

## CHAPTER II

### THEORETICAL BACKGROUND

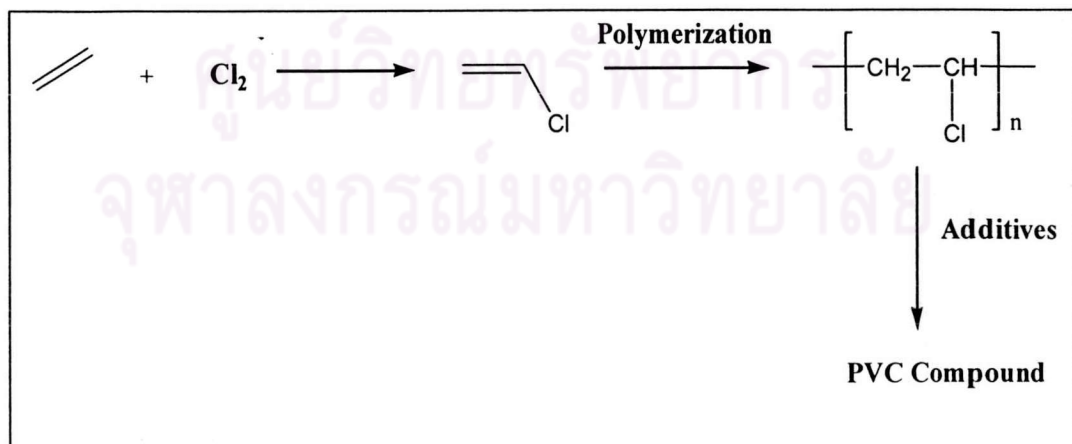
In order to improve the physical properties of PVC, the used rubber tire is utilized by mixing with PVC as a based resin. Background knowledge of each component and relate theory about blends are reviewed as follows.

#### 2.1 Polyvinyl chloride (PVC) [19]

PVC, a thermoplastic material, is produced via polymerization of vinyl chloride monomer (VCM), is a thermoplastic material.



VCM is a product of the reaction between ethylene from thermal cracking of crude oil and chlorine gas from electrolysis of sea water. Then PVC is produced by polymerization of VCM used as a monomer. The PVC compound production is shown in **Scheme 2.1**.



**Scheme 2.1** PVC compound production

### 2.1.1 Properties and application

The microstructure of PVC is atactic, PVC is an amorphous polymer. In addition it is a brittle polymer, glass-transition temperature ( $T_g$ ) is at 80-84 °C. Its specific gravity is 1.337 g/cm<sup>3</sup>. Since its physical properties and mechanical properties of this material is not suitable enough to use for producing the plastic ware, properties of such PVC are improved by adding additives. Then the compounded PVC is called as PVC compound.

There are two types of compounded PVC, i.e. rigid PVC (unplasticized PVC or R-PVC) and soft PVC (plasticized PVC or S-PVC). Commonly R-PVC is consisted of pure PVC as a based polymer, stabilizer, lubricants and modifiers. Sometime plasticizer is also mixed to improve the physical properties of R-PVC and S-PVC. The amount of plasticizer is less than 20 phr (part(s) per hundred resin). The rigid PVC is very hard, brittle and very difficult to make a material for use, but its chemical and environmental resistance is very high. Such R-PVC is usually used for outdoor application, pipe, a chemical container and so on.

To produce the S-PVC, the plasticizer added in the range of 20-50 phr is used for mixing in PVC based polymer. Its flexibility and processibility is better than the R-PVC. However, its hardness, thermal resistance, and environment resistance are less than the rigid one. The plasticized or soft PVC is applied for the electrical insulators, waterproof films, rain coats, boot, etc.

### 2.1.2 Compounding of PVC [21]

When PVC is contacted with heat higher than 100°C, the thermal degradation process is taken place. This phenomenon is a cause of the change in physical properties. Generally additives; for example, stabilizers, lubricants, plasticizers, fillers, processing aids, pigments, etc., are filled to modify its physical properties.

### Stabilizers

When the thermal degradation of PVC occurs, not only hydrogen chloride gas is generated but the physical appearance especially its color is changed as well. Whenever the process of degradation takes place, it is very difficult to halt this phenomenon. Therefore the stabilizers are added in order to inhibit the degradation process. Mostly stabilizers are metal salts such as lead stabilizers as a single salt and a mixed salt for example barium/cadmium stabilizers, barium/cadmium/zinc stabilizers, barium/zinc stabilizers, calcium/zinc stabilizers, and so on.

### Lubricants

According to PVC is not only a hard and brittle polymer but thermal sensitive polymer as well. Therefore the processing of PVC is very difficult to handle. Lubricating agent is used for reducing the friction of melted PVC molecule. There are two kinds of lubricants, internal and external lubricants. The external one decreases the viscosity of the melted PVC molecule. Whereas the other decrease the attractive force between the melted PVC molecule and the surface of machine. Furthermore, the amount of lubricants should be proper. If it is not enough lubricant, the PVC molecule is degraded because of heat. On the other hand, if lubricants are over loading, it will be difficult to melt. The example of lubricants for PVC compound are stearic acid, metal soap, paraffin wax and oils, low molecular weight polyethylene, oxidized polyethylene wax mineral natural and synthetic waxes, etc.

### Plasticizers

The aim of plasticizers for PVC is the increasing of flexibility of polymer molecule. It means that PVC compound can be used for several applications such as pipe PVC, medical tubing and also gum boots. There are a lot of plasticizers that is phthalate ester, trimellitate ester, phosphate ester, adipate, sebacated ester, and polymeric plasticizer.

### Fillers

Normally fillers are added to PVC compound for reducing the production cost. Besides fillers result in the physical properties especially impact strength of PVC. It is called as a reinforced filler if the impact of based polymer is increased. The examples of fillers are talc, wollustonite, china clays, calcium carbonate, rubber and so on.

### Processing aids

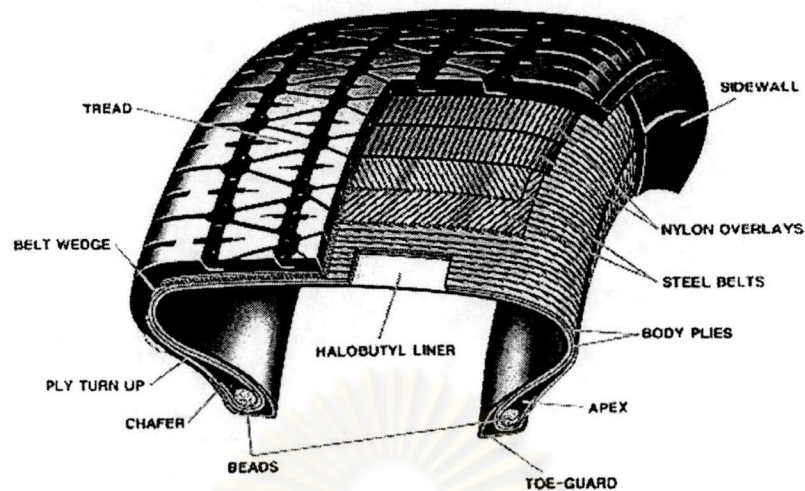
The processing aids of R-PVC is an acrylic resin or hydrocarbon resin, low molecular weight. The function of processing aids is the same as the plasticizer. Moreover, the melting of PVC becomes more homogenous and uniformed.

### Pigments

In general pigments effect on the resistance properties of thermal, light and melting behavior which results in the homogeneity of PVC. For the observation of homogeneity the melting behavior of PVC observed by using a torque from brabender plasticordor is obviously exhibited.

## **2.2 Recycled Tire Rubber**

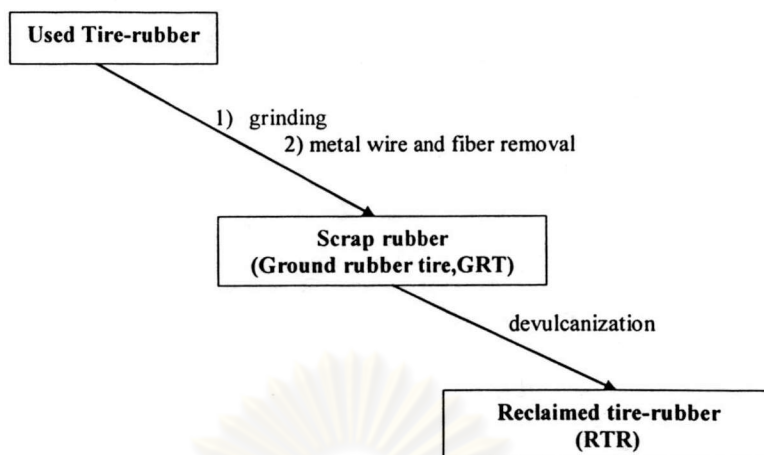
Tire rubbers shown in **Figure 2.1** comprise of composite materials topped with rubber. General components are carcass, made with chemical cords that is polyester, rayon or aramid, and breakers which is made of plated steel cords. Other components are made up of rubber compounds of natural rubber (NR), styrene-butadiene rubber (SBR) or butadiene rubber (BR). In order to improve the mechanical properties rubbers are vulcanized before producing the tire rubber.



**Figure 2.1** Tire construction [22]

Once the tires are worn out after a long usage, they must be thrown away. Increase of tire waste in the world has led to many researches that aim to recycle the used tires. Reclaimed tire rubber (RTR) is one of many products from the tire waste. The waste vulcanized scrap rubber tire is treated to produce a plastic material, which can be easily processed, compounded and vulcanized with/with out the addition of either natural or synthetic rubbers. The production of RTR begins with a size reduction of tire scrap. The tire bead wire is either cut from the carcass before grinding or manually removed after the first pass through the cracker. To remove remaining bead wire and steel belt wire, the ground rubber is passed over magnetic separation equipment. Moreover the fiber from the coarse-ground tires is removed by some sort of fluidized-bed. The action of controlled streams of air moving through a bed of ground rubber on an inclined gyrating of special design causes the fiber to separate from the clean rubber. So the ground rubber scrap is called as ground rubber tire (GRT). The size of the rubber particles may now be further reduce to perhaps 20 or 30 mesh by fine grinding.

Then the ground rubber scrap or GRT is processed further in order to achieve the application in a plastic material by devulcanization. There are three processes for producing reclaimed tire rubbers explained as below.



**Figure 2.2** Tire-rubber wastes production diagram.

### 2.2.1 Digesting Process

The coarsely group scrap is submerged in a solution of water and reclaiming agents. These agent may include many types of light and/or heavy oils, plasticizer, tackifier and chemical peptizing agents. Until the advent of synthetic rubber, the digesting solution also includes caustic soda to remove free sulfur and to act as a defibering agent. The process was generally referred to as the alkali digester method. Moreover, the scrap rubber containing SBR was totally incompatible with alkali cooks so the industry developed the neutral process, in which zinc of calcium chloride are used as the defibering agents.

Weighed scrap, water, and reclaiming and defibering agents are dumped into the digester and the cook cycle is started. Steam is injected in to the jacket of the vessel for a digestion period that may be from 5 to 24 hours. During this time, the rubber became devulcanized and the fiber becomes hydrolyzed. After digestion, the charge is blown down and washed to remove the decomposed fiber and caustic soda or metallic chloride. The washed, devulcanized rubber particles are conveyed to a dewatering press and then to a dryer. The material is now ready for the final, refining stage of the reclaimed tire rubber manufacturing process.

### **2.2.2 Heater or Pan Process**

The ground rubber is mixed with reclaiming agents in an open ribbon mixer then placed into containers rolled into the vessel. The main consideration is to allow an even penetration of heat in the mass of rubber. To achieve this uniform steam penetration, shallow panes are used as the stock containers. Line steam at pressure of 100 to 250 psi. with cycle times of 5 to 12 hours are typical.

This process yields fairly good results with some types of rubber scraps such as butyl inner tubes and marginal quality with other types such as find ground tires or low-specific-gravity natural-rubber scrap.

### **2.2.3 Reclaimator Process**

The reclaimator process is the only commercially successful continuous technique for devulcanizing tire scrap; all the others are batch process. Tires are ground, the metal and fiber are mechanically separated, and then the rubber is further ground to a fine particles size. This fine-ground rubber and the various reclaiming agents are all metered into a blending system and conveyed to the reclaimator.

The reclaimator is a special type of screw-extrusion machine. It is jacketed to provide for several zones of controlled temperature using either hot oil or cooling water; furthermore, the clearances between the screw and the chamber wall are close and adjustable. The object is to subject the rubber to a controlled amount of high heat and pressure in a continuously moving environment. The residence time of the rubber in the machine is less than 5 minutes. During this period, the rubber undergoes devulcanization. After the softened rubber is discharged from the head of the machine, it is cooled and further processed in refining mills just as is done in other reclaiming methods.

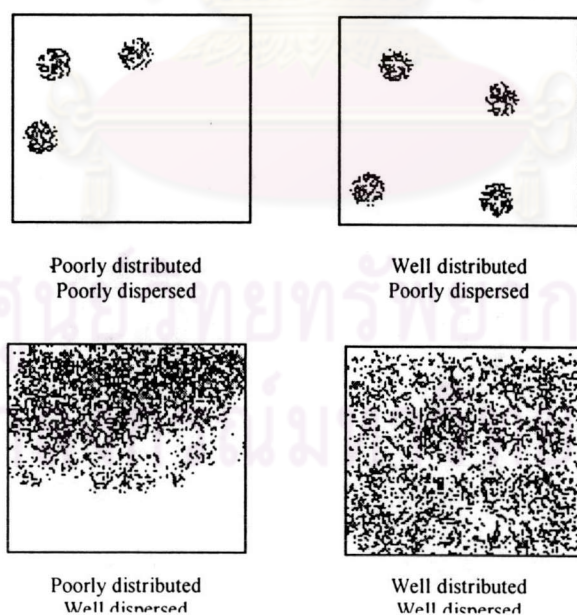
### **2.2.4 Further Advantages of Reclaiming and Applications**

Reclaimed tire rubber can be expected to break down in mixing much more indirect savings in the form of greater productivity more product using less labor and

overhead cost per unit. Furthermore, the reduced mixing time also reduces power consumption during mixing. Other advantages also include the conservation of petrochemical raw materials, conservation of the energy required to convert the petrochemicals into synthetic rubber, and conservation of the foreign exchange needed to pay for imported oil, a large proportion of the petrochemical's source [23].

### 2.3 Blending Method

On the whole polymer blends have been prepared commercially by melt mixing, solution blending or latex mixing. Elastomer-plastic blends of the type have generally been prepared by melt-mixing techniques. Melt mixing avoids problems of contamination, solvent or water removal, etc. Banbury mixers, mixing extruders and the newer twin-screw mixers are proper for melt-mixing elastomer with plastics. However, the dispersing of the mixed particle is always concerned. There are four types of dispersions shown in **Figure 2.3**. For well distributed and well dispersed, it is called as “dispersed particle morphology”. The theory of polymer blend is discussed as follows.



**Figure 2.3** The distribution pattern of blended polymer [24]

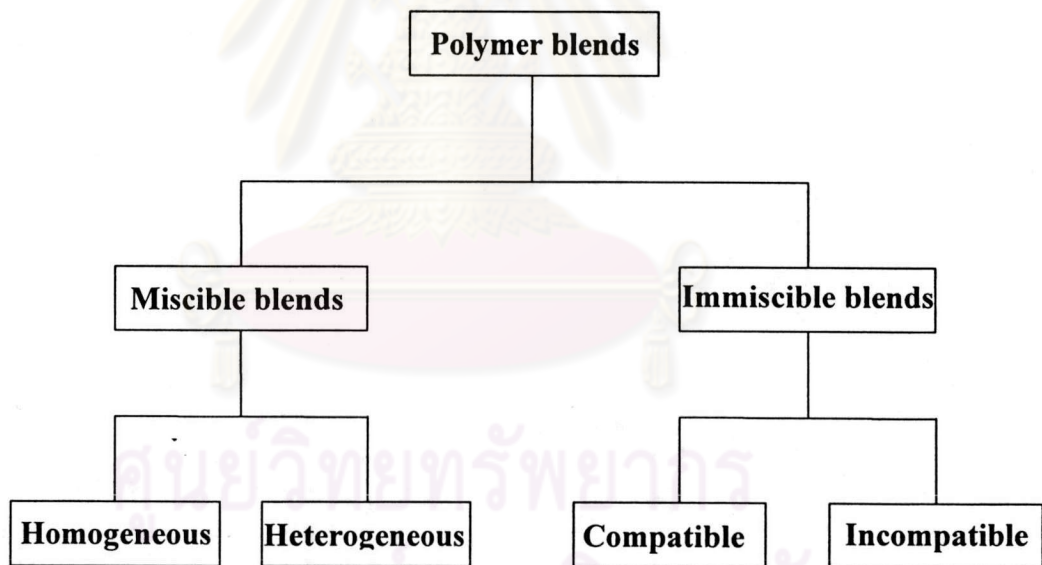


## 2.4 Polymer Blend [25]

Once two or more polymers are mixed together, normally the interaction, a physical interaction more than a chemical one, is taken place along each polymer chain. Because of this, the properties of blended polymer are different from a pure one. The aim of polymer blending is

- 1) To improve the properties of polymer, impact or weathering resistance, but low cost.
- 2) To extend the performance of blended polymer for replacing an expensive one.
- 3) To recycle the used or waste polymer.

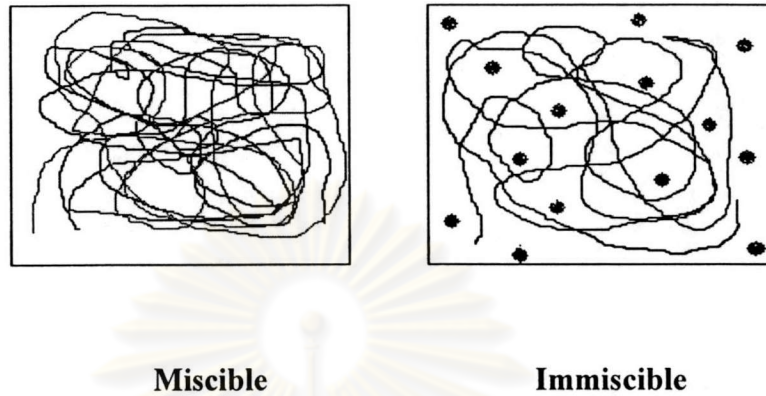
Normally, blended polymers are classified as the following chart.



**Scheme 2.2** Classification of blended polymers

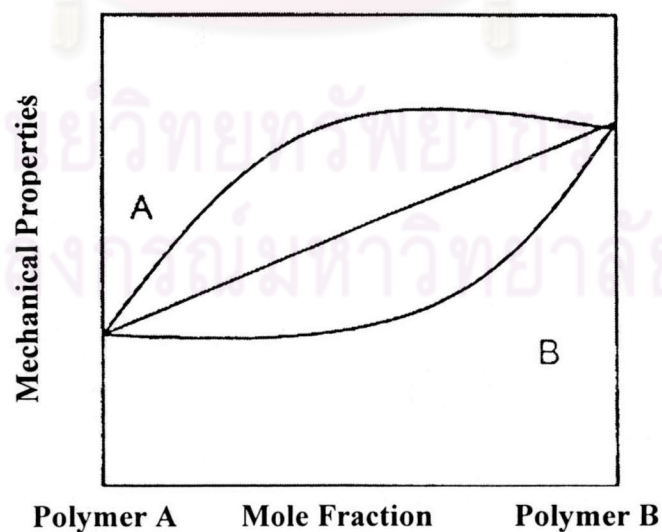
As above, there are two categories: a polymer which each phase cannot be distinguished by using SEM and shown only one glass transition temperature ( $T_g$ ), so called “miscible blends”. On the other hand, a mixed polymer exhibiting multiphase is call “immiscible blend”. From **Figure 2.4**, in the case of miscible blends polymer A

can be mixed in polymer B homogeneously, whereas in the case of immiscible blends polymer A cannot dissolve in polymer B.



**Figure 2.4** The microstructure of blended polymers

In the former category, the miscible blends are divided into two types. First, homogeneous miscible blends consist of the same kind of polymer but different in mechanical properties. Second, heterogeneous miscible blends consist of different kind of polymers. For the miscible blends, their mechanical properties depend upon the quantity of main and minor components (**Figure 2.5**).



**Figure 2.5** The relationship between the mechanical properties and the mixing ratio of polymer A and B which are miscible blended polymer [25]

From above, it indicates that the qualities of each polymer will affect the mechanical properties of blended polymer. Moreover, Tg of blended polymers is estimated by using the equation.

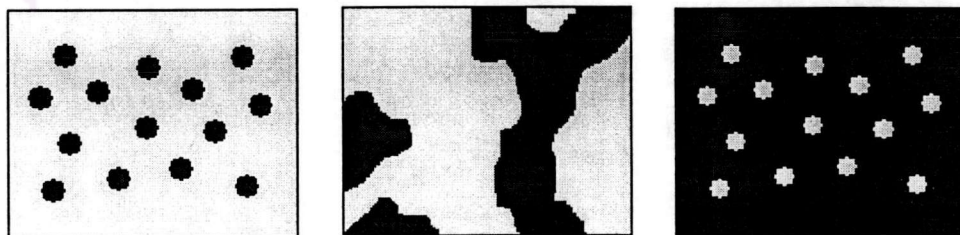
$$T_{g_b} = \frac{T_{g_A} W_A + T_{g_B} W_B}{W_A + W_B}$$

Where

- T<sub>g<sub>b</sub></sub>: Glass transition temperature of blended polymer
- T<sub>g<sub>A</sub></sub>: Glass transition temperature of polymer A
- T<sub>g<sub>B</sub></sub>: Glass transition temperature of polymer B
- W<sub>A</sub>: Weight fraction of A
- W<sub>B</sub>: Weight fraction of B

In the above equations, it commonly expresses the Tg-composition relationships for miscible copolymers and plasticizer-polymer compositions [26].

Most immiscible polymers form coarse mixtures with comparatively large domain sizes and shape interface, as a result of the high interfacial tension between the components. This leads to poor interfacial adhesion. The properties of blend depend not only on the mechanical behavior of the interface, but on the size of the respective polymer phase as well. When there is a lot more polymer A than polymer B, polymer B separates into little spherical globs. The sphere of polymer B will be separated from each other by the matrix of polymer A, as shown in **Figure 2.6**. In this case, polymer A is called the major component and polymer B is the minor component.



**Figure 2.6** Phase morphology of immiscible polymer blends.

When more polymer B is put into the immiscible blend system, the spheres will get bigger until they join together and form a co-continuous phase (the middle picture of **Figure 2.6**) or a region of phase inversion. And if more polymer B is added, the co-continuous phase of polymer B will become a major phase or a matrix phase, and polymer A will become a minor phase or a dispersed phase [27].

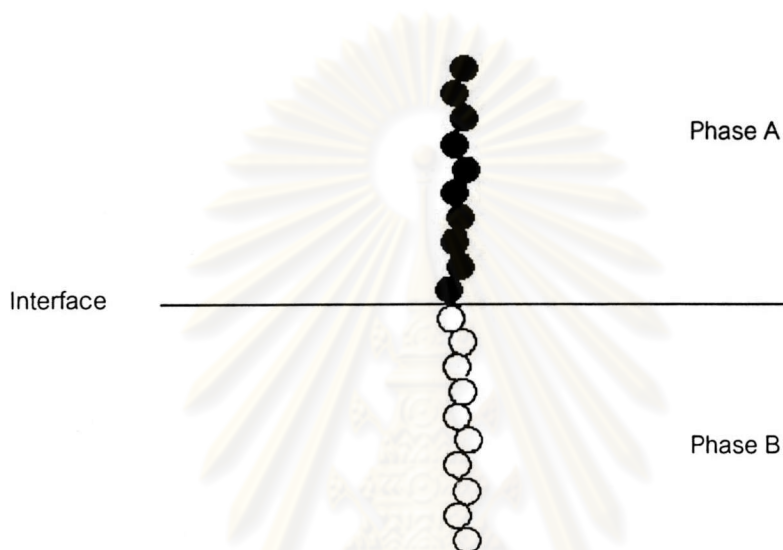
Normally, immiscible blends are divided into two types: compatible blends, the mixed polymer containing a strong interfacial force of both difference phases, and incompatible blend. The properties of the later one depend on the structure of major component.

## **2.5 Rubber toughened plastics**

Amorphous polymers such as PMMA, PS and PVC which have high glass-transition temperature ( $T_g$ ) are usually brittle full step. For PVCs, a plasticizer is not usually used for improving their toughness because the tensile strength, modulus, and hardness of modified PVCs are reduced. In order to enhance the toughness of a brittle plastic, rubbers are added to such plastic for this purpose. The dispersing of rubber particles called dispersed particle morphology is taken place when the amount of loading rubber is suitable. Moreover, its particle size, shape, and adhesion at the surface of rubber particle also affect the mechanical properties of a mixing polymer. A finer dispersion of one phase in another can be obtained by enhance adhesion by coupling the phase together, and stabilizing the dispersed the dispersed phase against coalescence [28]. Copolymers represent the most extensive use as a compatibilizer for the stabilization of phase structures. They may be added separately or form during compounding mastication or polymerization of a monomer in the presence of another polymer. The copolymer compatibilizers often contain segments, which are either chemically similar to those in blend components (non-reactive compatibilizer) or miscible or adhered to one of the components in the blend (reactive compatibitlizer). In case of a reactive copolymer compatibilizer, the segments of the copolymer are capable of forming strong bonds (covalent or ionic) with at least one of compounds in the blend. In the non-reactive copolymer compatibilizer, the segments of the copolymer are miscible with each of the blend components. The classical view of how

such copolymers locate at interfaces is shown in **Figure 2.7**. Copolymer structure and molecular weight impose important influence on their effectiveness [29].

The behavior of small amounts of copolymer-compatibilizer in an immiscible blend has been described as a classical emulsifying agent, similar to the soap molecules at an oil-water.



**Figure 2.7** Location of copolymer at phase interfaces.

### 2.5.1 Rubber Toughening Mechanisms

Toughening is a very important property for many materials. There are two categories of toughening mechanisms in dispersed systems: the energy is absorbed mainly by formation of craze at the rubber particles or through shear yielding between the modifier particles. Therefore, mechanism of deformation can be classified to be due to the following effects, energy absorption by rubber particles, matrix crazing, shear yielding or a combination of shear yielding and crazing.

#### 2.5.1.1 Energy Absorption by Rubber Particles [30].

Merz, Claver and Baer [29] proposed the idea of rubber particles absorbing energy for the toughening mechanism of toughened polymers. They observed that in

high-impact polystyrene (HIPS) an increase in volume and stress whitening accompanied elongation of the material and concluded that these phenomena were associated with the formation of many microcracks. More recently Kunz-Douglass, Beaumont, and Ashby [32, 33] have proposed a similar mechanism for rubber modified epoxies in which the elastic energy stored in the rubber particles during stretching is dissipated irreversibly when the particles rupture. However, the main disadvantage of these proposed theories is that they are primarily concerned with the rubber rather than with the matrix. It has been calculated [34] that the total amount of energy associated with the deformation of the rubbery phase accounts for no more than a small fraction of the observed enhanced impact energies. Consequently, this mechanism plays only a minor role in the toughening of multiphase polymers. Further toughening theories concentrated on the deformation mechanism associated with the matrix, which are enhanced by the presence of the rubber phase.

### 2.5.1.2 Matrix Crazing

Crazing is a more localized form of yielding and occurs in planes normal to the tensile stress. Crazes grow by macroscopic internal drawing of materials from the craze walls to increase the fibril length. A craze consists of polymer microfibrils (0.6 to 30 nm. in diameter) stretched in the direction of tensile deformation. The microfibrils are surrounded by void space, which can represent as much as 90% of the total volume of the craze.

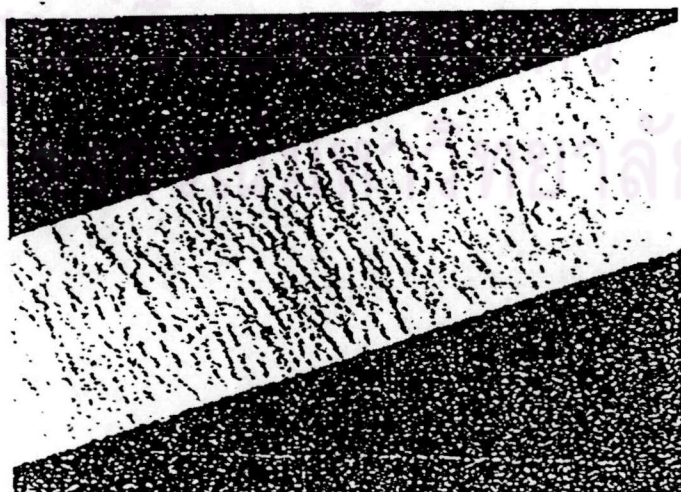
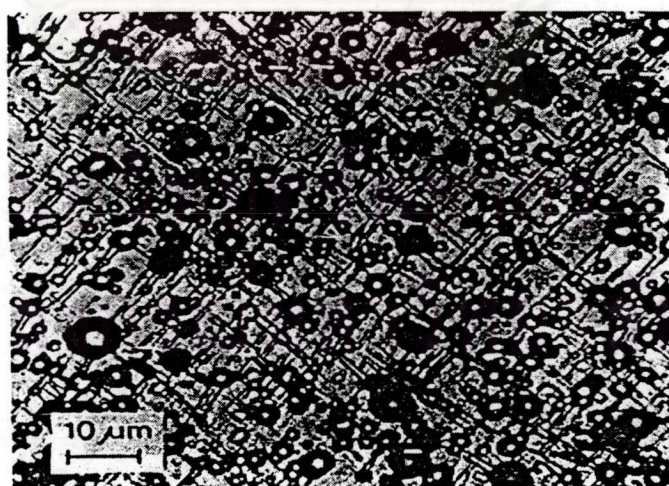


Figure 2.8 An example of craze fibrils [29]

From the above figure, it reveals the cross section of a craze showing its discontinuous structure and expanded volume. The craze consists of highly drawn treads of polymer associated with empty space. This means that the craze occupies roughly double the volume of the undrawn polymer and it achieves this by doubling only one dimension. When plastic materials fail principally by crazing, the impact modifier must initiate a large amount of crazing, the same modifier must then also terminate the craze. If it does not terminate the crazes a critically large void could form from that would lead to formation of a crack and hence failure. The ability of an impact modifier to initiate and terminate craze is related to the size of its particles where they are distributed in polymer matrix.

### 2.5.1.3 Shear Yielding

Shear yielding in the matrix phase also plays a major role in the mechanism of rubber toughening in polymer blends; shear yielding involves macroscopic drawing of material without a change in volume. The polymer will form regions of localized shear deformation, shear bands, which develop at an angle of  $45^\circ$  to the stretch direction. As a matter of fact, shear band formation is a dominant mode of deformation during tensile yielding of ductile polymers.



**Figure 2.9** An example of shear banding [28]

An example of shear banding is shown in **Figure 2.9**, a host of shear bands developed in conjunction with rubber particles. As before, the rubber particles provide

stress field perturbations, but the rubber by itself adds an extra feature, compression of the matrix. Shear yielding usually occurs in addition to elastic deformation. Not only does this phenomena act as an energy absorbing process but also the shear bands present a barrier to the propagation of crazes and hence crack growth, therefore delaying failure of the material.

Although cavitations of the rubber particles involve energy absorption, the enhanced shear yielding of the matrix is the major absorbing mechanism. However, cavitations of the rubber particles is a prerequisite for enhanced toughness where shear yielding is the principal mechanism.

#### **2.5.1.4 Crazing and Shear Yield**

Crazing and shear yielding may occur simultaneously in many rubber toughened plastic. The dominant mechanism is the one by which the unmodified matrix would typically fail. However, the contribution of each mechanism to the toughening of the system depend upon a number of variables such as the rubber particle size and dispersion, the concentration of the rubber particles and the rate and temperature of the test. The contribution of each mechanism to the toughening process can be assessed to some extent by using tensile dilatometer. It is assumed that deformations such as voiding and crazing are dilatational processes, which manifest themselves by an increase in volume strain. Unfortunately, if both voiding and crazing occur simultaneously, it is impossible to separate their contributions to volume strain. However, when shear yielding occurs, a decrease in the volume strain rate occurs since shear yielding is a non-dilatational or constant volume process.

#### **2.6 Parameters affecting the toughening**

Due to the rubber particles act as stress concentrators in rubber toughened plastics, the impact properties and tensile properties are and tensile properties significantly dependent upon the parameters of the rubber.



### 2.6.1. Rubber type

The effect of the rubber is difficult to evaluate as it depends on the mechanism by which toughening is believed to occur, be it as a stress concentrator to initiate crazes or shear bands or to alleviate local hydrostatic stress by cavitations. When the modulus difference between the rubber and matrix,  $G_R/G_M > 0.1$  Where  $G_R$  and  $G_M$  are the shear moduli of rubber and matrix, respectively, the stress concentration of the particle-matrix interface occurred, these will be improvement in toughening [35]. The modulus difference will cause the concentration of stress around the particles, leading to a nucleation of crazes or shear bands [36].

### 2.6.2 Loading of rubber.

The percent loading of the rubber was the major factor that affected mechanical properties of the blends. Increasing the loading of the rubber phase decreases the blend modulus and tensile strength irrespective of whether the matrix is brittle or pseudo-ductile. The main finding are that up to 30% rubber the  $T_g$  values of the two phase are not affected by rubber concentration in PA6-EPDM blends, but the brittle-bough transition temperature  $T_{BT}$  is reduced as the loading of rubber is increased [37].

### 2.6.3 Particle size and distribution of rubber.

The particle size and distribution of the dispersed phase significantly influences the deformation and failure properties of heterogeneous blends. The rubbery phase can act as an effective stress concentration and enhances both crazing and shear yielding in the matrix when highly dispersed. Ultimately the optimization of the size distribution of the dispersed phase depends on identifying the preferred deformation mechanism of the matrix polymer. A crazing mechanism is better suited to a higher particle size than a shear yielding mechanism. Generally, for the rubber to be effective the particle size has to be small (0.1-2  $\mu\text{m}$ ). Very small particle sizes are not effective.

#### **2.6.4. Rubber-matrix adhesion.**

When the bond between the rubber and the matrix is weak to make the craze termination mechanism also fails. Instead of stabilizing the craze, a weakly bonded rubber particle is pulled away from the matrix, leaving a hole from which the craze can propagate further, and from which breakdown of the craze to form a crack is probable. When there is good adhesion between the rubber and the surrounding matrix, fracture surfaces reveal rubber particles that have fractured into halves along the equatorial plane.

#### **2.6.5. Matrix type.**

If the molecular weight of the matrix is higher the melt viscosity increases and a fine dispersion is obtained more easily. The high molecular weight has also the advantage that the number of entanglements per chain is higher. In this way the material is more resistant to craze formation and some what higher impact strength can be expected.

#### **2.7 Literature review.**

Up to now there are several reports relating to the toughness improvement of thermoplastic like PVC by using rubbers, tire-rubber waste and even modified rubber. Here are a numbers of examples who are interested in this research area. Their studies are exhibited as the following:

Zainal and coworker [38] reported an optimum condition to improve the physical properties of PVCs was by using epoxidized natural rubbers. The proper ratio was 80/20 which PVC was a major component. Moreover, the effect of modified rubber or waste tire rubber on mechanical properties of thermoplastic polymer was studied.

Naskar and Bhomick [39] found that the surface chlorination of GRT could be performed by using trichloroisocyanuric acid (TCICA). Moreover, the dielectric

constant of chlorinated GRT increased depending on the chlorination and reached a maximum at an optimum degree of chlorination, beyond which it decreased. Chlorinated GRT, when molded, formed a biphasic morphology consisting of the rubbery phase and a hard phase, which was formed by the dipolar interaction. In spite of the loopy nature of GRT and chlorinated GRT (as compared to the PVC compound), their blends with the plasticized PVC compound did not show a high dielectric loss factor. This indicated that the blends could be used as dielectric material. While the activation energy for the dielectric relaxation of the PVC phase was not influenced by the presence of GRT in the compound. The presence of chlorinated GRT lowered the activation energy, indicating a higher degree of compatibility through dipole-dipole interaction between PVC and chlorinated GRT.

From Ref. [40], it indicated that chlorinated ground rubber tire powders (Cl-GRT) could be used as a filler in a plasticized PVC compound. Maximum 40 phr of Cl-GRT could be loaded, beyond which physical properties like tensile strength, ultimate elongation, and tear strength were adversely affected. SEM photomicrographs indicated that filler particles were dispersed in the PVC matrix. Stress relaxation study of the compositions showed improved adhesion between PVC and Cl-GRT, which restricts dewetting at the interface by the application of strain. Results of DMTA and solvent swelling study provide evidence for enhanced interaction between PVC and Cl-GRT compared to PVC-GRT interaction. The PVC/Cl-GRT composite also exhibited reprocessability characteristics of a melt-processable rubber.

In addition, the effect of GRT particle was also investigated by Naskar A. K. and his group [3]. It was found that smaller particles contain less polymer, but have higher amounts of fillers and metals with respect to polymer. NR compound containing smaller GRT particles showed better physical properties, but poorer aging characteristics.

From a few papers above, the concentration are on the utilization of RTR with PVC. From this point of view, this study concentrated on the effect of modified RTR on the mechanical properties of rigid PVC. The results of this study are discussed in the next section.