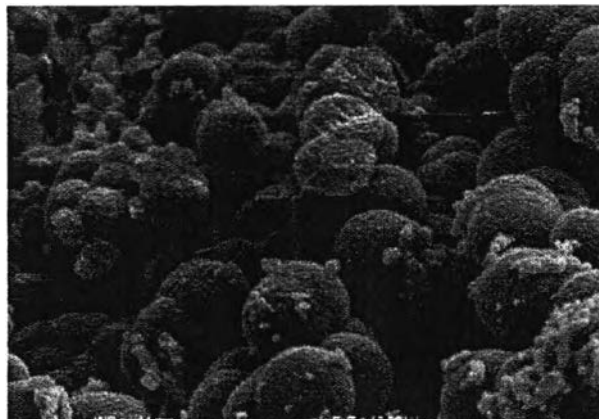
Table 2.4 Variations of swelling index (Yamoun C., 2010)

Sample	Swelling Index							
	Biodiesel (B5)		Gasohol (E20)		Gasohol 91		Gasohol 95	
	Room Temp.	100°C	Room Temp.	100°C	Room Temp	100°C	Room Temp	100°C
WI10	1.23	1.45	1.22	1.52	1.26	1.38	1.25	1.39
WI15	1.32	1.56	1.3	1.67	1.34	1.53	1.29	1.45
WI20	1.46	1.59	1.38	1.74	1.43	1.68	1.43	1.52
WI35	1.65	1.85	1.52	1.89	1.57	1.79	1.58	1.68
DC10	1.09	1.36	1.15	1.50	1.17	1.31	1.19	1.30
DC15	1.25	1.48	1.21	1.57	1.22	1.44	1.22	1.32
DC20	1.38	1.50	1.29	1.62	1.30	1.59	1.32	1.41
DC35	1.63	1.78	1.42	1.80	1.50	1.74	1.50	1.60
DB1	1.09	1.30	1.12	1.45	1.12	1.26	1.13	1.24
DB15	1.16	1.42	1.15	1.53	1.17	1.39	1.17	1.25
DB20	1.19	1.43	1.23	1.59	1.22	1.53	1.21	1.28
DB35	1.51	1.73	1.39	1.71	1.46	1.69	1.43	1.53

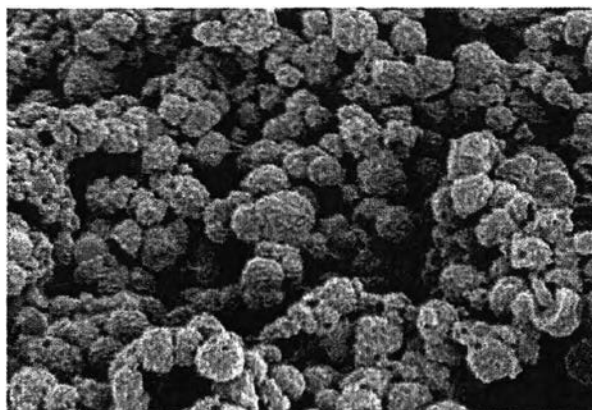
The results suggest that DBPH works better as a curing agent for the dynamic vulcanization system than DCP. The optimum mechanical properties and oil resistance were revealed in 30/50/20 and 30/60/10 HDPE/FKM/NR, being dynamic vulcanized with DBPH, respectively. In addition, was found that a dispersed HDPE phase shows the percent crystallinity in the range of 53–55% upon increasing the NR content. The SEM micrographs reveal the NR phase is well dispersed in FKM as small particles at low NR content and becomes co-continuous phase at high NR content.

Joy K. Mishra *et al.* (2011) found, polycaprolactone (PCL)/epoxidized natural rubber (ENR) blends (PCL/ENR = 70/30, 50/50 wt/wt) were prepared by a melt mixing in an internal mixer in the presence of a small amount (0.5 and 1 phr) of dicumyl peroxide (DCP). The effect of peroxide crosslinking on thermal, mechanical, and rheological properties of the blends was investigated. It was revealed that peroxide crosslinking enhanced degree of crystallinity of PCL phase and its non-isothermal melt crystallization temperature. The crosslinked blends behave like a thermoplastic elastomer exhibiting high elongation-at-break and fairly good elastic recovery as well as melt processibility. From melt rheological analysis, the peroxide crosslinked blends showed more pronounced shear thinning effect and higher elasticity compared to simple blends.

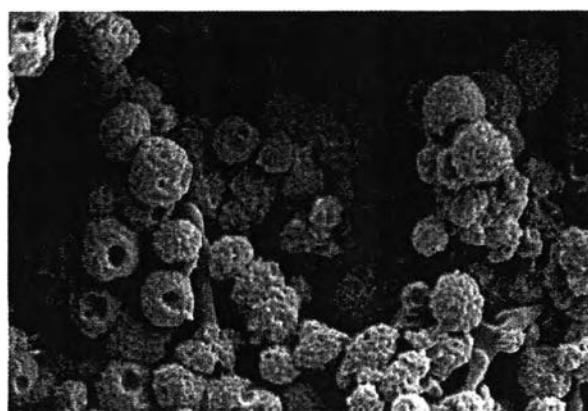
C. Nakason *et al.* (2006) studied, epoxidized natural rubber with 30% epoxidized was synthesized and used to prepare thermoplastic vulcanizates based on 75/25 ENR/PP blends with Ph-PP compatibilizer. Influences of various curing systems (i.e., sulfur, peroxide and a mixture of sulfur and peroxide-cured systems) were investigated. We found that the mixing torque, shear stress, shear viscosity, tensile strength and elongation at break of the TPVs using the mixed-cure system exhibited higher values than those of the sulfur and peroxide-cured systems, respectively. This may be attributed to a formation of S–S, C–S combination with C–C linkages in the ENR phase. The curing systems did not affect the hardness properties and solvent resistance of the TPVs. We also found that the dispersed vulcanized rubber domains of TPV with the peroxide-cured system were smaller rubber particles than those of the mixed and sulfur-cure systems. The SEM micrographs are shown in Figure 2.16.



(a) Sulfur system



(b) Peroxide system



(c) Mixed system

Figure 2.16 SEM micrographs of TPVs based on 75/25 ENR/PP blends using Ph-PP compatibilizer and various vulcanization systems (C. Nakason *et al.*, 2006).

2.3 Poly(vinylidene fluoride) (PVDF)

Poly-1,1-difluoroethene or poly(vinylidene fluoride) (PVDF) is a thermo plastic materials in the fluoropolymer family that was showed chemical structure in Figure 2.17. 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).

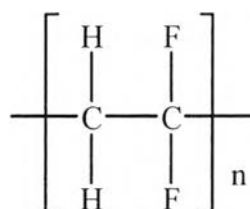


Figure 2.17 Chemical structure of PVDF.

❖ Properties of PVDF

The PVDF is 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.

❖ Literature Review Regarding to PVDF

The blending ability of PVDF with another polymer has several carried out. Hsin-Chieh Chen *et al.* (2011) found, PVDF can be miscible with PLA which called as biocompatibility by spun into nonwoven mats via electrospinning technique using a co-solvent system of DMF and acetone. This work provides a new method of blending PVDF with other materials to improve the brittle property. From the results, the PVDF/PLA mats exhibited higher melting temperature but lower crystallinity

than both PVDF and PLA. The tensile strength of PVDF/PLA was lower than those of PVDF and PLA. However, PVDF/PLA exhibited higher breaking elongation than PLA. The conclusion was included the potential of PVDF/PLA electrospun mats for biomedical applications.

Chen MH *et al.* (2005) found, a tubular PVDF scaffold with dense outer surface to prevent saliva leakage and with porous inner surface for the cell growth was proposed to serve as an artificial salivary gland for future use in the treatment of patients with salivary hypofunction. In addition, porous PVDF had higher cell growth compared with dense PVDF. Therefore, the hydrophobic PVDF with a porous structure was the best substrate for culturing acinar cells.

Chen RS *et al.* (2007) explored, the effect of biomaterial on tooth germ cell adhesion and proliferation. The purpose of this study is to evaluate the effects of cell-surface interactions of tooth germ cells on biomaterials with various surface hydrophilicities. The biomaterials used in this study included polyvinylidene fluoride (PVDF). The results indicated that adhesion and proliferation of tooth germ cells to biomaterials with moderate hydrophilicity/hydrophobicity was superior compared to most hydrophobic material PVDF or most hydrophilic material PVA in this study.

For other properties of PVDF, it is a highly non-reactive fluoropolymer. It has an excellent chemical resistance, anti-wear, and extraordinary electrical properties such as ferro-, piezo-, and pyro-electricity. 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 such as 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.

❖ General Applications

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 filtration, waste water treatment, and gas separation.

It is commonly can use 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.

It is very good for fuel lines because PVDF can resistant to 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 available in a conductive version.

It can also be used as a protective coating over carbon steel fuel and brake fluid lines, and in 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.

2.4 Epoxidized Natural Rubber (ENR)

Epoxidized Natural Rubber (ENR) is derived from the partial epoxidation of the natural rubber molecule which epoxide groups are randomly distributed along the natural rubber molecule. When natural rubber is epoxidized under carefully controlled conditions, it can be converted to a totally new polymer or new type of elastomer with some properties more akin to speciality rubbers and some properties that appear to be advantageous for tire treads. The chemical structure of ENR is shown in Figure 2.18.

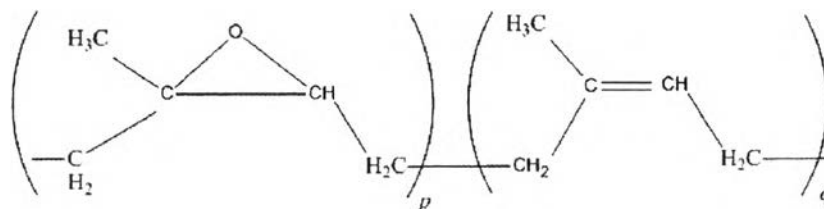


Figure 2.18 Chemical structure of ENR.

Due to most applications of Natural Rubber (NR) are limited owing to the low stability to heat, oxygen, sunlight, etc. and the high solubility in most hydrocarbon/hydrophobic solvents including oils. Those limitations result from NR chemical structure (cis-1,4-polyisoprene) which contains double bonds and hydrocarbon atoms that is shown in Figure 2.19.

The chemical modification at double bonds and introduction of hydrophilic groups along NR backbone are alternative strategies to improve the stability of NR and to provide widespread applications. So ENR is an ideal material since the introduction of epoxirane ring not only reduces the number of double bonds but also increases the hydrophilicity of NR. The preparation of ENR is used peracids such as performic and peracetic acids.

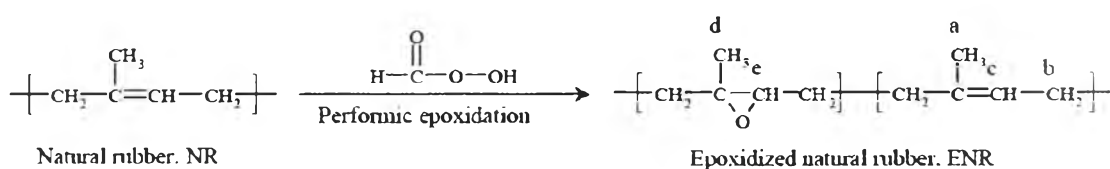


Figure 2.19 Performic epoxidation of NR (Yoksan R., 2008).

Three levels of epoxidation have been extensively evaluated. They were 50, 25 and 10 mole% epoxidized NR referred to as ENR-50, ENR-25 and ENR-10 respectively. ENR-50 has been found to undergo strain crystallization like NR, but with oil resistance similar to a medium acrylonitrile NBR and gas permeability similar to butyl rubber. It is a highly damping rubber with very low room-temperature resilience.

ENR-50 and ENR-25 both exhibit good wet grip characteristics and have been examined as tire tread materials. In particular, ENR-25 compounds containing silica or silica/black have been found to give lower rolling resistance than NR. ENR-25 and ENR-50 exhibit this unique feature with silica of reinforcement equivalent to black without the use of a coupling reagent.

❖ **Properties and Applications of ENR**

Thus, these rubbers have potential of providing white or colored vulcanizates with properties previously associated only with black-filled compounds, so extending applicational areas, or even resulting in colored tires or other automotive parts. ENR-10 provides a damping grade of NR when lower resilience are required. Alternatively, blends of ENR-25 or -50 with NR may be used. Many engineering applications are calling for reduced resilience.

Epoxidation results in a systematic increase in the polarity and glass transition temperature. These increasing are reflected in the vulcanizate properties. Property changes with increasing level of epoxidation which include an increased in damping, a reduction in swelling in hydrocarbon oils, a decreased in gas permeability, an increased in silica reinforcement, improved compatibility with polar polymers like polyvinyl chloride, reduced rolling resistance and increased wet grip.

❖ **Literature Review Regarding to ENR**

Due to the material which can resist deteriorating from gasohol is limited and NR and PHBV do not dissolve in ethanol. Phothiphon K. (2010) investigated, the blending between NR and PHBV which can be developed to be a thermoplastic vulcanizate (TPV) incorporated with PVDF, the high chemical resistance. The TPV is derived from dynamic vulcanization process which occur a melt mixing of polymers and crosslinking reaction at the same time. The results found that the increasing amount of DBPH provides the high mechanical properties and reduce the degree of swelling in gasohol. The addition of ESO can improve the mechanical properties and the swelling resistances from gasohol with percentages lower 50 and 150% at the temperature of 25 and 100°C, respectively. The morphology of TPV was also improved. The rubber phase formed into particles with sized of 1 micron and had well dispersed in thermoplastic phase.

Jiamjitsiripong K. and Pattamaprom C. (2011) studied, the mechanical properties and gas permeability of natural rubber/bromobutyl rubber blends were investigated when using epoxidized natural rubber (ENR) as a compatibilizer. They found that, ENR could promote faster cure and could improve the mechanical properties, compression set, and abrasion resistance of the composites with significant improvement in its gas barrier property.

Kaushik Pal *et al.* (2009) investigated, epoxidized natural rubber(ENR) and organoclay nanocomposites (Cloisite 20A) were prepared by solution mixing in this study. The obtained nanocomposites were incorporated in natural rubber (NR) and high styrene rubber (HSR) blends in presence of ISAF and SRF types of carbon black as reinforcing fillers. Morphology, curing characteristics, mechanical and thermal properties and wear characteristics of the nanocomposites were analyzed. The morphology of the ENR/nanoclay showed a highly intercalated structure. The nanocomposites containing SRF type of carbon black has showed increase in cross-link density, maximum torque and cure rate index compared to ISAF type of carbon black. The overall mechanical properties and thermal stability was higher for the nanocomposites containing SRF type of carbon blacks. The compounds containing ENR-nanoclay composites (EC) in NR–HSR have higher barrier properties compared to without EC. EC with SRF carbon black has showed minimum compression set value due to the increased formation of effective network chains due to higher reinforcing efficiency of the nanoclay in the rubber matrix. EC with SRF type of carbon black showed high abrasion resistance property.

Hana Ismail *et al.* (2001) studied, the effect of a compatibilizer, styrene-(epoxidized butadiene)-styrene triblock copolymer (ESBS) on curing characteristics, mechanical properties and oil resistance of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR) blends. The results indicate that the increasing compositions of ENR and the presence of ESBS improve processability, tensile strength, tear strength and tensile modulus of SBR/ENR blends. The scorch time, t_2 and cure time, t_{90} decrease with increasing compositions of ENR in the blend. The presence of ESBS exhibits a beneficial effect by increasing the scorch time and decreasing the cure time of the SBR/ENR blends. The presence of ESBS also

resulted in SBR/ENR blends having an oil resistance better than the similar blends without ESBS.

H. Ismail *et al.* (2000) studied, the dynamic properties, curing characteristics and swelling behaviour of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR) blends. The incorporation of ENR50 in the blends improved processability, stiffness, resilience and reduced the damping property. In terms of curing characteristics, the scorch time, t_2 and curing time, t_{90} of the SBR/ENR blends decrease with increasing ENR content. At room temperature (23°C) and at 100°C the swelling degree of the SBR/ENR blends decreases with increasing ENR content.

5. Acrylonitrile Butadiene Rubber (NBR)

Acrylonitrile Butadiene Rubber (NBR) is commonly considered the materials of the industrial and automotive rubber products industries. NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. Chemical structure and repeating unit of NBR are shown in Figure 2.20 and 2.21, respectively.

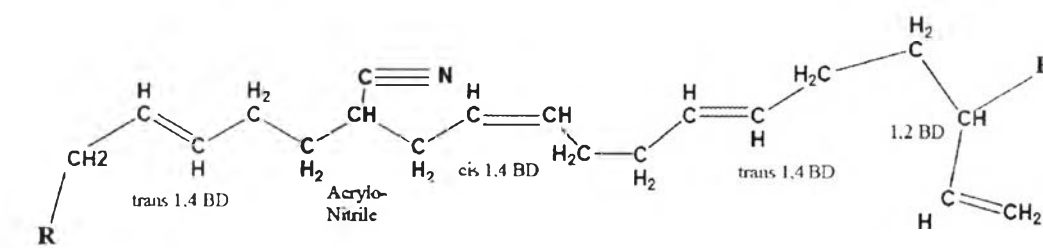


Figure 2.20 Chemical structure of NBR.

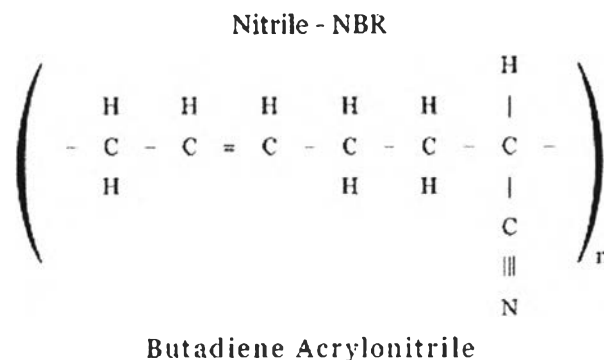


Figure 2.21 Repeating unit of NBR.

The acrylonitrile content of nitrile sealing compounds varies considerably (18% to 50%) and influences the physical properties of the finished material. The higher the acrylonitrile content, the better the resistance to oil and fuel. At the same time, elasticity and resistance to compression set is adversely affected. NBR has good mechanical properties when compared with other elastomers and high wear resistance. NBR is not resistant to weathering and ozone

By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of application areas requiring oil, fuel, and chemical resistance.

❖ Applications and Processing of NBR

In the automotive area, NBR is used in fuel and oil handling hose, seals and grommets, and water handling applications. With a temperature range of -40°C to $+125^{\circ}\text{C}$, NBR materials can withstand all but the most severe automotive applications. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications.

Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful articles. Additional ingredients typically include reinforcement fillers, plasticizers, protectants, and vulcanization packages. Processing includes mixing, pre-forming to required shape,

application of substrates, extrusion, and vulcanization to make the finished rubber article.

Mixing and processing are typically performed on open mills, internal mixers, extruders, and calenders. Finished products are found in the marketplace as injection or transfer molded products (seals and grommets), extruded hose or tubing, calendered sheet goods (floor mats and industrial belting), or various sponge articles.

❖ Literature Review Regarding to NBR

Supri *et al.* (2006) investigated the effects of dynamic vulcanization and glycidyl methacrylate (GMA) on mechanical and thermal properties, swelling index and morphology properties of the thermoplastic elastomers (TPEs) blends between recycled poly(vinyl chloride) (PVCr) and acrylonitrile butadiene rubber (NBR). It was found that dynamic cross-linking has enhanced the peak stress, stress at 100% elongation, thermal stability and swelling resistance of dynamically vulcanized PVCr/NBR+GMA blends compared to PVCr/NBR blends. Peak stress, elongation at break and stress at 100% elongation result are shown in Figure 2.22, 2.23 and 2.24 respectively. Table of swelling index data is shown in Table 2.5. Due to the introduction of cross-links into elastomer phase and better compatibility between PVCr and NBR are responsible for the enhancement of mechanical properties.

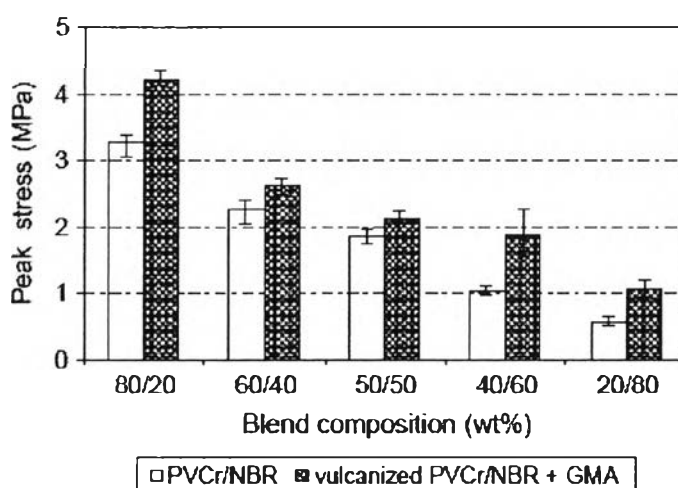


Figure 2.22 Peak stress vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR+GMA blends (Supri *et al.*, 2006).

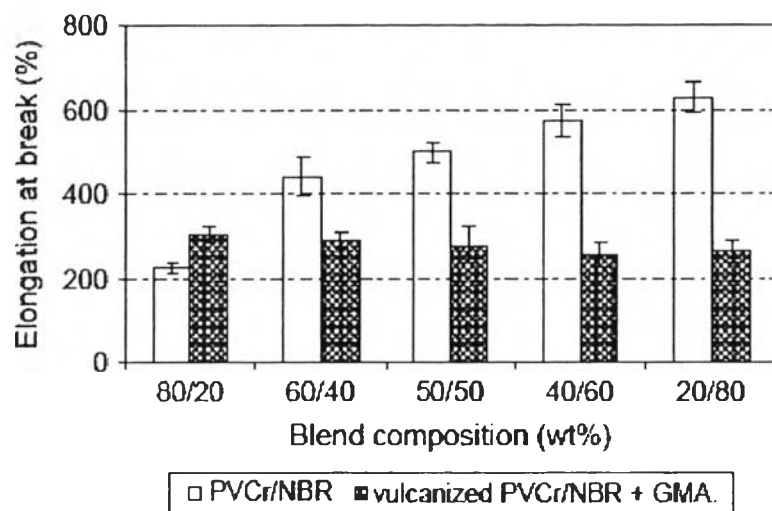


Figure 2.23 Elongation at break vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR+GMA blends (Supri *et al.*, 2006).

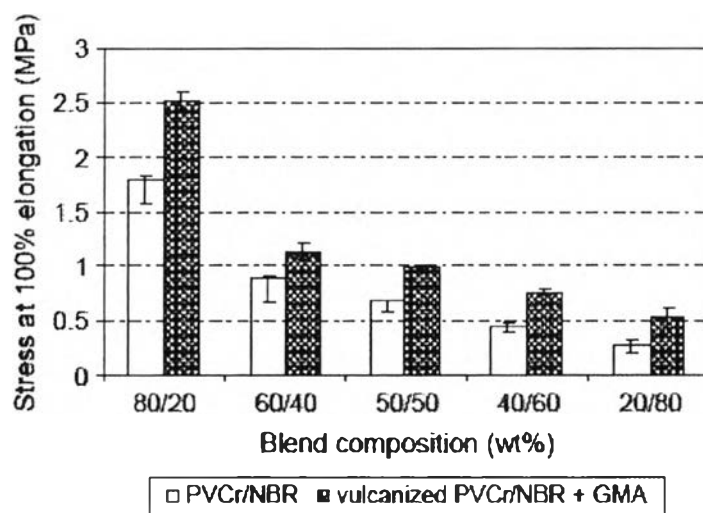


Figure 2.24 Stress at 100% elongation vs. blend composition of PVCr/NBR blends and dynamically vulcanized PVCr/NBR+GMA blends (Supri *et al.*, 2006).

Table 2.5 Data of swelling index of PVCr/NBR blends and dynamically vulcanized PVCr/NBR+GMA blends in toluene for 46 h (Supri *et al.*, 2006)

Experimental	Blend composition (wt%)	Swelling index
PVCr/NBR	80/20	1.70 ± 0.05
	50/50	2.86 ± 0.08
	20/80	5.12 ± 0.14
Dynamically vulcanized PVCr/NBR + GMA	80/20	1.58 ± 0.01
	50/50	2.20 ± 0.09
	20/80	3.30 ± 0.09

M.C. Senake Perera *et al.* (2001) studied, the structure and dynamics of the binary blends PVC/NBR and PVC/ENR, and the PVC/ENR/NBR ternary blend were investigated by dynamic mechanical analysis and solid state NMR. Samples were prepared by mechanical blending at 150°C. The effect of the change in the composition of the polymer blends, on the $\tan \delta$ peak width, the $\tan \delta_{\max}$ and area under the $\tan \delta$ curve were used to understand the miscibility and damping properties. Results confirmed heterogeneity in these blends and phase separation which indicated immiscibility in the range of 1-6 nm in all the three blends. The result from DMA indicated some degree of heterogeneity and reduces molecular mobility in all the three blends studied. PVC/ENR blend was found to have higher molecular mobility than the PVC/NBR and PVC/NBR/ENR blends. PVC/ENR blend also shows less heterogeneity than the PVC/NBR blends. Least destruction of the glassy structure was observed in the PVC/NBR blend.

Ahmad Mousa *et al.* (2005) studied, dynamically cured poly(vinyl chloride)/nitrile butadiene rubber (PVC/NBR), thermoplastic elastomers (TPEs) were melt mixed at 150°C at 50 rev.min⁻¹ with a Brabender Plasticorder. Curatives concentration was varied from 0 to 1 phr in order to study the effect of dynamic curing on the oil resistance. The compounds were characterized in respect to their mass swell, tensile properties, tear strength and hardness. The PVC/NBR formulations have been exposed to air and oil under identical conditions. The influences of oil and thermo-oxidative ageing on the mechanical properties were

characterized at room temperature and 100°C. It was found that at ambient temperature the samples immersed in oil possessed similar properties to those that were exposed to air. Profound enhancement in mechanical properties was observed for both environments at 100°C. The observed plan has been attributed to the increase in the degree of curing which was accompanied by a steady reduction in % mass swell with increased sulfur loading. The excellent mechanical behavior of the PVC/NBR TPEs even after immersing the samples in oil at 100°C evidenced for the good oil resistance of the materials.

2.6 Polylactic Acid (PLA)

Poly(lactic acid) or polylactide (PLA) is a highly versatile, biodegradable, thermoplastic aliphatic polyester derived from 100% renewable resources such as corn, tapioca products, sugarcane and sugar beets. PLA offers great promise in a wide range of commodity applications. Chemical structure of PLA is shown in Figure 2.25.

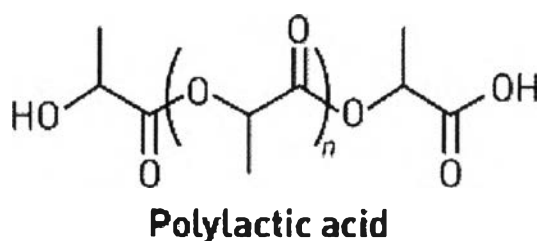


Figure 2.25 Chemical structure of PLA

In spite of its excellent balance of properties, the commercial viability has historically been limited by high production costs. Until now PLA has enjoyed little success in replacing petroleum-based plastics in commodity applications, with most initial uses limited to biomedical applications such as sutures.

❖ Degradation of PLA

The environmental degradation of PLA occurs by a two step process. During the initial phases of degradation, the high molecular polyester chains hydrolyze to

lower molecular weight oligomers. This reaction can be accelerated by acids or bases and is affected by both temperature and moisture levels. Brittleness of the plastic occurs during this step at a point where the Mn decreases to less than about 40,000. At about this same Mn, microorganisms in the environment continue the degradation process by converting these lower molecular weight components to carbon dioxide, water, and humus. The structural integrity of molded PLA articles decreases as the molecular weight drops and eventually the article disintegrates. A typical degradation curve of PLA under composting conditions is shown in Figure 2.26.

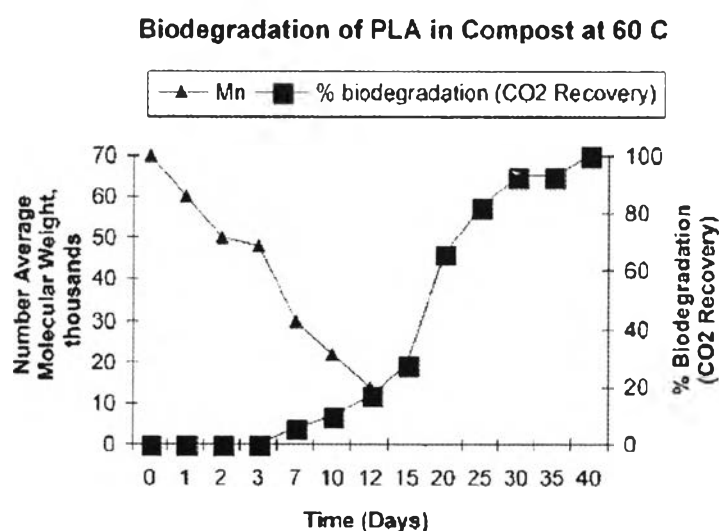


Figure 2.26 Degradation of PLA at 60°C (Ray E. Drumright *et al.*)

❖ Processing of PLA

PLA resins can be tailor-made for different fabrication processes, including injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning. Injection molding of heat-resistant PLA products requires rapid crystallization rates, which can be achieved by PLA that contains less than 1% D-isomer and often with the addition of nucleating agents. These compositions allow high levels of crystallinity to develop during the fast cooling cycle in the mold. Thus the rheological characteristics and physical properties of PLA can be tailored for use in a variety of processes and applications.

❖ Applications of PLA

Low-cost polylactic acid products are finding uses in many applications, including packaging, paper coating, fibers, films and a host of molded articles. The use of polylactic acid in these applications is not based solely on its biodegradability or because it is made from renewable resources. PLA is being used because it works very well and provides excellent properties at a low price. The use of PLA as a cost-effective alternative to commodity petrochemical-based plastics will increase demand for agricultural products such as corn and sugar beets, and will lessen the dependence of plastics on oil.

❖ Literature Review Regarding to PLA

G.H. Yew *et al.* (2009) studied, the composites consisting of PLA, rice starch (RS), and epoxidized natural rubber (ENR50) are compounded using a twin screw extruder followed by compression molding. Natural weathering tests are performed on the composites for 2 months. The average mean temperature and mean relative humidity are 29°C and 70%, respectively. The retention-ability of the PLA composites are relatively low, which may be attributed to the photo-degradation of PLA, chain scission of PLA, oxidation degradation on ENR, moisture absorption of RS, and leaching of RS particles. The extent of degradation is increased by the addition of ENR, owing to the fact that ENR is susceptible to oxygen attack, and consequently facilitates degradation. The morphological properties are transformed to a more brittle behavior, indicating that severe degradation has occurred on the PLA/RS composites.

KlinKlai W. *et al.* (2009) studied, Natural Rubber/Polylactic acid/Epoxidized Natural Rubber (NR/PLA/ENR) blends with various ratios. The ENR having 33 mol% epoxy group, then, was blended with NR and PLA in a Torque Rheometer at 170°C. The composition of NR/PLA/ENR blend was 100/100/0, 100/90/10, 100/70/30, 100/50/50, 100/30/70, 100/10/90 and 100/0/100 wt%, respectively. The NR/PLA/ENR was characterized through FTIR spectroscopy. FTIR spectrum revealed that there is no change in epoxy group content after blending. The effect of the blend ratio on the processing, physical properties, and thermal properties has been investigated. Density of the blend increases with the increase of PLA content. Glass transition temperature and melting temperature of the blends were independent

upon blend ratio. Tensile strength and % Elongation at break of NR/PLA blend increased as epoxidized natural rubber content increased. Blending of NR and PLA in the presence of ENR leads to the improvement in mechanical properties and thermal stability. Mechanical Properties values of blending is shown in Table 2.6.

Table 2.6 Mechanical Properties of blending as a function of blending ratio of PLA/NR/ENR (KlinKlai W. *et al.*, 2009)

Sample	NR (%wt)	PLA (%wt)	ENR (%wt)	Tensile strength (MPa)	Impact strength (kJ/m ²)	Density (g/cm ³)
1	100	100	0	8.61	5.5	1.108
2	100	90	10	11.32	9.0	1.050
3	100	70	30	19.60	17.2	1.029
4	100	50	50	14.36	14.6	1.007
5	100	30	70	15.23	12.0	0.994
6	100	10	90	12.65	7.6	0.964
7	100	0	100	10.50	-	0.960

2.7 Triacetin

Triacetin is the triester of glycerol and acetic acid. Somebody may know in name of glycerin triacetate, triglyceride and 1,2,3-triacetoxypropane. The chemical structure of triacetin is showed in figure 2.27.

Triacetin is a clear, colorless acetate ester used for example in the manufacture of cigarette filters. Triacetin is also used for plasticising NBR and cellulose derivatives. Storage stability is available under suitable conditions and can be stored for one year in a stainless steel tank.

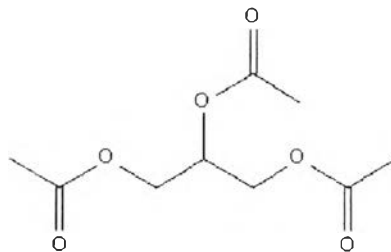


Figure 2.27 Chemical structure of triacetin

Triacetin is readily soluble in aromatic hydrocarbons and most organic solvents. It is insoluble in aliphatic hydrocarbons, mineral oils and vegetable and animal oils. Solubility in water is low.

❖ **General Properties**

The major features of triacetin are excellent suitability for the solidification of acetyl cellulose fibres for the manufacture of cigarette filters, very good dissolving power for a number of organic substances, good plasticising effect for various plastics such as celluloseacetates or celluloseacetobutyrate, good plasticising effect for cellulose-based paints, good compatibility with natural and synthetic rubber and good light resistance.

❖ **Applications**

Triacetin is used for the solidification of acetyl cellulose fibres in the manufacture of cigarette filters. The water content must be kept constant to achieve constant solidification. Triacetin is also used as a support for flavourings and essences in the food industry and as a plasticiser for chewing gum. In technical applications, triacetin is used for example as a core sand binder in the metal foundry sector. Another application is inks and printing inks. Triacetin is used as a highly-effective plasticiser for cellulose-based plastics.

❖ **Literature Review Regarding to Triacetin**

Nor Azowa Ibrahim *et al.* (2010) were studied the effect of triacetin on poly(lactic acid) reinforced kenaf bast fiber composites. The results shown that triacetin acts as a good plasticizer due to the increase of tensile strength, improvement of thermal stability, increase of storage modulus, decrease of softening

temperature. Moreover, from the SEM micrographs demonstrated that better adhesion between the fibers and the matrix. Finally, they found that the optimum fiber loading was 30 % wt kenaf fibers in the PLA matrix with the addition of 5 % triacetin.

Frank M. McMillan and De Loss E. Winkler (1952) studied the softening agent for rubber and resultant rubber composition. They found that the softening agents for natural rubber exhibit a plasticizing as well as softening and tackifying action, in some cases it may also be desirable to use additional plasticizers of which triacetin, stearic acid and dibutyl phthalate.

2.8 Organoclays

Organoclays are manufactured by modifying bentonite with quaternary amines, a type of surfactant that contains a nitrogen ion. The nitrogen end of the quaternary amine, the hydrophilic end, is positively charged, and ion exchanges onto the clay platelet for sodium or calcium. The amines used are of the long chain type with 12-18 carbon atoms. After some 30 percent of the clay surface is coated with these amines it becomes hydrophobic and, with certain amines, organophilic.

In this work, organoclay made from DEHYQUART® F 75 surfactant type containing distearoylethyl hydroxyethylmonium methosulfate and cetearyl alcohol. The main component of organoclay is bentonite, a chemically altered volcanic ash that consists primarily of the clay mineral montmorillonite. The bentonite in its natural state can absorb up to seven times its weight in water, after treatment can absorb only 5 to 10 percent of its weight in water, but 40 to 70 percent in oil, grease, and other sparingly-soluble, hydrophobic chlorinated hydrocarbons. As the organoclay is introduced into water, the quaternary amine is activated and extends perpendicularly off the clay platelets into the water. A chlorine or bromine ion is loosely attached to the carbon chain. Since the sodium ions that were replaced by the nitrogen are positively charged, they bond with the chlorine ion, resulting in sodium salt that is washed away. The result is a neutral surfactant with a solid base, which is the organoclay. The hydrophilic end of the amine dissolves into the oil droplet

because "like dissolves like," thus removing that droplet from water. Because the partition reaction takes place "outside" of the clay particle (in contrast to adsorption of oil by carbon, which takes place inside its pores), the organoclay does not foul quickly. Organophilic clay can function as a prepolymer to activated carbon, ion exchange resins, and membranes (to prevent fouling), and as a post polisher to oil/water separators, dissolved air flotation (DAF) units, evaporators, membranes, and skimmers. Organophilic clay powder can be a component or the main staple of a flocculent clay powder. They are excellent adsorbers for the removal of oil, surfactants, and solvents, including methyl ethyl ketone, t-butyl alcohol (TBA), and others.

❖ Applications

By removing oil and greases at an extremely high volume/weight ratio, organophilic clays can save an end user fifty per cent or more of operations costs. Organophilic clay may be disposed of through landfilling, fuel blending, asphalt plants, or stabilization. As long as the clay passes the liquid paint filtration test, it can be disposed of in the dumpster of a facility whose contents are landfilled. Environmental applications of organophilic clays include groundwater cleanup at old disposal sites and underground storage tank sites as well as the treatment of landfill leachates.

In processing field, organoclay can be used as reinforcing agent, filler and compatibilizer, i.e., added organoclay into NR sulfur-cured system to increase mechanical properties, added organoclay into PLA/ENR to increase compatibility and used as reinforcement fillers in PP/EPDM and NR/SBR blends.

❖ Literature Review Regarding to Organoclay

Ranumas Thipmanee, Rathanawan Magaraphan and Tarinee Nampitch (2009) were studied mechanical properties and morphology of poly(lactic acid) (PLA) / epoxidized natural rubber (ENR) / organoclay nanocomposites. The results found that the addition of organoclay improved the tensile strength and modulus of the PLA/ENR blend because the organoclay acted as reinforcing agent. At the twice-functionalized organoclay (TFC) content of 5 and 7 % wt improved the better results than that of C25A. This result suggested that the epoxy group grafted onto TFC

helped increase the compatibility of ENR and PLA by interaction with the epoxide group and the hydroxyl group.

P. L. TEH *et al.* (2003) were studied cure characteristics and mechanical properties of natural rubber/organoclay nanocomposites. They found that cure time (t_{90}) decreased with increasing filler content from 0 -10 phr but showed slight increases in maximum torque. The mechanical properties: tensile strength increased gradually up to 2 phr filler loading due to uniformly dispersed in the natural rubber matrix. The filler has high aspect ratio which tends to improve interfacial bonding and form filler-rubber interaction because of the high specific surface area of the filler. Further increase in filler loading after 6 phr of organoclay resulted in a reduction in the tensile properties because when the filler content is high, the filler tends to form agglomerate. The same trends are observed for elongation at breaks and tear strength.

H. Ismail and R. Ramli (2012) were studied organoclay filled natural rubber nanocomposites: the effects of filler loading and mixing method. The results shown that there is cure enhancement of organoclay filled NR nanocomposites with increased filler loading. Cure time and scorch time of NR nanocomposites prepared by solution mixing are shorter than those prepared by mechanical mixing. The maximum torque increases with increasing filler loading. Moreover, addition of organoclay in NR nanocomposites increases the tensile modulus, elongation at break and tensile strength (until 4 phr of filler).

L. E. Yahaya *et al.* (2010) were studied natural rubber/organoclay nanocomposites: effects of filler dosage on the physicomechanical properties of vulcanizates. They found that there was remarkable enhancement in the tensile and tear properties of the NR vulcanizates with increasing filler loading. This can be attributed to the strong rubber-filler interaction. Further, evidence of the interaction was obtained from the swelling behavior, which decreased as filler loading increases and the chemical crosslink density of the nanocomposites increases with increasing dosage until an optimum of 6 phr was attained. Evidence from SEM indicates that the failure mechanism is strongly dependent on the reinforcement effect on the modified filler marked by a higher extent of filler-rubber matrix interaction.