



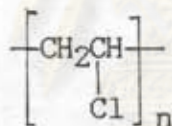
CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Poly(vinyl chloride)

2.1.1 Production

Poly(vinyl chloride) or PVC is produced by the free-radical polymerization of vinyl chloride monomer, PVC has the following basic structure:



where the degree of polymerization(n) ranges from 300 to 1500.

PVC is insoluble in vinyl chloride monomer and the polymer precipitates from the monomer phase at 0.1 % conversion. This phase separation of polymer from monomer is also found for acrylonitrile and vinylidene chloride. The phase separation of the polymer from the monomer affects both the polymerization kinetics and particle morphology of the poly(vinyl chloride) resin.

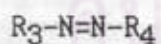
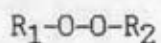
Classical free-radical polymerization

A. Initiation

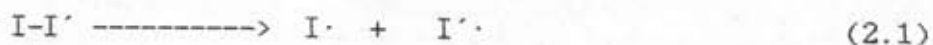
The polymerization process begins with the generation of a high energy species which is capable of interacting with the olefinic double bond of the vinyl chloride monomer. The source of this high energy species is a molecule called an initiator which can be represented by the form



The initiator may or may not be symmetrical. The only requirements for an initiator are that the chemical bond between I and I' must have a low bond energy. The consequences of these requirements have been to limit the initiator types which are useful commercially in the polymerization of vinyl chloride to those based on structures such as peroxide and azo compounds.



Homolytic bond scission occurs at the O-O bond for the peroxide and with the release of N₂ for azo compound. The bond energy for these homolytic scissions are approximately 25 to 40 kcal/mol at 25°C. The formation of the free-radical species by thermally induced homolytic bond breaking can be represented below.



B. Propagation

The propagation step is a series of sequential additions of monomer units in a fashion depicted below

Step 1: Formation of polymer with one unit(M_1):

$$dM_1/dt = K_{p1}[I\cdot] [M] - K_{p2} [M_1\cdot] [M] \quad (2.2)$$

Step 2: Formation of polymer with two units(M_2):

$$dM_2/dt = K_{p2}[M_1\cdot] [M] - K_{p3} [M_2\cdot] [M] \quad (2.3)$$

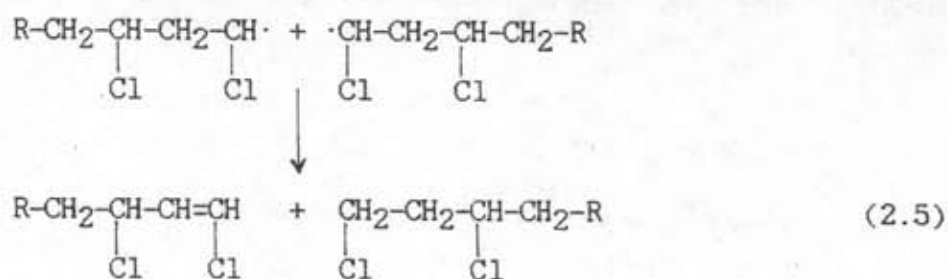
Step i: Formation of polymer with i units(M_i):

$$dM_i/dt = K_{pi}[M_{i-1}\cdot] [M] - K_{pi+1} [M_i\cdot] [M] \quad (2.4)$$

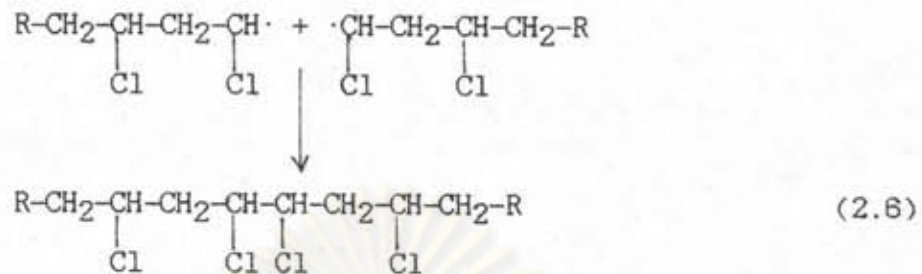
C. Other reactions of the free radical chain end

The termination steps in a free radical polymerization are all the reactions that results in a total loss of active chain ends. Free radical reactions can occur either through the use of a chain terminating reagent(also called a short stop agent) or by the mutual reactions of two active chain ends. Termination reactions can be of two forms: disproportionation reaction or combination reaction.

In disproportionation two active ends interact as



In combination reaction, the two active ends combine to form.



The free radical polymerization of PVC can be used in different processes such as suspension, bulk, or emulsion polymerization processes in which there are different conditions, recipe, equipment, capacity, and the particle sizes of PVC resin.

2.1.2 Physical and chemical properties

PVC is a thermoplastic which can soften and melt at elevated temperatures. Thus, by the application of heat and pressure, PVC may be extruded or molded into any desired shape. Processing can be formed from 150 to 200°C, depending upon the molecular weight of the resin and formulation.

PVC is uniquely responsive to functional additives which permit the generation of rigid and flexible products, useful in novelties at low cost and in designed engineering applications.

PVC is used in a wide range of applications because of its combined physical properties of:

- Compounding versatility as rigids or flexibles

- High modulus(unplasticized)
- Ease of fabrication
- Low flammability
- Low cost

PVC is sensitive to environmental attack, and vigorous programs to develop cost-effective ultraviolet stabilizers are an on-going area of research.

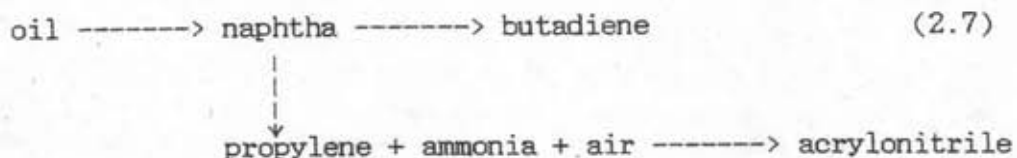
2.1.3 Applications

Because of the compounding versatility of PVC, consequently, they can be used in many applications such as wire insulation, tube, film, sheet, footwear, toys, hose, and many other applications.

2.2 Acrylonitrile-butadiene rubber

2.2.1 Production

Acrylonitrile-butadiene rubbers (NBR or Nitrile rubbers) are manufactured by emulsion copolymerization of butadiene with acrylonitrile in processes similar to those used for other emulsion polymers, such as SBR. The main raw materials required are the monomers, butadiene and acrylonitrile. Both monomers may be synthesised from naphtha obtained from oil.

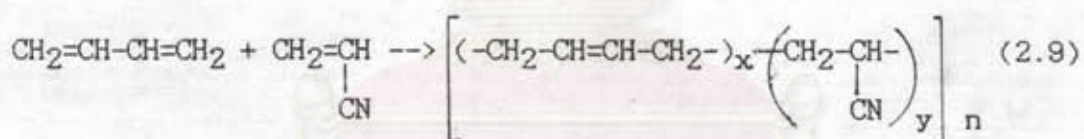


At present, approximately 75% of the world production of acrylonitrile utilises the Sohio process (Veatch et al., 1962; Schmidt, 1969), in which ammonia, propylene, steam, and air are passed through a fluidised bed of finely divided catalyst at about 450 - 500°C. This and other similar processes are based on the reaction shown below.



The use of propylene as the basis for the production of acrylonitrile has superseded older routes involving acetylene and hydrogen cyanide, for example, mainly on economic grounds.

In theory, the polymerization reaction can be written



The values of n and y depend on the precise polymerization recipe and the temperature of polymerization. It is important to bear in mind that, except under azeotropic conditions, the ratio of the two monomer units in the final polymer will not normally be the same as the ratio in which the monomers were charged into the reaction vessel. As the ratio of butadiene to acrylonitrile in the polymer largely controls its properties, as will be seen later, the design of the polymerization recipe and the temperature at which this is carried out are important features of nitrile rubber production. The properties of the product may be influenced by other details of the recipe, such as the nature and amount of modifiers

and emulsifiers.

The early nitrile rubbers were all polymerised at about 25-50°C, and these hot polymers were characterised by their toughness resulting from the presence of a degree of branching of the polymer chains often referred to as 'gel'. By analogy with the development in the emulsion polymerization of SBR, since the early 1950's an increasing number of nitrile rubbers are being produced by 'cold' polymerization at about 5°C, this results in more linear polymers containing little or no gel and which are easier to process than "hot" polymers.

2.2.2 Physical and chemical properties [3]

Nitrile rubbers are classified as specialty rather than general purpose elastomers, as the vulcanized forms are used primarily for their oil, solvent and chemical resistance.

Nitrile rubber grades available in the marketplace have a 20-50 % acrylonitrile content. When properly compounded and cured, the fuel and solvent resistance, abrasion resistance and resistance to gas permeation increase with increasing acrylonitrile content, but with decreasing acrylonitrile content the low temperature properties and resilience improve. A second controlled variable in the manufacture of NBR is Mooney viscosity, a measure of average molecular weight ranging in commercial polymers from 30 to 90 arbitrary units. At the low end of this range processability is superior but dynamic mechanical properties may be poorer.

The fluid resistance of compounds containing NBR, as measured by volume swelling in laboratory immersion or by actual performance tests, is proportional to acrylonitrile content, or the polarity imparted by the -CN groups on the polymer chains, and also is a function of the chemical nature of the oil or solvent. As a polar rubber, NBR is most resistant to hydrocarbons but is less resistant to polar fluids.

Low temperature behavior is improved as the acrylonitrile content of NBR is reduced. Since oil resistance also declines with reduced acrylonitrile level, the selection of an appropriate NBR type must often involve a compromise depending upon the given service condition.

Two other processes that impart ozone resistance and have assumed commercial importance are blending with poly(vinyl chloride) (PVC) or with ethylene propylene diene elastomer (EPDM). For the former, several commercial blends, containing 30% of dispersed PVC, are available. In compounding, the stiffening influence of PVC is compensated by the use of ester plasticizers.

The other properties of nitrile rubbers can be summarized as shown in Table 2.1.

Table 2.1 The effect of acrylonitrile content on properties of nitrile rubbers.

High	<----- Acrylonitrile ----->	Low
<-----	Resistance to fuels and oil improves	
<-----	Tensile strength improves	
<-----	Abrasion resistance and hardness increase	
<-----	Compatibility with plastics improves	
	Low-temperature flexibility improves	----->
	Resilience and elasticity increase	----->

2.2.3 Compounding & vulcanization

Nitrile rubber is compounds along lines similar to those practised with NR and SBR. There are a few noteworthy points. The vulcanization systems should be considered before compounding rubber because vulcanization is a process which transform the plastic material (can be processed like thermoplastic) to elastomeric material (can not be processed like thermoset). Thus, the vulcanization systems are important for rubber compounding and processing.

The conventional vulcanization systems always have sulphur as vulcanizing agent, which can crosslink the rubber chains in order to form the rubber network (vulcanized rubber or elastomeric material) illustrated in Figure 2.1. However, vulcanization systems should have activators and accelerators for reducing time of crosslinking.

The onset of crosslinking so called scorch time or scorch resistance can be measured by Mooney viscometer(Figure 2.2 (a)). It consists of a rotating disk in a cavity which contains the test rubber. The temperature is selected to be a typical, or average, processing temperature. When the time reaches to scorch time, the Mooney viscosity increase rapidly(Figure 2.2 (b)). The extent and rate of vulcanization are measured by determination of mechanical properties after various cure periods.



Figure 2.1 Structural features of vulcanizate network.

At present time, rheometers(or cure meters) illustrated in Figure 2.3 (a) have been used. These devices are capable of measuring the extent of cure of a single sample at a given temperature on a continuous basis as illustrated in Figure 2.3 (b).

Generally less sulphur and more accelerator are used with nitrile rubbers than with natural rubber. The most important vulcanizing agents are elemental sulfur and sulfur donors. Organic peroxides are also used as cross-linking agents and they impart good high temperature resistance. Other chemicals that may be required to balance the vulcanization system are activators, such as zinc oxide and stearic acid, and accelerators which reduce the time and temperature requirements for sulfur cure. The latter include the

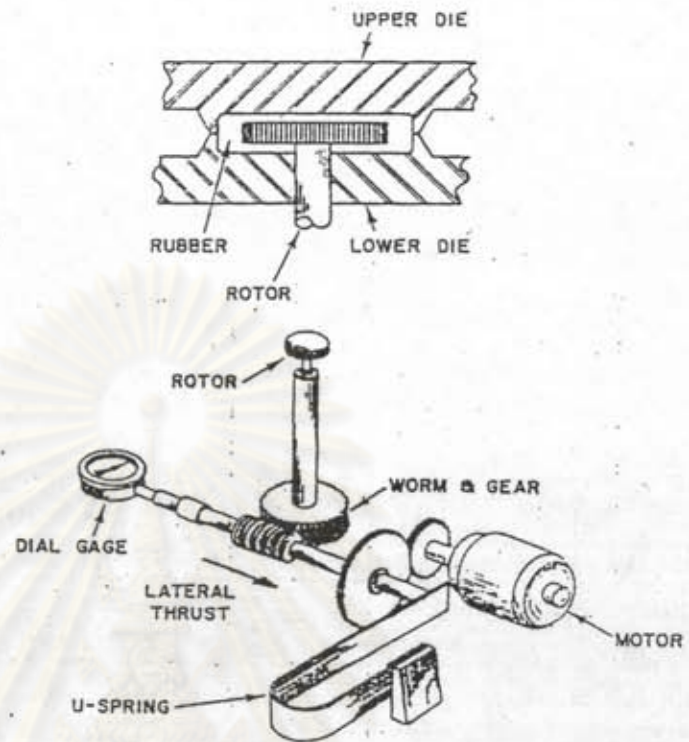


Figure 2.2(a) Mooney viscometer.

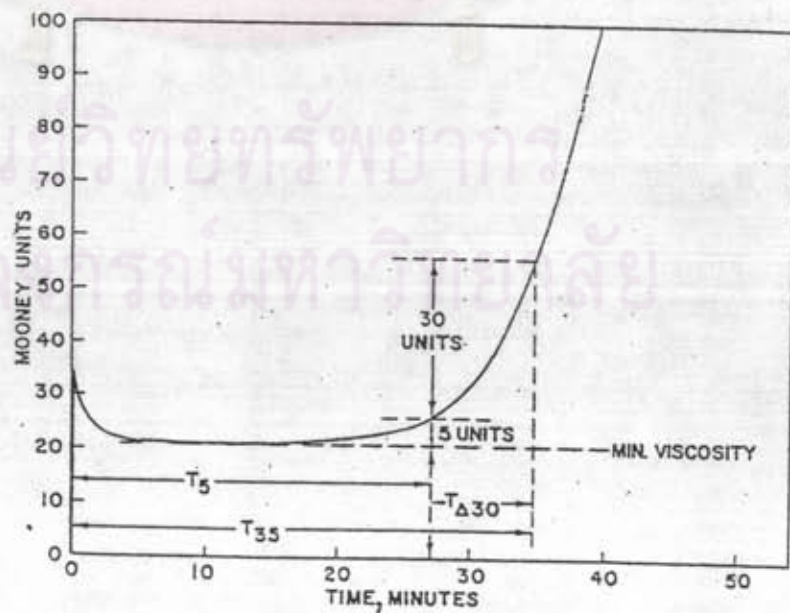


Figure 2.2(b) The effect of scorch on Mooney viscosity.

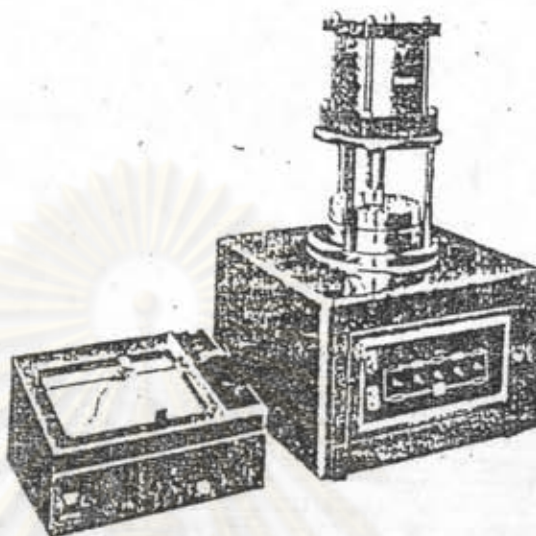


Figure 2.3(a) Oscillating disk type curemeter.

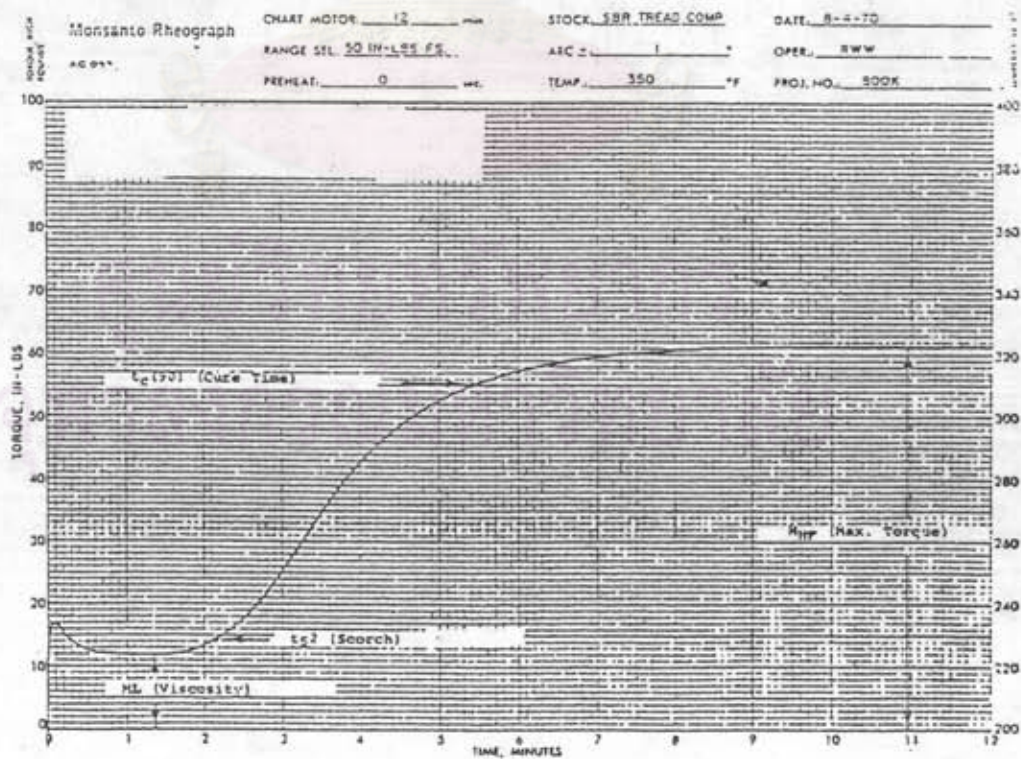


Figure 2.3(b) Torque curve measured by curemeter

very numerous thiazoles, sulfenamides, thioureas, guanidines, dithiocarbamates, thiuram disulfides, aldehyde-amine reaction products and combination of these.

The total compound of polymer, fillers, plasticizer and cure system may be mixed in conventional rubber equipment, such as open mills or internal mixers, then sheeted-off for molding, calendering or extrusion. Some precautions during these operations are often required to ensure good dispersion of ingredients and to prevent premature cure or scorching of stocks.

The choice of accelerator is particularly important when compounding for the frequently required low compression set; one such system is TMTD 3 phr, CBS 3 phr, sulphur 0.5 phr (parts per hundreds of rubber). Accelerator systems are comprehensively covered by Hofman (1963, 1964).

Ester and polymeric plasticizers are widely used in NBR because they influence not only processing but also such properties as hardness, low temperature flexibility, and oil resistance. Small quantities of aromatic process oils can occasionally be used, particularly with those NBR types which do not contain more than about 30% acrylonitrile.

Nitrile polymers are amorphous, not crystalline, and like SBR, need reinforcement by fillers in order to obtain optimum properties. These fillers may be carbon black or non-black mineral types, the choice depending upon the end use and the requirement of finished products properties.

All types of carbon black and non-black fillers may be used with nitrile rubber. The most common practice is to use mainly the reinforcing and/or semi-reinforcing varieties in order to obtain the products with suitable physical properties allied to low raw material costs. Nitrile black masterbatches in a crumb form are commercially available to enable compounders to maintain a clean working environment, with the advantage of shorter mixing cycles (Yelland, 1967). Silica and clays are used where non-black compounds are required, but compression set performance is not so good as a black-reinforced compounds unless silane treated silicas are used.

2.2.4 Applications

Nitrile rubbers are excellent in resistance to oil, chemicals, heat and water, they allow wide applications ranging from oil resistant rubber products to adhesives and PVC blends. They are used in such oil resistant rubber products as oil resistant hoses, packagings, gaskets, diaphragms, shock absorbers, rubber rolls, oil resistant shoe soles, rubber sheets and many other products.

2.3 Processing

2.3.1 Dry blending of PVC compounds[4]

Poly(vinyl chloride) dry blending has long been one of the most important methods of mixing rigid PVC powder blends, and the high-speed intensive mixer has also been a boom to the PVC powder formulator who needs to disperse plasticizers, fillers, stabilizers,

pigments, and colorants.

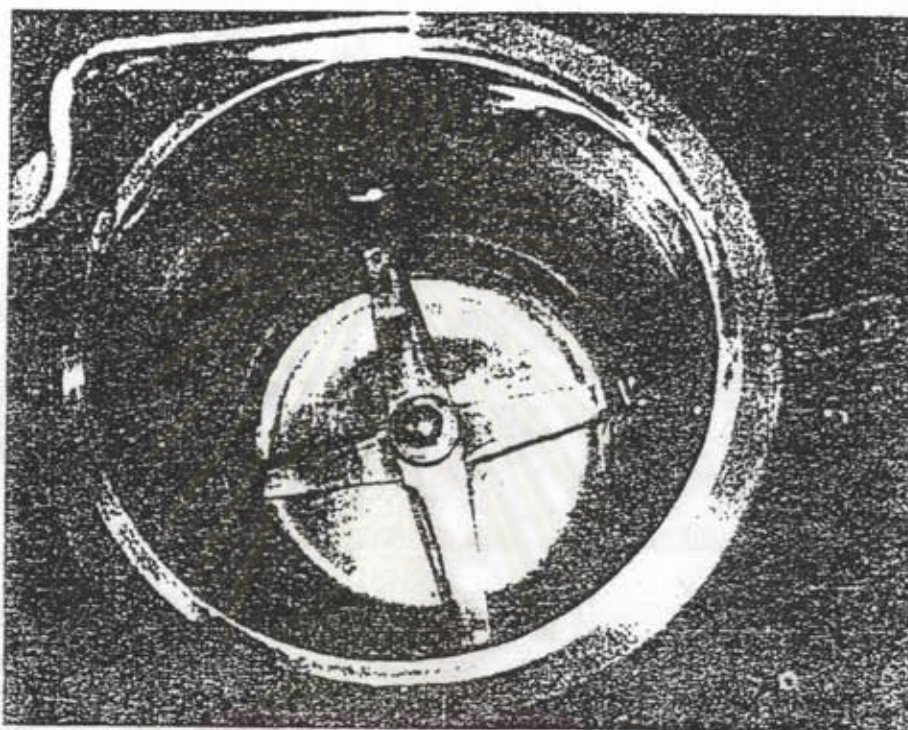


Figure 2.4 Prodex-Henschel high-intensity mixer, opened with the rotors showing at the bottom of the mix bowl.

The Prodex-Henschel mixer operates on the principle of vertical mixing with extremely high shear rates. When the powder mix is fluidized, two types of flow patterns are set up—circular around the circumference of the bowl, and tidal, where the material is subjected to an "under and over" and a "down towards the center" type of movement.

The high horsepower input per unit volume (8 hp/cu.ft.) results

in rapid heating of the PVC powder blends, permitting rapid addition sequence of ingredients, including plasticizers, with cycles of 6-8 minutes of final compound temperatures from 190-260°F(87-127°C). Mixing cycles vary from 3-8 minutes, depending on the type of formulation and the required temperature of the mix.

Prodex supplies five standard-model intensive mixers with capacities ranging from 0.2 to 24 cu.ft., and horsepower ranging from 2.5 for the smallest to 100-200 hp. for the largest model. The working capacities of the cooling mixers range from 5 cu.ft. for the smallest to 24 cu.ft. for the largest unit. A cooling mixer for the laboratory size intensive mixer is not available.

Dry blending involves incorporation of the plasticizer into the PVC particles by stirring at 50 to 110°C to yield a dry powder barely distinguishable in outward appearance from the original resin. For this, certain grades of resins with a high degree of porosity in the resin particles are preferred for their absorption power. The method of polymerization, types and amount of surface contaminants will influence the rate of plasticizer uptake. Dry blending takes place most readily when the mixture is heated above the glass temperature(T_g) of resin (about 80°C for homopolymers) but well below the fusion temperature (Table 2.2) under conditions free from pressure on the particles. Plasticizer diffusion into the amorphous regions of the particles above or even below T_g is the rate controlling step. Below T_g , years may be required for the diffusion of plasticizers of usual molecular volume.

Table 2.2 Ease of fusion of PVC with different plasticizers.

Plasticizer	Relative ^a fusion temp.(°C)	Minimum ^b fluxing temp.(°C)	Clear ^c point (°C)
Phthalates			
Diethyl(DEP)	58	54	
Dibutyl(DBP)	62	68	97
Di-n-hexyl(DHP)	84	75	113
Diisooctyl(DIOP)	85		126
Di-2-ethylhexyl (DOP)	84	105	127

^a The temperature at which torque in a Plasticorder torque rheometer begins to increase rapidly at the onset of fusion.

^b The lowest temperature at which a plastisol develops sufficient physical integrity to permit being lifted from the fusion plate.

^c The temperature at which a plastisol becomes clear.

The time required to obtain a dry blend is very dependent on the temperature as well as on the plasticizers. Plasticizers having a high molecular volume or being very viscous require a longer time or a higher temperature, or both, for dry blending. Diethyl and dibutyl phthalates are small enough to dry blends quite well below

the T_g of the resin. For di-2-ethylhexyl phthalate, the fusion time in Plasticorder is 186 seconds or about 3 minutes. It takes a longer time in Henschel mixer(462 seconds or about 8 minutes).

Rubber powder such as NBR powder can be also mixed with additives or PVC resin in dry blends mixing and followed by injection molding or extrusion by which time and energy in processing are saved.

2.3.2 Mixing in Brabender Plasticorder[5]

The C. W. Brabender Plasticorder instrument(Figure 2.5 (a) and Figure 2.5(b)) is a table top pilot plant designed to permit the study of all types of rubber and plastic materials under the same conditions of shear force, shear rate and temperature as anticipated in processing. Mixing, extrusion, calendering and molding characteristics can be pre-determined in this manner. Test samples may be in the form of strips, pellets or crumbs.

The heart of the instrument is one of the numerous variable speed recording torque dynamometers operating in the speed range of 2 to 200 rpm(rounds per minute). The reaction torque forces, developed in the measuring head during the test are transmitted to the torque dynamometer. The action-reaction principle is used and the torque is converted to a read-out through a mechanical array of lever arms. Torque, in terms of gram-meters, is indicated on a scale, as well as being recorded continuously on a strip chart.

The Plasticorder has been used most frequently in the rubber industry with the Cam Measuring Head(manufacturer's name), a small

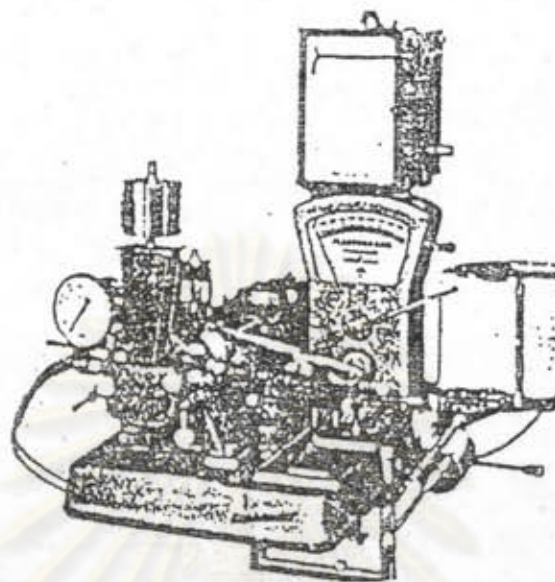


Figure 2.5(a) Brabender Plasticorder.

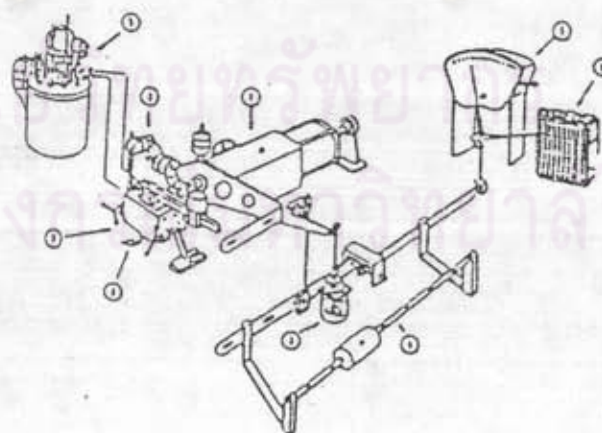


Figure 2.5(b) Assembly of Brabender Plasticorder.

stainless steel internal mixer with a rotor of configuration similar to that of a Banbury mixer. Compounding studies covering the range of up to 200-ML Mooney units can be accomplished in the Cam Head at a single instrument setting. Break down energies for various polymers can be identified in terms of the area under the torque-time curve. Effects of reinforcing agents, process oils, plasticizers, peptizers, stabilizers and other additives can be observed as corresponding increases or decreases in torque. Data obtained by employing this "mixing-in-miniature" principle can be used to estimate breakdown times and energies as well as mixing rates on production equipment.

2.4 Theory of polymer blends and composites

2.4.1 Thermoplastic elastomers

From the introduction part, definition of thermoplastic elastomers(TPE) was described but the classes of TPE are not mentioned. Consequently, in this part, TPE are classified into six different commercial classes. These classes are depicted in Figure 2.6 in an order of increasing performance and cost. The properties of six classes of TPE are summarized in Table 2.3[2].

A) Styrene block copolymer: These materials are based on an ABA block copolymer where A is a polystyrene chain and B is a diene chain, such as polybutadiene or polyisoprene. The styrene/diene molar ratio can range from 50/50 to 15/85. The useful temperature range is from -70°C to 100°C .

B) Polyolefin blends: These TPE are primarily blends of

polyolefins (most commonly polypropylene and polyethylene) and rubbers (most commonly EPDM). Some less common rubbers are natural rubber, nitrile rubber, and EVA.

C) Elastomeric alloy(EA): These materials contain two or more different polymer systems combined synergistically to obtain the more beneficial properties of each. EA are subdivided into two different types. The first of these is a two-phase synergistic alloy of a rubber and a thermoplastic (such as Monsanto's Santoprene and Geolast). The second type, melt-processable rubbers(MPR), are single-phase alloys of chlorinated polyolefin-EVA-polyacrylate ester with significant plasticizer content(such as Du Pont's Alcryn).

D) Thermoplastic polyurethanes(TPU): TPU are also block copolymers, they result from the reaction of a diisocyanate with a medium to high molecular weight/polyol(either polyether or polyester) and a low molecular weight glycol chain extender, such as 1,4-butanediol. TPUs are sensitive to moisture, acidic and basic solutions, which can cause hydrolytic cleavage of polymer chains.

E) Thermoplastic copolyesters(TPEs): These block copolymer TPEs contain ester and ether linkages rather than urethane(carbamate) linkages. They have excellent physical properties but are somewhat susceptible to attack by moisture, acids, and bases at higher temperatures.

F) Thermoplastic polyamides: Introduced in 1982, these materials contain amide(nylon) and ester linkages. This is the most expensive and highest performance group of TPE. As expected, these

materials are also susceptible to hydrolytic degradation.

Commercially available TPE cover essentially the entire rubber hardness range (30-90 Shore A). Many classes of TPE, such as EAs (Figure 2.7) also extend into the range of soft plastics (90 shore A to 75 Shore D).

2.4.2 Processing and economics of TPE

TPE clearly excel over conventional thermoset rubbers in their capability of being processed more rapidly, efficiently, and economically. Table 2.4 shows an actual cost estimation for injection molding of automotive vacuum connectors versus compression molding of these connectors from thermoset EPDM rubber. Even though the raw material cost is substantially lower for EPDM, the faster cycle time and recyclability of TPE scrap generate nearly a 50 % cost reduction in these parts. In addition to these advantages, TPE scrap can be recycled as regrind. When blended with virgin material, 100 % of clean regrind can be used. For example, Figure 2.8 shows the properties retention of an EA after five regrind cycles. Generally, longer drying times will be necessary prior to remolding.

However, TPE have also some disadvantages such as higher compression set, loss of elasticity compare to conventional thermoset rubber. Consequently, there are needs for researchs and developments so as to improve the properties of TPE.

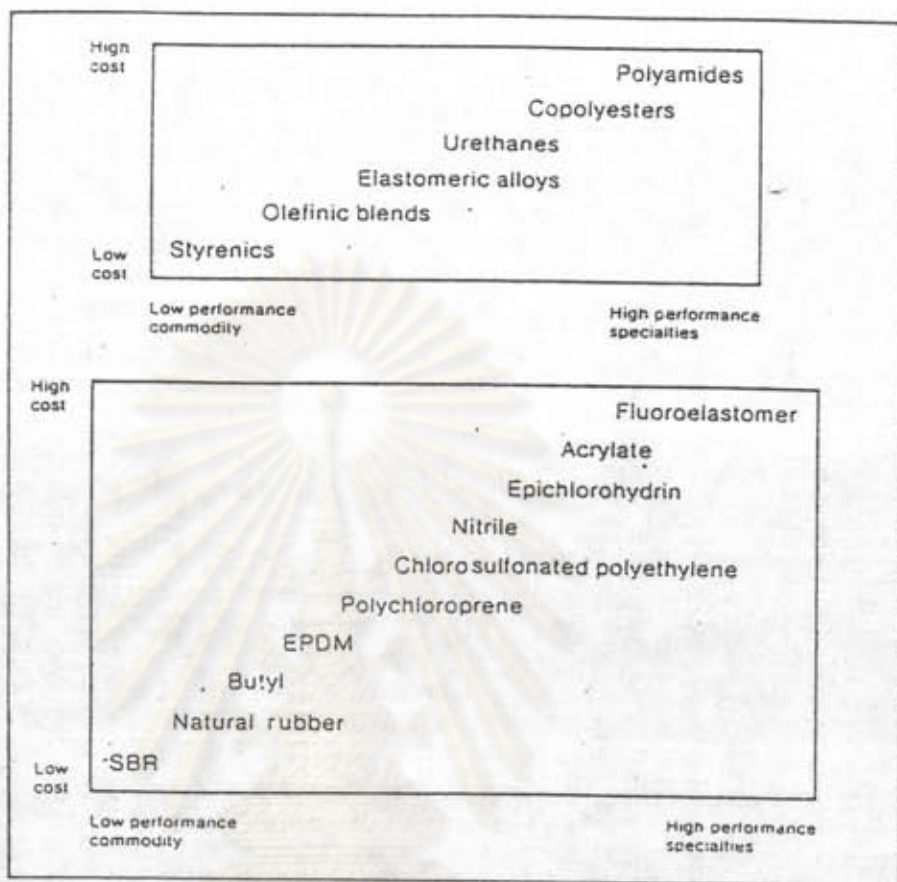


Figure 2.6 Cost/performance of TPE and thermoset rubbers.

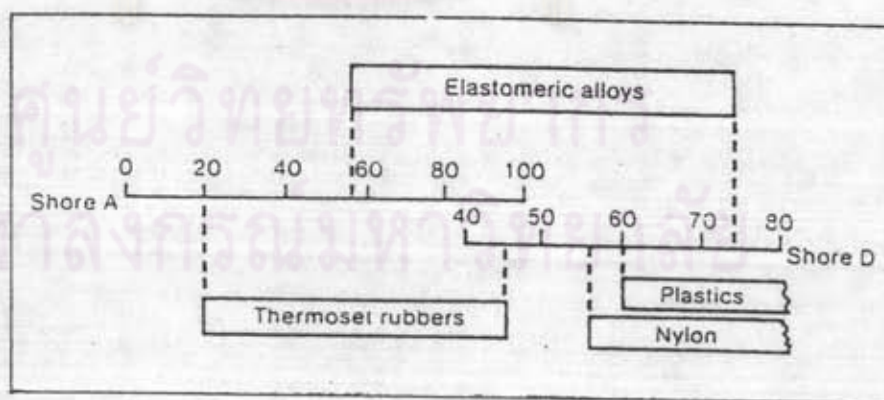


Figure 2.7 Hardness ranges of elastomeric alloys.

Table 2.3 Key properties of thermoplastic elastomers

Property	Styrenic	Poly-olefinic	Elastomeric alloys		Poly-urethane	Copoly-ester	Poly-amide
			2-Phase	MPRs			
Specific gravity*	0.90-1.1	0.89-1.00	0.94-1.0	1.2-1.3	1.1-1.3	1.1-1.3	1.0-1.2
Shore hardness	30A-75D	60A-75D	55A-50D	55A-80A	60A-55D	40-72D	75A-60D
Low temp. limit	-70°C	-60°C	-60°C	-40°C	-50°C	-65°C	-40°C
High temp. limit (continuous)	100°C	120°C	135°C	125°C	120°C	125°C	170°C
Compression set resistance at 100°C	P	P	G/E	F	F/G	F	F/G
Resistance to hydrocarbon fluids	P	P	F/E	G/E	F/E	G/E	G/E
Resistance to aqueous fluids	G/E	G/E	G/E	F/G	F/G	P/G	F/G

P = Poor, F = Fair, G = Good, E = Excellent.

*Does not include grades to which a special flame-retardant package has been added. This package generally raises the specific gravity 20% to 30%.

Table 2.4 Cost estimates for injection molding of vacuum connector automotive parts

	Thermoset rubber (EPDM)	Thermoplastic elastomeric alloy
Tool size, number of cavities	120	16
Tooling cost, dollars	12,400	13,000
Manufacturing capacity, parts/day	7800	19,200
Piece price, dollars	0.085	0.045

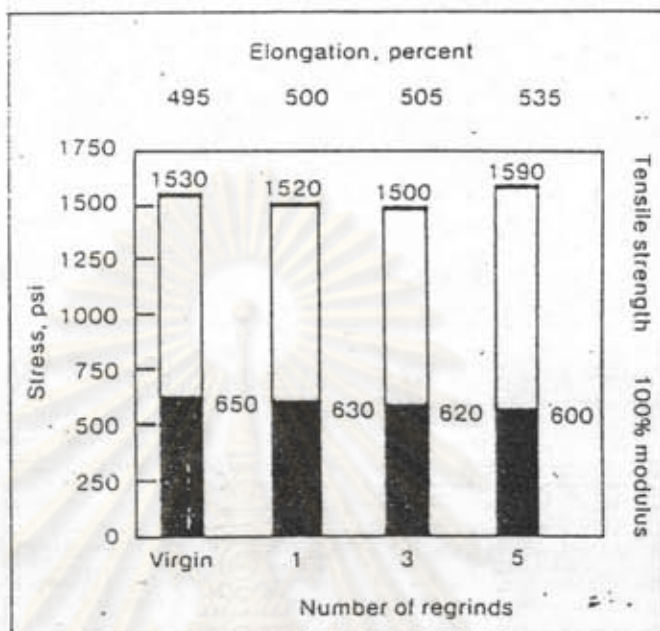


Figure 2.8 Repeated recycling of two-phase elastomeric alloy results in no significant loss of properties.

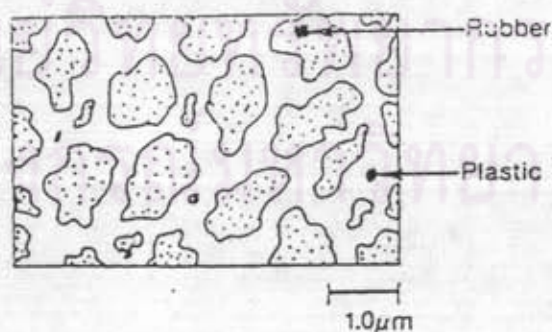


Figure 2.9 Morphology of thermoplastic vulcanizate.

2.4.3 Elastomeric alloy thermoplastic vulcanizates(EA-TPVs)

Charles P. Rader(at Monsanto Chemical Company) described that EA-TPVs are a category of TPE made of a rubber/plastic polymer mixture in which the rubber phase is highly vulcanized. They are demonstrably different from polymer blends TPE, which have a rubber phase that is either unvulcanized(no crosslinking of polymer chains) or only partially vulcanized. EA-TPVs (abbreviated as TPVs) are commonly described as "completely cured", "crosslinked", and so on.

The plastic phase of a TPV is commonly a polyolefin (especially polypropylene), and the rubber phase is often an ethylene-propylene elastomer or a nitrile rubber. The vulcanization of the rubber phase of TPV results in numerous property improvements. Essentially insoluble in ordinary rubber solvents, the TPV is swelled by these solvents to a much smaller extent than a comparable unvulcanized rubber/plastic blends.

2.4.4 Dynamic vulcanization

The preferred process for generating thermoplastic vulcanizates is dynamic vulcanization, a process that is not well known in spite of having existed for a quarter of a century. Pioneered by Gessler and Fischer, dynamic vulcanization has been extensively explored and practiced by Coran and Patel and their numerous coworkers at Monsanto Company.

Static vulcanization used commercially since the days of Charles Goodyear involves the heating of a rubber stock(fully

compounded) and mixed with a cure system (at a temperature 130-180°C for a specified time) during which chemical crosslinks are formed between the macromolecules of the elastomer (natural rubber, nitrile rubber, etc.). This process transforms the rubber into a tough, elastic, durable thermoset material.

Dynamic vulcanization, on the other hand, embraces the curing of a rubber composition during its mixing or mastication and one of the ingredients of this rubber composition must be a thermoplastic resin. It is important that the mixing be continuous during the masticating step, or a thermoset material result. The temperature reached during the mixing must be sufficient high to melt thermoplastic resin and affect the chemistry of the crosslink reaction. Good dispersion is generally favored if the viscosities of the rubber and plastic phases are comparable.

Commercial thermoplastic elastomers are based on either block copolymers or blends of a thermoplastic with an elastomer. By far the most important TPE blends are based on polyolefin (especially polypropylene) with either EPDM (ethylene propylene diene terpolymer) or a diene rubber. Elastomeric alloy TPV differ from simple elastomer blends TPE in the degree of vulcanization of the rubber phase. The high degree of vulcanization of a TPV produces a number of improvements in material properties.

The introduction of Monsanto's Santoprene thermoplastic rubber (in 1981) is a TPV in which the plastic phase is polypropylene and the rubber phase is EPDM rubber. It consists primarily of a fine dispersion of highly vulcanized EPDM rubber in a matrix of

polypropylene as the continuous phase. Figure 2.9 depicts the morphology of this TPV. The particles of vulcanized EPDM are distributed uniformly throughout the polypropylene matrix. The importance of crosslink density to improved properties is illustrated in Figure 2.10, which gives the variation of tensile strength and tension set (plastic deformation under tensile stress). A commercial TPV has a crosslink density on the right side of these plots.

Of equal importance to the improved properties of a TPV is the size of the particles of vulcanized EPDM. As the particle size decreases, the properties progressively improve such as tensile strength and ultimate strength. Although dynamic vulcanization is the preferred method for preparing TPV, it is possible to prepare these materials by grinding a cured thermoset rubber to a fine particle size and dispersing this powder in the thermoplastic.

The EPDM and polypropylene in Santoprene rubber are adequately miscible (nearly equivalent solubility parameters) to give a rubber dispersion sufficiently fine to provide desired material properties. Attainment of this morphology with less thermodynamically compatible rubber/plastic systems (such as the nitrile rubber/polypropylene system) requires the use of a compatibilizer. The action of a compatibilizer, is analogous to that of a surfactant. The compatibilizer may be a block copolymer with the more polar block associating with the more polar polymer of the rubber/plastic system and the less polar block associating with the less polar polymer. Compatibilization is often assisted by each of the blocks being chemically bonded to their respective

polymer phases.

2.4.5 PVC/nitrile rubber blends [6]

There are three principal ways of preparing blends with toughness or high impact resistance. The original method involved blending by mechanical techniques (the first method). Blends of poly(vinyl chloride) with nitrile rubber are presently manufactured by a variation of this technique. The second method is a solution-graft copolymer, in which the elastomer component is first dissolved in the styrene monomer and then the latter is polymerized with agitation. The last method is emulsion polymerization such as polymerization of ABS (acrylonitrile-butadiene-styrene) polymers.

PVC blends with nitrile rubber is the mechanical blends. PVC homopolymer is a stiff, rather brittle plastic with a glass temperature of about 80°C. So it is still important to blend PVC with elastomer system to improve toughness such as MBS (methacrylate-butadiene styrene) elastomers can impart impact resistance and also optical clarity.

The PVC and nitrile rubber blends are the mixture of elastomeric with plastic resins or plastic compounds is based on PVC as the plastic component, and random copolymer of butadiene and acrylonitrile as the elastomer component (Matsuo, 1968). On incorporation of this elastomeric phase, PVC is ordinarily stiff and brittle plastic which can be toughened greatly. A nonpolar homopolymer rubber such as polybutadiene is incompatible with the polar PVC. Indeed, electron microscopy shows well defined two phase

systems for simple blends of PVC with polybutadiene. However, the introduction of a small amount of acrylonitrile as a comonomer in the polybutadiene component results in the more polar, and more compatible with PVC. As shown dramatically by Matsuo(1968), the addition of 20% AN to polybutadiene (NBR-20) causes the phase boundaries to become less distinct and indicate more compatibility. Addition of AN to a level of 40%(NBR-40) destroys the phase boundaries entirely, resulting in the microheterogeneous system (illustrated in Figure 2.11, Figure 2.12, Figure 2.13 respectively).

2.4.6 Reinforcement in elastomer

Reinforced elastomers are one of the oldest and most important classes of composite materials (Ruffell, 1952; Sellers and Toonder, 1965; Stern, 1968). When the automobile first became popular, the need to toughen tire rubber, especially against abrasion, became obvious. Although zinc oxide had already attained widespread use as a rubber colorant, in 1905, Ditmar realized the true importance of this material as a reinforcing agent for rubber. Many industry experts can still remember when tires had white treads. However, the tire treads usually lasted less than 5000 miles, and the need for further improvements was necessary. In 1904, Mote had already discovered the reinforcing value of very fine carbon blacks. Carbon black proved much superior to zinc oxide for rubber reinforcement, and replaced the latter in tires between 1910 and 1915. At first, only small amounts of carbon black were used. At the present time, this has increased to 50 % or more, and tire treads lasting up to 40,000 miles are now common.

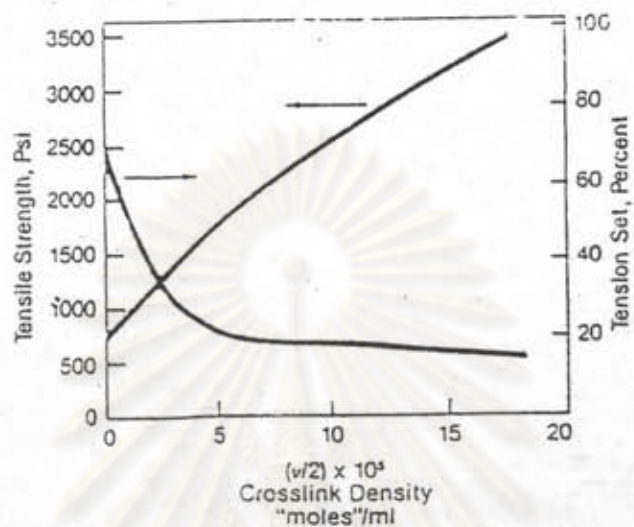


Figure 2.10 Effect of crosslink density on tensile strength and tensile set of elastomeric alloy - TPV.

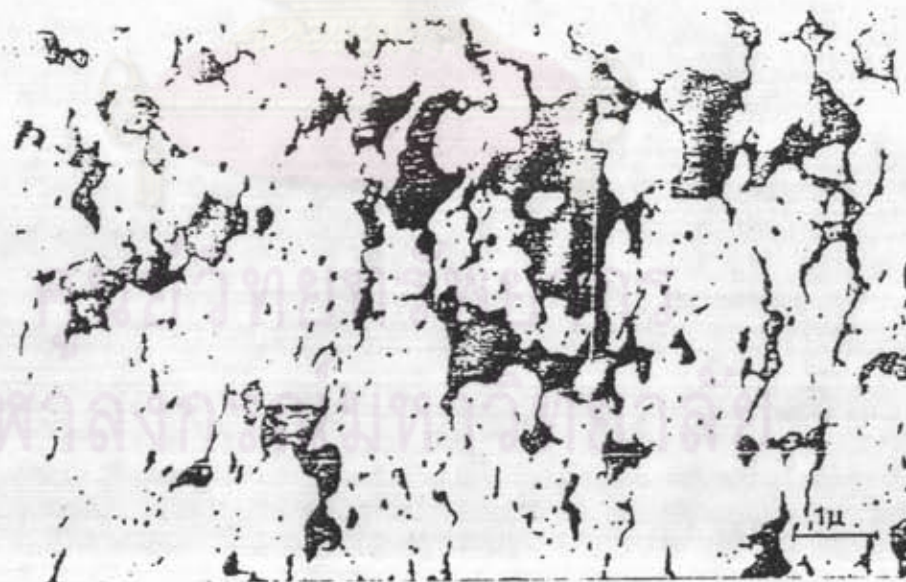


Figure 2.11 Electron micrograph of ultrathin section of a PVC/PB blend(100/15), rubber particles(dark areas) dispersed in the PVC matrix.

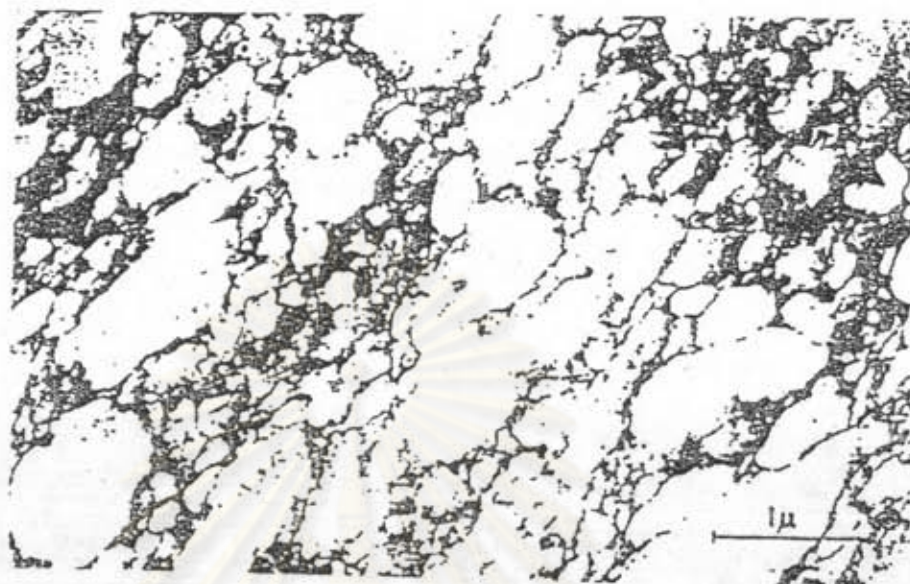


Figure 2.12 Electron micrograph of ultrathin section of a PVC/NBR blends (20 % acrylonitrile content)

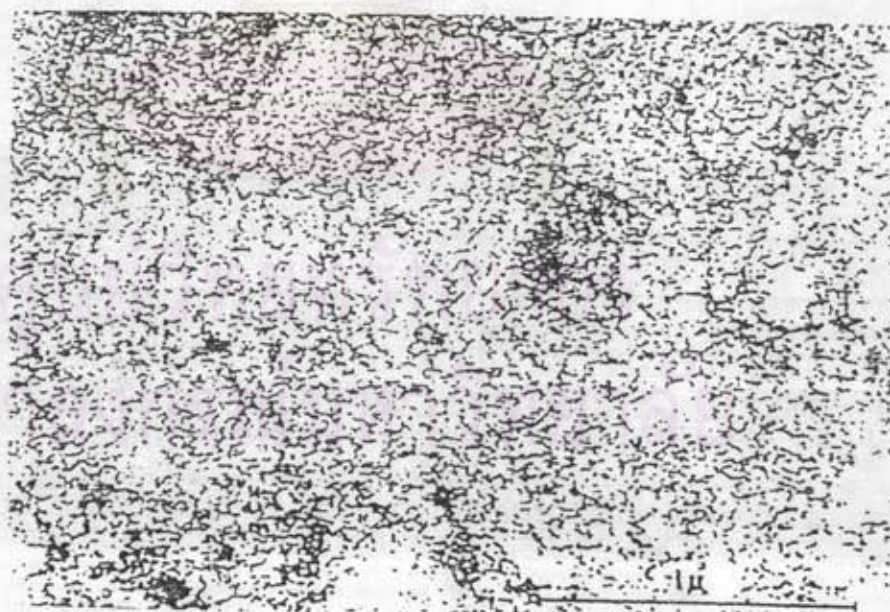


Figure 2.13 Electron micrograph of ultrathin section of a PVC/NBR blends (40% acrylonitrile content)

In the period between 1939-1949, several types of silica were introduced as rubber reinforcing agents. Finely divided silicas give degrees of reinforcement approaching those of the carbon blacks, and have found widespread use in rubber shoe heels and soles, in food packaging, and in many other applications where carbon blacks are objectionable.

The reinforcing effect of carbon black on stress-strain behavior of natural rubber is depicted in Figure 2.14. The reinforced material has a higher modulus (is stiffer) and is less extensible.

About the present use of zinc oxide in rubber manufacture. The discovery early in this century that many organic vulcanization accelerators are not effective without zinc oxide led to continued usage of this material for purposes other than reinforcement. By far the major use of zinc oxide in the rubber industry today is for activation of organic accelerators, and not for reinforcement.

Types of fillers

Carbon exists in two crystalline forms[7], and numerous so-called amorphous, less ordered forms as illustrated in Figure 2.15. The crystalline forms are diamond and graphite, and the less ordered forms are mainly cokes and chars.

All forms of industrial carbons other than diamond and graphite, including carbon black, can be classified as amorphous carbons characterized by degenerating or imperfect graphitic structures. Table 2.5 lists some of the basic structural and

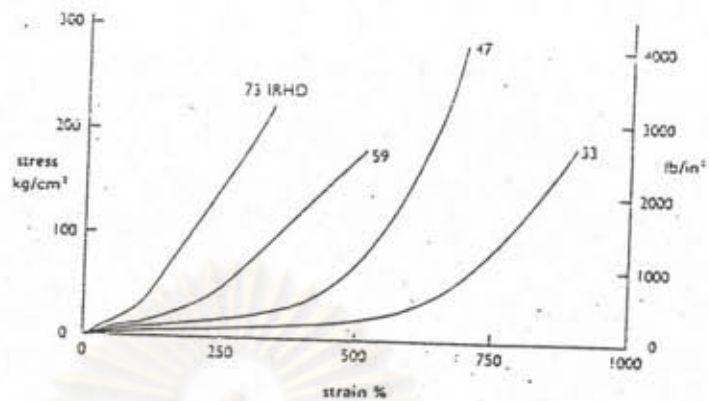


Figure 2.14 Tensile stress-strain curves for four natural rubber compounds of different hardnesses: 73 IRHD contains 50 parts of a reinforcing black.

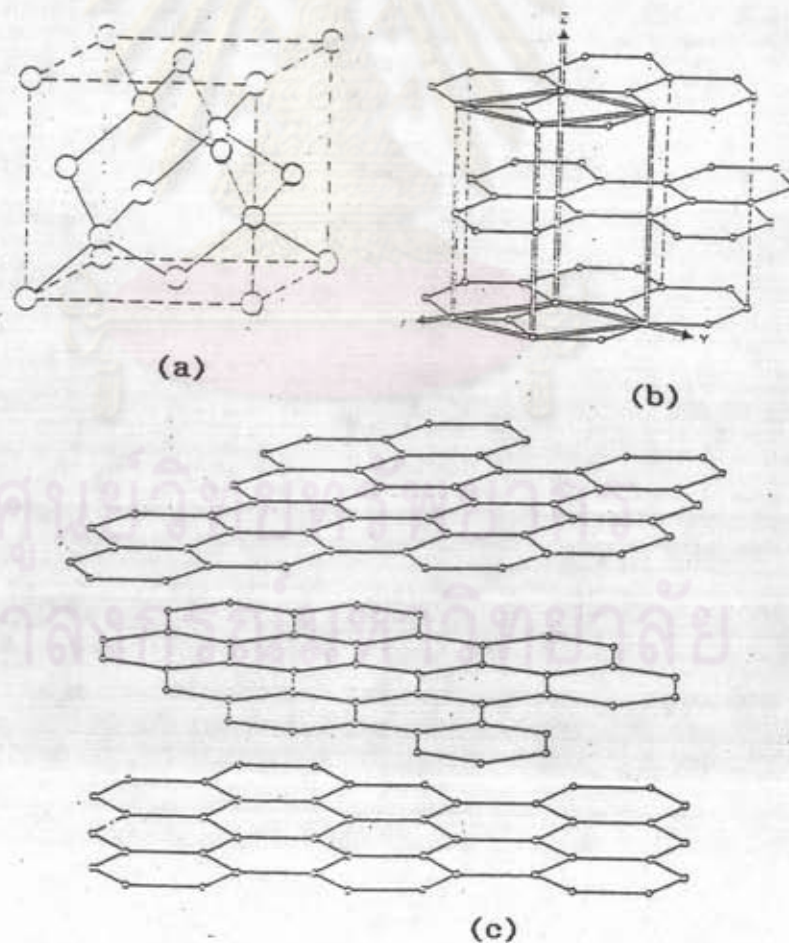


Figure 2.15 Crystallographic arrangement of carbon atoms in:
a) diamond b) graphite c) carbon black

crystalline properties of the carbons.

Table 2.5 Forms of carbon and characteristics.

Form	Crystal system	Sp.Gr.	C - C diameter (nm)	Layer distance (nm)
diamond	cubical	3.52	0.155	
graphite	hexagonal	2.27	0.142	0.335
carbon black	hexagonal- turbostatic	1.86-2.04	0.142	0.365

Carbon blacks[8] are prepared by incomplete combustion of hydrocarbon or by thermal cracking. Thus, there are several processes for producing carbon blacks such as oil furnace process, thermal decomposition process, channel black process, etc.

The American Society of Testing Materials has established a carbon black classification system based essentially on particle size and degree of surface oxidation (the factor that primarily affects the curing time of rubber carbon black compounds) with the intention of replacing an earlier letter type nomenclature. The N series comprises "normal-curing" furnace and thermal blacks. the S series "slow-curing" channel blacks and deliberately oxidized furnace blacks. A three-digit suffix identifies particle size as shown in the accompanying tabulation. Different ASTM numbers inside each

category identify blacks by other characteristics, mainly "structure". For example, the designation N-220 immediately identifies a carbon black as normal curing with particle size in the 20-25 nm size range, but additional specifications are needed to distinguish it from N-234 as shown in Table 2.6.

Table 2.6 The classification of carbon black filler.

Range of ASTM numbers	Nominal number average particle diameter(nm.)	Old classification
900-999	201-500	MT
800-899	101-200	FT
700-799	61-100	SRF
600-699	49-60	GPF, HMF
500-599	40-48	FEF
400-499	31-39	FF
300-399	26-30	HAF, EPC
200-299	20-25	ISAF
100-199	11-19	SAF

With respect to silica systems[6], the four major types are based on the so-called pyrogenic(PP), thermal(TP), and wet(WP) process as well as on the natural product(N). A second set of symbols represents the degree of reinforcement: low reinforcing(LR), medium reinforcing(MR), high reinforcing(HR), super reinforcing(SR), and extremely reinforcing(ER).

For example, the commercial product "Aerosil" would be classified as PP-SiO₂-ER. A selective list of commercial reinforcing silicas is given in Table 2.7, together with specific surface area measurements.

There appears to be only the most general correlation between surface area and reinforcement in silicas, provided the area is above 50 m²/g.

Table 2.7
Silica Surface Areas

Trade name	Surface area, m ² /g
Purosil UR	180 ± 20
Purosil URL	150 ± 20
Aerosil	175
Cab-O-Sil M-5	200
HiSil 233	150
Silene D	40

Size and surface characteristics of elastomer reinforces

Filler size dimensions are usually given in terms of surface area per gram because the first widely used modern technique for measuring small particles was the BET nitrogen adsorption method. Significant elastomer reinforcement begins when particles have greater than 50 m²/g of surface area. Assuming simple spheres,

this corresponds to particles approximately 500\AA in diameter, which is the same order of magnitude as the distance between crosslink sites in the matrix elastomer, as illustrates in Figure 2.16. Apparently, when the particles become larger than the average end-to-end distance between crosslinks, reinforcement declines due to rubber and particle adhesion failure when the attached chains become highly extended during deformation.

A great deal of attention has been paid to reactive sites on the filler and types of bonds formed. Although most investigators think that good bonding is essential to reinforcement, two major ideas of thought have appeared (Kraus, 1965). The first idea hold that primary chemical bonds are essential to reinforcement, while the second idea holds that secondary physical forces are sufficient. However, There are some persons (Peterson and Kwei, 1961; Rowland et al., 1965) discovered that the low strength physical forces to attach chains to filler surfaces quite firmly.

Morphology and microstructure of carbon blacks

Electron micrographs of furnace blacks, for example, as shown in Figure 2.17. Heat treatment causes a marked improvement in layer alignment and orientation, attaining the highly ordered capsular structure of graphitized black shown in Figure 2.18. Surprisingly, while the relatively disordered structure of Figure 2.17 yields a highly reinforcing black, the structure illustrated in Figure 2.18 is essentially nonreinforcing.

Aggregation and agglomeration

Up to this point the surface chemistry and size of the primary filler particles have been examined. However, important evidence exists that these particles are not randomly distributed throughout the elastomeric matrix. Indeed, much evidence shows that a complex state of aggregation is important for reinforcement in both carbon black and silica fillers. Two levels of structure have been identified in reinforcing fillers beyond the primary particles: aggregates of primary particles, which are bonded together rather strongly, and weakly bonded collections of these aggregates, which are sometimes called agglomerates.

Structure in carbon blacks

Many types of carbon black exhibit a characteristic chainlike structure, aggregation, as shown in Figure 2.19 and Figure 2.20 (Kraus, 1971; Medalia, 1970; Sambrook, 1970, 1971). These structures are carried over into the rubber compound (Sweitzer, 1961). Carbon blacks exhibiting a high degree of chainlike aggregation produce high degrees of shear during mixing, which aids in proper dispersion. This type of aggregation also results in higher modulus and abrasion resistance. The optimum degree of aggregation depends on the chemical nature of the elastomer, butyl compounds requiring less structure than styrene-butadiene rubber (SBR) (Ford et al., 1963)

Dispersion of carbon black within the elastomer

Dispersed within the rubber as a reinforcing filler, carbon



Figure 2.16 Filler particle size in relation to crosslink density.

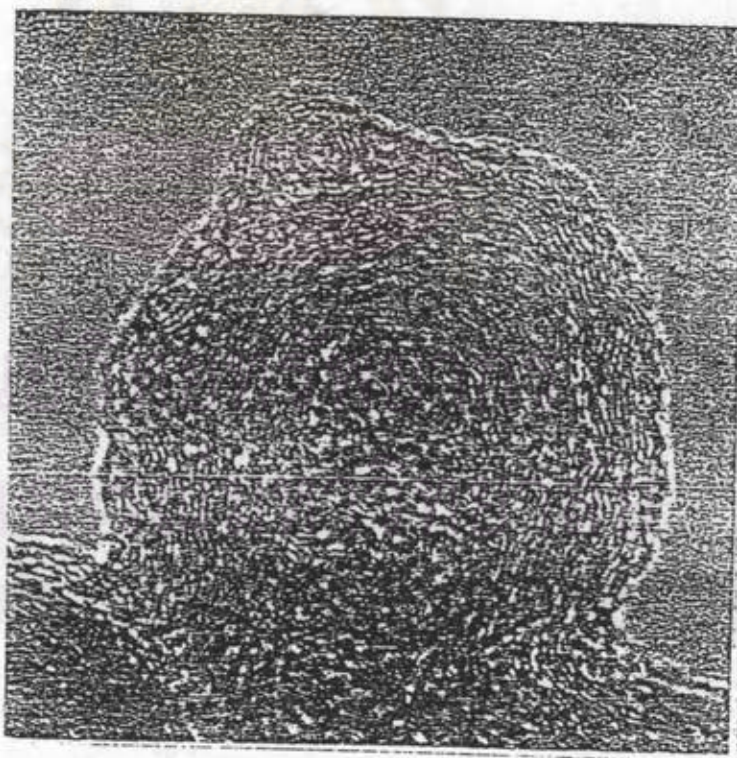


Figure 2.17 High-resolution electron micrograph of a furnace black particle which received no heat treatment. (Rivin, 1971)



Figure 2.18 High-resolution electron micrograph after extensive heat treatment (2700°C), the graphitized furnace black shows improved layer alignment

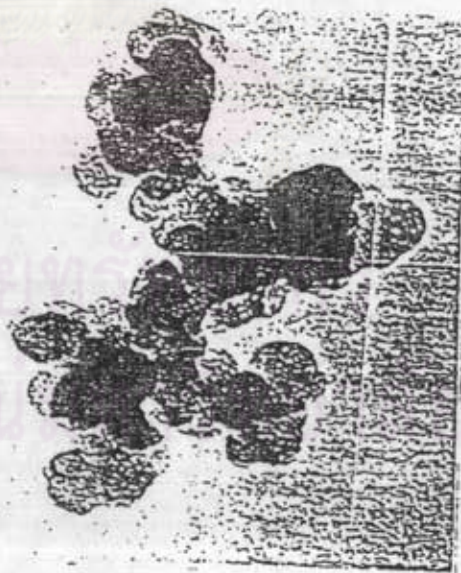


Figure 2.19 HAF carbon black exhibits a high degree of aggregation as seen by electron microscopy.

black retains much of the aggregation displayed by the pure phase. In addition, a more complex state of agglomeration develops within the rubber, as shown in Figure 2.21. These structures often appear like elongated strings or chains of interconnected carbon black particles. In a review paper, Kraus pointed out that secondary aggregation (agglomeration) is responsible for the large increase in the modulus of filled elastomers at low strains. The breakdown in agglomeration at high strains substantially reduces the modulus, usually permanently.

The high reinforcement results not only from the aggregation of the filler particles (structure), but also from the filler particle size which must be the same size or smaller than the chain end-to-end distance for maximum reinforcement. The close interlocking of filler aggregate and polymer network, both structures having similar dimensions, allows for maximum reinforcement.

Bound rubber

The phenomenon of bound rubber has played a crucial role in the chemistry of elastomer reinforcement. Very simply, if vulcanized rubber is masterbatched with a reinforcing filler, a certain fraction of the rubber is found to become insoluble, and to remain as a gel. This gel, a swollen mass of rubber and dispersed carbon particles, is called bound rubber. The percentage of bound rubber depends, of course, on the quantity of filler employed[6], and also on mixing conditions and choice of solvent (typically benzene).

There are several reactions postulated as being important in

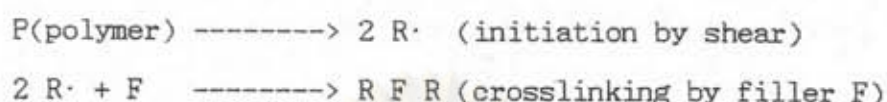


Figure 2.20 Three dimensional model of the particle shown in Figure 19, model constructed by Medalia and Sambrook(1970)



Figure 2.21 Electron micrograph of ALS-HAF in butyl vulcanizate.

bound rubber besides physical adsorption. For example, mastication under shear causes degradation of organic polymer molecules with the formation of free radicals (Casale and Porter, 1971; Watson, 1955):



The percentage of bound rubber increases with increasing unsaturation of the polymer.

Structure in silica fillers

The state of aggregation and agglomeration of reinforcing silicas also appears complex. In 1970, Galanti and Sperling reported on the agglomeration characteristics of several silicas milled into silicone elastomers under conditions approaching those employed industrially. Figure 2.22 shows the state of dispersion of HiSil in silicone elastomer as a function of filler level.

The smallest particles visible average $5\mu\text{m}$. in diameter, and appear roughly spherical. Some of these, in turn, appear clustered together further to form agglomerates of $20\text{-}30\mu\text{m}$. in diameter. It should be observed here that the actual size of the individual particles is 200\AA , as seen in the electron microscope. Thus this study strongly suggests that the three level structural organization previously observed by Vold (1963) may be carried over into elastomer dispersion. The three levels of dispersion are:

- (1) individual primary particles of about 200\AA diameter
- (2) aggregates of $5\mu\text{m}$. in diameter, and

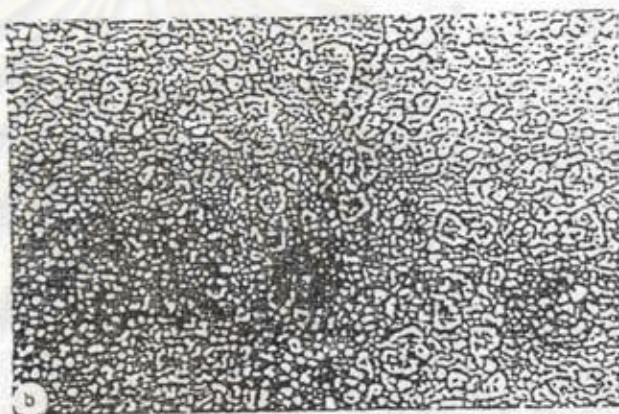


Figure 2.22 Silica filled silicone rubber at (a) 2.4 vol%;
(b) 7.5 vol %; (c) 15.5 vol %. Magnification 100 x

(3) agglomerates of 20-30 μm . in diameter

Scorching

The cure system must permit the stock to be processed in normal manner without premature vulcanization (scorch). Consequently, the scorch control is very important in rubber compounding. Carbon black promotes scorch, as illustrated dramatically in Table 2.8[8].

The high structure versions of these blacks are more scorchy in the factory than the regular structure blacks because they increase the viscosity of the batch more than the blacks of regular structure. Thus, while high structure blacks give improved dispersion, they also give rise to higher mixing and processing temperatures, and thus to earlier scorching.

Table 2.8 General scorchiness of sulfur-cured stocks containing various types of carbon black.

Type of black in increasing scorch tendency
Thermal blacks
Channel blacks
HAF blacks
ISAF blacks
SAF blacks

2.4.7 Fillers and reinforcements in thermoplastic

2.4.7.1 Calcium Carbonate: [9] The inert filler, calcium carbonate plays an important role in the search for a balance between a low price and the retention of physicomechanical values. High quality carbonate fillers are distinguished by the following properties:

- High chemical purity, no heavy metal ions that can catalyze the aging process in polymers.
- No tendency to form agglomerates
- High degree of whiteness, hence the processability of partial substitution of expensive white pigments.
- Increase in stiffness and modulus of elasticity.
- Reduced shrinkage, higher color fastness.
- Improvement in the surface of the article.
- Lower plate-out
- Increased impact strength, in particular through the use of coated grades.
- Non-toxic, odorless, heat-resistance up to 600°C.
- Modify rheological properties
- Low cost

2.4.7.2 Carbon black: [9] The filler for centuries has been used as a black pigment. Its use as a reinforcing filler did not commence until the start of this century. Carbon black is the most important reinforcing filler employed by the rubber industry. As regards their use in plastics, carbon blacks are classified according to their particle size and color intensity. Carbon blacks with

small particle size are usually more difficult to disperse than coarser types. Carbon black is frequently utilized as a protection against UV radiation and as a black pigment in thermoplastics.

2.4.7.3 Silica: [9] In all the manufacturing processes, synthetic silica is very fine and generally spherical primary particles, which as secondary particles form aggregates and agglomerates. Depending on the manufacturing process, the surface may be very large and attain value of 50 to 800 m^2/g . Silicas are likewise supplied with various silane coatings.

In contrast to silicas of natural origin, which as fillers are mainly used in the form of quartz flour, synthetic silicas can already be employed in low quantities to achieve specific effects. In thermoplastics, silicas perform the following functions:

- Reduction in shrinkage and crack formation.
- Reinforcement.
- Prevention of film blocking.
- Improvement in dimensional stability under heat.
- Reduction in the coefficient of linear thermal expansion.
- Improvement in electrical properties.
- Increase in hardness.
- Reduction of die swell during extrusion.
- Thickening, rheological and thixotropic effects.

2.5 Literature review

Blends of nitrile rubber and PVC were first evaluated by Konrad in 1937 and the properties of blends containing up to 50 % PVC were discussed in detail by Abrams[10] in 1962. Since then these blends have attracted much commercial and academic attention.

Matsuo, Nozaki and Jyo [11] described NBR-PVC blends as "semi-compatible" when NBR was used at 20 % acrylonitrile content and "almost homogeneous" at 40 %. Jordan and coworkers found that the softening temperature of PVC decreased and approached that of the rubber with increasing NBR content, which suggested compatibility. On the other hand, DSC analysis showed the T_g for both components in the blend, indicating incompatibility. This paradox was resolved by the hypothesis that DSC sees a smaller volume element than mechanical spectroscopy.

Woods, Morsek and Whittington[12] point out that tensile strength of PVC modified with crosslinked NBR is greater than that obtained when regular NBR is used.

J.R. Dunn[13] studied the heat and fuel resistance of NBR and NBR-PVC blends. He described that 70/30 NBR/PVC blend is required for good ozone resistance and such blends are used for fuel hose. The polar nature of PVC enhances the fuel and oil resistance of NBR but addition of PVC has a detrimental effect on low temperature flexibility.

Takashi Inoue and others[14] studied the structures of PVC/nitrile rubber blends cast from tetrahydrofuran solutions by X-ray diffraction, radiothermoluminescence, light scattering and DSC. No evidence was found for molecular miscibility in the blends. The two phase nature of the blends was maintained at the higher temperature up to 150°C. The spacial arrangement of the microphases in the PVC/nitrile rubber(26 %AN) blend is fairly regular in the range of 1.36 μ m.

K. E. George, Rani Joseph and D. Joseph Francis[15] studied the optimum temperature exists for the formation of a particular blend and shows that magnesium oxide, zinc oxide, and stearic acid was found to be useful in PVC/nitrile rubber blends. In addition, they investigated the using of natural rubber, styrene-butadiene rubber to replace part of the nitrile rubber in a 70/30 Nitrile rubber/PVC blend[16]. Such replacement up to 15 % of the total weight of the blend improved the mechanical properties, while decreasing the cost of the blend. Styrene-butadiene rubber could replace nitrile rubber up to 30 % of the total weight of the blend without deterioration in the mechanical properties.

Kushida et. al.[17] explained the previous works about PVC thermoplastic elastomers composition. Plasticized PVC have strong creep tendency and large compression set and thus are poor in the restorability when the compression force has been removed. In order to reduce the compression set for improvement, it has been attempted to use such a plasticized PVC in combination with a partially cross-linked NBR as a component to reduce the compression set of plasticized PVC. However, there will be a drawback that other

important properties such as tensile strength, elongation, and tear strength tend to deteriorate, although the compression set may be reduced to a level of about 40 %. The present inventors have conducted various studies to obtain a PVC thermoplastic elastomer composition having a low compression set and high strength while maintaining the desired properties as the thermoplastic elastomer. As a result, they have found it possible to obtain a thermoplastic elastomer having the compression set and breaking stress improved while maintaining the thermoplasticity by adding a usual curing agent for rubber to a system comprising PVC resin, a nitrile rubber, a plasticizer and filler by reacting the mixture under kneading.

P. Ramesh and S. K. De[18] studied melt mixed blends of PVC and carboxylated nitrile rubber are crosslinked during moulding at elevated temperatures in the absence of any crosslinking agent. Such a system of self-crosslinkable plastic/rubber blend is partially miscible as is evident from dynamic mechanical analysis. Such blends were found to have good oil resistance, high abrasion resistance, high modulus with moderate tensile and tear strength.

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