

CHAPTER II

THEORY AND LITERATURE SURVEYS

2.1. Rubber Modification of Plastics [1]

Efforts to reduce the resistance of amorphous, glassy polymers by an addition of particulate rubber date back to the 1940's and are still in progress. Commercial exploitation has outpaced the present understanding of the mechanism of impact enhancement. Earlier work was directed at modifying polystyrene but has since expanded to include most styrenic polymers; poly(methyl methacrylate); poly(phenylene oxide); cross-linked polymers of many types, for example, epoxies, acrylics and styrenated polyesters; and semicrystalline polymers with amorphous phase possessing low or high glass transition temperatures (T_g), for example, polypropylene, polyethylene, nylon, and poly(tetramethylene terephthalate).

In a sense, rubber modification competes with other chemical methods for achieving improved toughness, elongation to fracture, ductility or enhanced propensity to yield. These include the closely related block copolymerization, which also almost always yields a two-phase morphology but requires special synthesis procedure; random copolymerization with copolymers with a lower glass transition

temperature and miscibility with compatible liquid plasticizer or, in special cases, other polymers.

The various theories proposed thus far suggested that rubber toughening may be due to the following :-

- (a) Energy absorption by the rubber particles.
- (b) Energy absorption by yielding of the continuous phase; ductility enhanced by strain induced dilatation near the rubber occlusion.
- (c) Craze formation involving cavitation and polymer deformation within the craze.
- (d) Shear yielding as a source of energy absorption and crack termination.
- (e) Stress distribution.
- (f) Rubber particles acting as craze termination points and obstacles to crack propagation.

One of these proposed theories alone is considered inadequate to provide a total theory of rubber toughening. Moreover, the role of these elements are expected to vary with the polymer system and test conditions.

2.2. Rubbery Thermoplastic Blends [2]

Rubbery thermoplastic blends are thermoplastic material that are processable as a "melt" at elevated temperatures but exhibit properties similar to the vulcanized elastomer at the use temperature.

There are two basic types of rubbery thermoplastic blends namely the modified thermoplastic elastomers and the thermoplastic elastomers by polymer blending. The modified thermoplastic elastomers are blends of a compositionally homogeneous thermoplastic elastomer (TPE). The TPEs by polymer blending are polymer combinations that produce a rubbery thermoplastic from nonthermoplastic elastomer and plastic materials.

The distinction between thermoplastics as rubbery and nonrubbery is quite arbitrary. Three typical types of stress-strain properties for polymeric materials are illustrated in Fig 2.1. Polymer composites and blends have been developed such that they now encompass the complete spectrum of stress-strain properties from high-modulus materials for structural applications to crosslinked elastomers, which are low modulus and can be extended to several hundred percent and return to their original dimension on release of the applied stress. In general, however, materials are considered rubbery if they can be extended over 100% without failure and return to nearly their original dimensions in a short period of time. Modified thermoplastic elastomers and thermoelastic blends exhibit stress-strain characteristics that fall between the high modulus-yielding materials that undergo a high degree of plastic deformation, as shown by curve (b),

and the low modulus crosslinked elastomer, as shown by curve (c) in Fig 2.1.

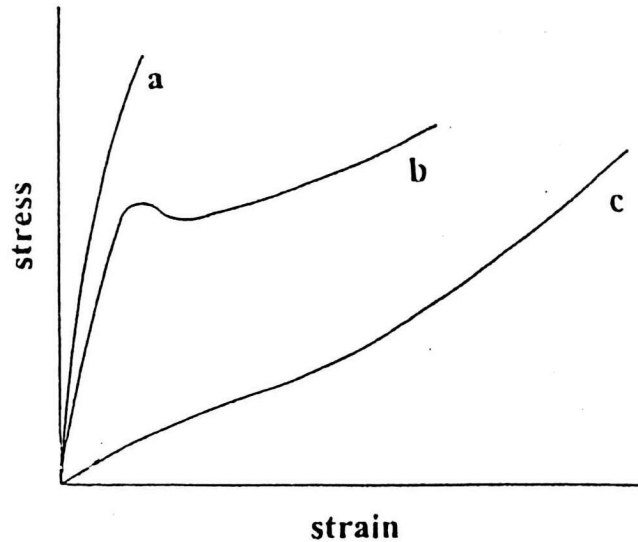
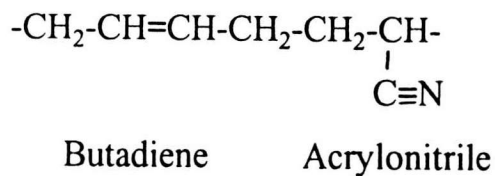


Fig 2.1: Three typical types of stress-strain curves for: a) high modulus polymer; b) high modulus polymer with yielding and poor recovery on return cycle and c) low modulus and rubbery polymer.

By the technique of polymer blends, physical properties can be altered to produce useful materials with a wide range of applications. Desirable properties can be achieved more easily in many instances by proper blend selection than by polymerization of a new polymer. This being the case, a major thrust of the technology on rubber thermoplastic blends is to provide materials which will meet specific applications as efficiently as possible. Moreover, certain rubbery thermoplastic blends possess a combination of physical and rheological properties that are unavailable in a single polymer.

2.3. Nitrile Butadiene Copolymer (NBR)

NBR is a copolymer which is prepared by copolymerization of acrylonitrile and butadiene. It was first produced in 1930 by E. Konrad and E. Tshunkur [3]. P. Stoecklin recognized the special technical advantage of NBR vulcanizates, which, unlike those from NR or SBR, does not swell in contact with gasoline, oils or fats. Full scale production of NBR commenced in 1934 in Germany, in 1939 in the U.S.A. (Goodrich), and thereafter in many other countries. A majority of NBR is 'cold rubber' although some 'hot NBR' is still being produced. A great number of NBR grades are produced, their acrylonitrile content ranges from 18 to 51% by weight. The chemical formular of NBR is as follows:



In 1985, the global production capacity of NBR was about 0.508 million tons, which represents roughly 4.0% of total SR capacity [4].

2.3.1. Production of NBR

There is a great similarity between the emulsion polymerization processes of butadiene with acrylonitrile and of butadiene with styrene and of the corresponding polymerization recipes [5], [6]. However, in the production of NBR, one has to take into account especially the different reactivity ratios of butadiene and acrylonitrile [7]. At 38% by weight acrylonitrile and 62% by weight of butadiene, there exists an azeotropic blend of the two monomers at 25°C, but the ratio changes somewhat depending on the polymerization temperature. For an azeotropic mixture, the relative concentrations of the components remain the same in the monomer phase of the emulsion and in the polymer throughout the whole polymerization process. If the acrylonitrile concentration in the monomer blend is less than the azeotropic concentration, the polymer will be rich in acrylonitrile at the start of the polymerization reaction, and similarly, if the acrylonitrile concentration in the monomer blend is above the azeotropic concentration, the polymer will have an acrylonitrile content below that of the relative acrylonitrile/butadiene ratio of the monomer charge. The difference between the concentration ratio of the monomers charge in the polymerization and in the polymer become greater, the further one deviates from the azeotropic concentration ratio for butadiene and acrylonitrile. In order to counteract this non-uniformity, the acrylonitrile is often added stepwise during the polymerization reaction this is known as an oligo increment production. Another difference between acrylonitrile and styrene is the greater water solubility of acrylonitrile, which of course, influences the NBR emulsion polymerization. There are many parameters that effect the production of NBR, resulting in a great variety of

commercially available grades. The viscosity of the rubber has an influence on the processibility. There is no difference in the solvent swell resistance and low temperature flexibility properties of vulcanizates from NBR's with different viscosities, as long as the nitrile content of the rubbers is the same.

NBR grades with extremely low viscosities or liquid NBRs can be used as compatible, non-volatile plasticizers in blends with other NBRs. During vulcanization, these plasticizers are then partially chemically bound to the rubber network, and therefore can not be easily extracted. The polymerization temperature not only has influence on the long chain branching, but also on the monomer sequence distribution, and the cis-1.4, trans-1.4, and 1.2 microstructure of the butadiene. For instance, a NBR polymerized at 28°C with 36% by weight of acrylonitrile in the polymer, has a butadiene component with randomly distributed microstructure of 12.4% cis-1.4, 77.6% trans-1.4, and 10% 1.2-trans. Due to the lack of compositional uniformity along polymer chains, it is not possible for NBR, nor for SBR, to form crystallines on extension. This lack of strain crystallization or lack of reinforcement results in relatively poor tensile properties of NBR gum vulcanizates. NBR grades produced at low polymerization temperatures or 'cold rubber' show less chain branching than the 'hot NBR' grade. Like viscosity, the polymerization temperature has also an influence on the processibility of the NBR's. The glass transition temperatures of polyacrylonitrile is +90°C while that of polybutadiene at -90°C. With an increasing amount of acrylonitrile in the polymer, the T_g of the NBR tends to rise, together with its brittleness temperature as shown in Fig 2.2. The elastic behaviour of NBR

vulcanizates also becomes poorer as the concentration of bound acrylonitrile in the NBR increases, but at the same time the copolymer becomes more thermoplastic, which is advantageous for the processibility of the compounds.

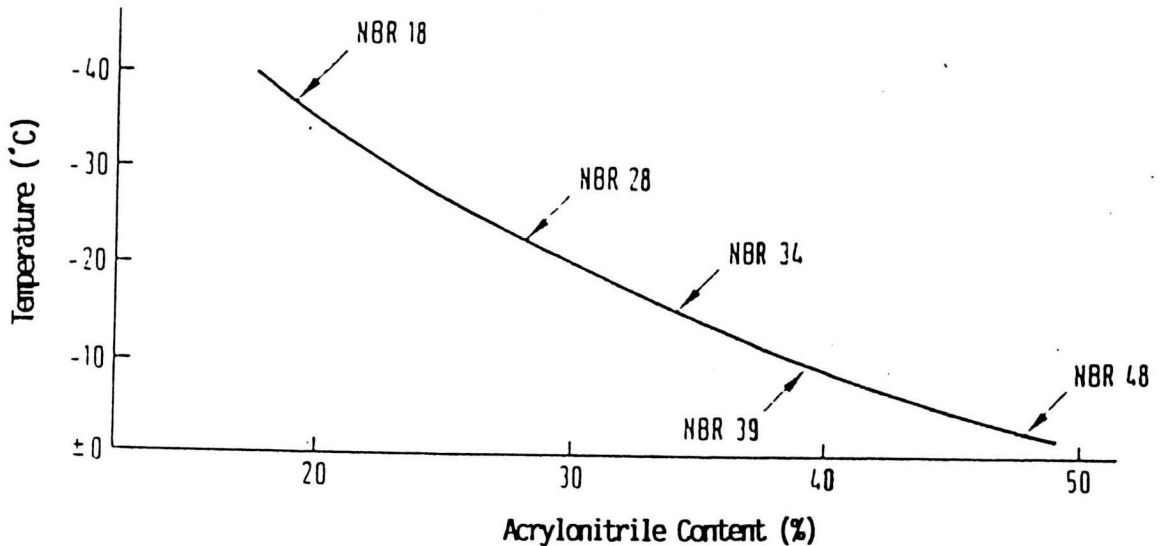


Fig 2.2: The influence of the acrylonitrile content on the glass transition temperature of NBR.

The polarities of acrylonitrile and butadiene are very different. The polarity of NBR becomes greater with increasing amount of acrylonitrile. The concentration of the acrylonitrile in the copolymer has therefore a considerable influence on the swell resistance of the vulcanizates in non-polar solvents. The greater the acrylonitrile content, the less the swell in the motor fuels, oils, fat, etc. However, the elasticity and the flexibility at low temperature also become poorer. For the same reason, the compatibility with polar plasticizers and polar plastic such as PVC improves with increasing acrylonitrile concentrations in the NBR. The

solubility of the polymers in non-polar solvent and the gas permeability of the vulcanizates become lower as the acrylonitrile concentration in the NBR becomes greater.

2.3.2. Thermoplastic NBR [8]

There have been many attempts to develop thermoplastic NBR's by various methods. Several investigators have attempted to achieve thermoplasticity through thermal or mechanical reversible crosslink structures. This, however, did not lead to commercial products. Another method is the blending of fully compounded NBR with polypropylene or polyamides, polystyrene or with PVC. The thermoplastic NBRs, which has recently emerged in the market.

2.4 Poly(Vinyl Chloride) (PVC) [9]

Vinyl chloride, the monomer from which PVC is made, was first synthesized in the laboratory of Justus von Liebig in 1835. One of his students, Victor Regnault, published a paper in 1839 detailing his observations of a white powder which formed in a sealed ampoule of vinyl chloride exposed to sunlight. The first report of an authentic vinyl halide polymer was published by Hoffmann in 1860 when he made polyvinyl bromide. PVC itself was synthesized by Baumann in 1872.

In 1912, Fritz Klatte discovered the basis for the technical production of PVC. Other chemists examined PVC and related polymers later in the century. Some even went so far as to patent them. However,

the earliest commercial production of PVC took place in the U.S.A. in the late 1920's, British production began in 1940s.

PVC has become the second largest commodity plastics after polyethylene. It is manufactured and traded worldwide. In 1991, the world production was in the region of 18 millions tonnes. Western Europe production was in the region of 5 million tonnes. In 1995, the world production of PVC has risen to about 25.5 million tonnes. Most of the growth concentrates in South America and Pacific rim. In Thailand, PVC production is ranked second among the commodity plastic. In 1995, the country's production of PVC is about 280,000 tonnes

2.4.1. Suspension Polymerization Process for PVC

With its boiling point at -13°C , VCM is a gas at ambient temperature but is handled as a liquid under pressure. VCM is relatively stable and shows little tendency to polymerize by itself. However, contamination with oxygen can give rise to vinyl chloride polyperoxide which decomposes and initiates polymerization of the VCM. Consequently, VCM manufacturers take steps to avoid contamination of oxygen, or if this is unavoidable, small quantities of stabilizer, usually phenol or phenol derivatives, can be added to prevent both peroxidation of the monomer and to inhibit polymerization. A very small quantity is normally sufficient to stabilize contaminated VCM against pre-polymerization and is sometimes used to prevent polymerization under long-term storage conditions. This stabilizer is not normally moved before the VCM is used in the

polymerization process. VCM is transported by pipeline from bulk storage or by road or rail tanker into the stock tanks on the PVC plant.

Since it is not economic to convert all the VCM charged to the polymerization vessel to PVC, VCM after polymerization process is always recovered from these vessels. This recovered VCM can be returned to the VCM plant for redistillation and blending with virgin VCM, or it can be used in subsequent polymerizations in which the recovered VCM is produced.

In the suspension polymerization process, VCM is dispersed as droplets in water in a suitably designed pressure vessel and polymerizes using free radical initiators until 80-90% of the VCM is converted to PVC. The residual VCM is then removed from the suspension of PVC in water by a process termed 'stripping'. The stripped slurry is dewatered using a centrifuge, dried and then stored as required. The outline of the process is shown diagrammatically in Fig 2.3.

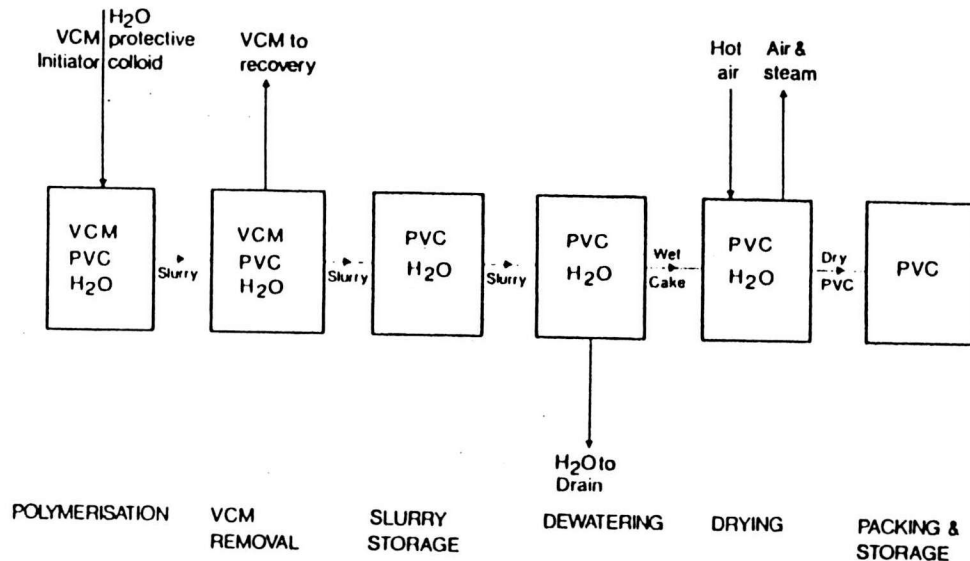


Fig 2.3: Suspension Polymerization of PVC.

In the typical suspension polymerization, a known quantity of water, normally demineralized water or water of a known high quality, is charged to a pressure vessel and other polymerization ingredients such as initiator, buffers and protective colloid are added. The autoclave is then sealed and evacuated. VCM is added either by metering, using a turbine meter, or by weighing using a suitable weighing vessel. A typical PVC formulation is shown in Table 2.1.

Table 2.1: Typical suspension polymerization recipe for a 10 m³ autoclave.

	Weight (kg)
Water	5000.0
Protective colloid	3.5
Buffer	0.7
Initiator	1.5
Vinyl Chloride	3500.0

Polymerize at 60 °C for up to 6 hours

The autoclave is heated up to the polymerization temperature using a mixture of steam and water in the autoclave jacket. Once the autoclave reaches the set temperature, polymerization starts and heat is evolved. The heat of polymerization of VCM liquid to PVC is -1,540 kJ/kg. This heat is removed by cooling water in the autoclave jacket. The autoclave pressure is steady at the autogeneous pressure of VCM from 6.3 bar for the polymerization temperature ranging at 40°C to 15 bar at 80°C until 75% conversion of VCM to PVC, when there is less free VCM phase remaining. The pressure then begins to fall as the equilibrium vapor pressure of the PVC/VCM phase falls as its PVC content rises. At a given pressure below the autogenous pressure, the polymerization is terminated, usually by venting off the excess VCM. Since the polymerization rate falls at high conversion, it is normally not economic to take the polymerization beyond

90%. Lower conversions are desirable for polymer quality reasons. Venting off the excess VCM reduces the polymerization rate markedly and effectively stops the polymerization. The remaining VCM is then stripped from the slurry either in the autoclave or in a separate stripping process. After discharge of the batch, the autoclave is cleaned to remove any polymer remaining in the autoclave. The autoclave is then ready for the next polymerization cycle.

2.4.1.1 Additive in Plasticized PVC

Poly(Vinyl Chloride)(PVC) is a hard and brittle polymeric material. It is easily degraded. Hence, PVC is never used alone. Generally, it is always mixed with other ingredients before being processed. Thus, the addition of additives to the PVC is very important. For plasticized PVC the additives often used are as follows:-

i) Plasticizers.

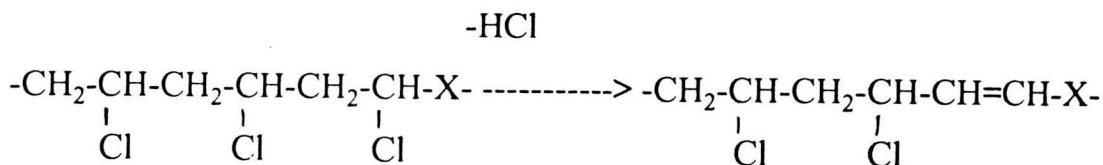
A plasticizer can effectively reduce the melt viscosity of PVC polymer. Plasticizers for PVC resin can be classified into several chemical classes such as phthalate, aliphatic diesters, organic phosphate and epoxides. Plasticizers that are highly compatible with the resin and do not exude to the surface of the product are called primary plasticizers. Those that are not highly compatible are called secondary plasticizers. Secondary plasticizers are commonly used in combination with the primary plasticizers to promote the compatibility between the polymer and the primary plasticizer. They can also act as heat stabilizer between the

polymer and the primary plasticizer. Epoxidized soya bean oil is an example of the secondary plasticizer generally used in PVC.

The interaction of the polymer and the plasticizer is an important parameter for determining the plasticized compound properties. The highly electronegative nature of the chlorine atom's strong dipoles along the polymer chain can lead to a high concentration of secondary valency forces, and therefore a reduction of chain flexibility. The simplest model of plasticization envisages the plasticizer molecules, which have polar or polarisable group, as bonding with the polymer dipoles. The result is a reduction the dipole between polymer chains and an increase in the freedom of molecular movement. However, lower levels of plasticizer can cause an increase in the stiffness or a phenomena known as 'anti-plasticization'. This is because the lower level of plasticizer can lead to an increase in the amount of crystallinity.

ii) Stabilizers

The degradation of PVC is an important problem in the processing of PVC. It is due initially to the loss of hydrogen chloride as shown in the following reaction:-



where X = Activating group

Elimination of the first molecule of hydrogen chloride and the subsequent formation of an unsaturated double bond on the PVC chain can activate the neighboring chlorine atom, and thus facilitates the subsequent elimination of another hydrogen chloride. So, stabilizers are necessary to prevent the degradation of PVC [10].

The ideal stabilizer for PVC should have functions as follows:-

- a) Absorption and neutralization of hydrogen chloride.
- b) Displacement of active, labile substituent groups, such as chlorine atom, attached to tertiary carbon, or an allylic chlorine.
- c) Neutralization or inactivation of stabilizer degradation products (e.g. heavy metal chlorides) which could function as degradation initiators.
- d) Chain reaction disruption, e.g. ability to disrupt progression of unsaturation.
- e) Neutralization or inactivation of resin impurities, contaminants, catalyst residue, etc.
- f) Provision of a shield, protection for ultraviolet radiation.

There are many types of stabilizers such as lead, barium cadmium, barium-cadmium zinc, barium-zinc and organotin stabilizer. Ba/Cd and Ba/Cd/Zn are general purpose stabilizers for plasticized PVC but they are not suitable for cable extrusion due to their inferior electrical properties. They exhibit synergism with phosphite chelators such as tris(nonyl phenyl)phosphite, and are often used with 3-5 phr of epoxidized vegetable oil as co-stabilizer. The ratio of barium to cadmium in a particular stabilizer is chosen to obtain the required balance between good initial

color and long term heat stability. The inclusion of a small amount of zinc can improve the initial color at the expense of long term heat stability.

iii) Filler

Most of the fillers used is calcium carbonate powder. Calcium carbonate can decrease some mechanical and processing properties. It decreases the mechanical properties such as tensile strength, elongation, and modulus but increases the electrical properties and opaqueness.

Calcium carbonate filler has high volume usage in the plastics industries. It is available in two crystalline forms, calcite and aragonite, Calcite is formed by crystallization of calcium carbonate at temperature below 30°C and occurs in lime-stone, marble, and chalk. Aragonite is obtained by crystallization at higher temperature. It may consist of a mixture of the two crystalline forms, calcite and aragonite. The calcite has a density of 2.71kg/m³ and a refractive index of 1.48 while those of the aragonite are 2.93 Kg/m³ and 1.53 respectively.

In PVC compound, calcium carbonate is generally used because it offers several advantages. Compared with other fillers, calcium carbonate is available at a much lower cost. It is non-toxic, non-irritating and odorless. It is white powder with low moisture content. PVC compounded with calcium carbonate can still be colored easily to any desirable shade. The calcium carbonate particles can be coated quite easily to improve the plastic melt rheology. As a soft filler, it is non-abrasive to machinery. Since it is an acid acceptor, it is capable of acting as a secondary stabilizer

to PVC to neutralizing chlorine ions. Calcium carbonate itself is quite stable over a wide range of temperature.

Aside from the above-mentioned advantages, calcium carbonate is available in a wide range of particle size. Calcium carbonate particle size distribution can be controlled to give optimal packing in each polymeric system. It can be mixed into formulation without difficulties; occasionally it also aids the mixing of other ingredients. Calcium carbonate has been known to reduce the shrinkage of the produced articles during processing. It also acts as a anti-plate-out agent, i.e. exerting a mild scouring action during processing. Due to its low stiffness, calcium carbonate can be used in higher volume when compared with other fillers.

However, calcium carbonate is a polar, reactive substance, having several disadvantages for plastic use. It is a salt that can be attacked by acids. The trigonal crystal shape of calcium carbonate provide little reinforce action. Therefore, a high level of calcium carbonate can lead to an increased stiffness and inferior mechanical properties such as tensile strength and elongation. The factors that appear to reduce the physical strength include particle shape, size and the lack of interaction at the filler and matrix interface.

2.4.2 Compounding of PVC

The compounding of PVC polymers is basically very simple. Apart from the polymer itself, the only essential ingredient is the stabilizer. Except for some rigid PVC compositions, it is normal and desirable to add

a plasticizer. To complete the trio of additives, a lubricant is often incorporated, usually for extrusion compounds.

Any compounding study must concentrate on an understanding of the four corners of PVC technology namely the polymer, plasticizer, stabilizer and lubricant. Subsidiary materials, added for special reasons, include mainly fillers, colorants, antistatic agent, UV light absorbers, blowing agent and extenders.

2.4.2.1 Compounding Technique for PVC

For processing PVC products, the first step is to select the resin suitable for the production, then one would select appropriate stabilizers, lubricants, colorants, filler, etc. At present there are a wide variety of PVC compounds for different applications available for the processors as shown in Table 2.2.

Table 2.2: The various applications of PVC.

Polymerization degree	Applications
2,500 - 3,000	Packaging products
1,300 - 1,700	Electrical wire
1,000 - 1,300	Film, sheet, synthetic leather, etc.
700 - 800	Pipe, bottle
400	Adhesive

2.5 Mixing of Polymers

The practical industrial chemist or engineer tends to define two polymers as 'compatible' or 'miscible' if, on mixing, they mix together sufficiently well that his particular purpose is satisfied. After blending together, polymer pairs may be qualitatively considered incompatibles, semi-compatible or compatible, depending on whether two distinct or immisible phases remain, partial mixing of two polymers take place at the molecular level, or a single thermodynamically stable phase is formed. True mutual solubility in a polymer mix is rare, due to the small entropy gain on mixing. Important guidelines in determining compatibility often involve, besides optical clarity, a single sharp glass-rubber transition.

2.5.1 Method of Mixing Polymer Pairs [11]

The principal methods of mixing two kinds of polymer molecules include mechanical blending, graft co-polymerization, block co-polymerization and interpenetration of two networks. The last two are often considered as sub groups of the graft method.

Polymer blends may be defined as intimate mixtures of two kinds of polymers, with no covalent bonds between them. Historically, the oldest and simplest method involves blending either on open rolls or through extruders that contain several percent of elastomer dispersed in plastic matrix.

In simple mechanical blends, the plastic component usually predominates, with the dispersed elastomer having dimensions of the order of several micrometers. The shear action of mechanical blending also generates free radicals through polymer degradation reaction.

The free radicals induced by the mechanical action subsequently react to form a small number of true chemical grafts between the two components. The quality and importance of such grafted material obviously depend on the exact mode of blending. Significant improvements in impact resistance and toughness are usually noted in such blends over the plain parent plastic, even in cases where no particular amount of grafting is noted. Several mixing processes are practised by plastics blending manufacturers.

2.5.1.1 Dry Blending Process

The initial random distribution mixing of plasticizer and all of the additives to the PVC resin is called the dry blending process. It is an important process for plasticizing PVC. The dry blend method is conducted by using a high speed mixer to mix the PVC with solid additives. The liquid additives are added when the temperature reaches 80°C and mixed until the temperature increases to 120°C. This is because PVC resin absorbs the plasticizer more effectively at this temperature. Then, the compound is cooled at a lower speed of mixing. Solid NBR should be added to the mixing during the cooling step in order to avoid plasticizer absorption and any crosslinking which can possibly occur at high temperature.

During the dry blending step, the solid additives which possess high melting points are not absorbed into PVC particles. Instead, they stay as a coating at the surface of PVC while the liquid plasticizer and stabilizer diffused into the PVC particle. Dry blending at high temperature will ensure the liquid additives have fully diffused into the PVC.

2.5.1.2 Melt Compounding

After the dry blending step, the compounds are dried to obtain free flowing powder which generally makes it easier to feed into subsequent steps of dispersive mixing or fabrication process. The dispersive mixing is obtained by compounding the plasticized PVC in a two-roll mill or an extruder.

A two roll mill consists of two opposite rotating parallel rollers moving at a specified speed in the opposite directions. There is a small gap that is adjustable between the rollers. The rollers are set at temperature around 140-170°C, depending on the composition. The PVC is fused by conductive heat and friction heat from shearing.

The main application of an extruder is in extrusion and pelletization of the PVC compound. The material flow depends on the friction against the barrel. The extruder consists of a screw that is divided into 4 sections, i.e. the conveying, mixing, kneading and venting sections. When the screw rotates, the material is forced between the screw and the barrel, resulting in an effective dispersing action due to shearing.

The gelation of the polymer and the development of the required properties in the extrudate depend critically on the properties, proportions, and interaction of the ingredients of the powder dryblend.

2.6 Literature Survey

Elastomeric copolymer of acrylonitrile and 1,3-butadiene (nitrile elastomer or NBR) have been mixed with PVC to achieve a number of purposes. Small amounts of nitrile elastomer in PVC can be used to improve the impact strength of rigid PVC compositions. Small amounts of PVC can be added to nitrile elastomers before vulcanization to improve the ozone resistance of the vulcanizates. Mixes of comparable amounts of nitrile elastomer and PVC can be used as thermoplastic elastomers or can be vulcanized to form thermoset elastomers.

The first use of a plasticizer in PVC is attributed to Fritz Klatte [12], [13] for the formation of semi-rigid sheets. The discovery that PVC could be converted to an elastomer by addition of a plasticizer was made more than ten years later in 1962 by Waldo Semon [12], [14], [15] while trying to dissolve the polymer. This discovery leads to the marketing of rubber plasticized PVC under the name Koroseal [16]. The plasticizers use were low molecular weight materials.

The first mention of the use of polymeric plasticizer in PVC in the form of nitrile elastomer was reported to have occurred in 1938 in trade literature from the Advance Solvents and Chemical Corporation [17], a distributor in the U.S. for nitrile elastomers manufactured in Germany by I. G. Farbenn Industries [18]. Badum [19] filed a patent application in Germany in 1937 and in the U.S. in 1938 on ozone resistance mixes of PVC and nitrile rubber containing 10-50% PVC. A composition of matter patent covering both vulcanized and unvulcanized mixes of 1,3-butadiene acrylonitrile copolymer with PVC was applied for in 1940 by D. E. Henderson [20] of Goodrich. The shortage of natural rubber which occurred during World War II stimulated research in the U.S. on the compounding and modification of plastics to form rubber-like material [21]. This work was persued after the end of World War II and resulted in the commercial marketing of NBR/PVC blends by Goodrich in 1947 under the name Geon Polyblend [22], [23]. These blends were initially prepared by mill mixing. The Polyblend products were furnished as light-yellow sheets which were soft, somewhat tacky and relatively weak. Prior to their end use, they had to be heat treated at some point in the processing

operation in order to develop their properties. At temperatures above about 150°C, the colloidal blends become homogeneous thermoplastic materials with good physical properties. An unvulcanized Polyblend having composition 45% NBR/55% PVC has a tensile strength of 13 MPa, an elongation at break of 430%, and a Shore A hardness equal to 93. Softer products were prepared by adding low molecular weight plasticizers. A latex version of Geon Polyblend was also available [24].

Also in 1947, Young and coworker [25] at Standard Oil Development Company reported on thermoplastic blends of nitrile elastomers, produced by Enjay, with 95% vinyl chloride/ 5% vinyl acetate copolymers, manufactured by the Bakelite Corporation. Further studies on blends of vinyl chloride/vinyl acetate copolymer with elastomers were published by Reed and Harding [26]. They evaluated 64 plasticizers, including two nitrile elastomers, in the vinyl chloride copolymer. The use of nitrile elastomers as a plasticizer resulted in blends with excellent resistance to swelling and to loss of plasticizer due to extraction or volatility. In a subsequent publication, Reed [27] stated that nitrile elastomers plasticized vinyl chloride polymers by solvation mechanism in the same manner as monomeric ester plasticizer. He pointed out that when powdered vinyl chloride polymer was added to nitrile elastomer and the batch was hot-milled, the blend became clear and behaved as a normal plasticized compound.

Factors affecting the processability and properties of NBR/PVC blends were addressed by Bolam [28]. For a nitrile elastomer to be an efficient PVC plasticizer, he felt it should possess a minimum of nerve.

This calls for nitrile elastomer having a low gel content and a low Mooney viscosity as discussed in a patent by Wheelock [29]. Others advocated an alternative approach claiming that nitrile elastomer having 50-75% contents of tight gel produce NBR/PVC blends with improved processing properties. In a talk on thermoplastic NBR/PVC compounds, Beekley [30] pointed out that difficulties in processing can arise from the long backdown periods required for the nitrile elastomer, causing excessive frictional heat build-up, leading to degraded PVC and excessively crosslinked nitrile elastomer. To reduce these processing problems, Goodyear introduced a low molecular weight PVC and an easy processing nitrile elastomer for the preparation of blends. The mechanical properties of mill-mixed blends of PVC with various amounts of nitrile elastomer containing 40% acrylonitrile were reported by Byl'ev and Voskresenski [31], Pedley [32] pointed out the advantages and availability of preblended, prefluxed, easy processing NBR/PVC blends and described the compounding, processing and applications of these materials. When powdered nitrile elastomers became available, they were combined with powdered PVC compounds to make possible the processing of NBR/PVC blends in powder form. The advantages of powder processing are discussed in several publications [33], [34], [35], [36], [37]. The use of precrosslinked and powdered nitrile elastomer is reported to be effective in reducing the elastic memory (nerve) of NBR/PVC blends [23], [24], [27].

The status of PVC thermoplastic elastomers in Japan was reviewed by Kawashima [38]. PVC thermoplastic elastomers have gained major interest in the Japanese market particularly in automotive applications. New types are being introduced with substantially improved properties.

Gel-containing PVC, prepared by polymerizing vinyl chloride in the presence of a polyfunctional monomer, has been mixed with partially crosslinked nitrile elastomer to form NBR/PVC compositions with substantially improved compression set, permanent set, resiliency and high temperature shape retention. Thermoplastic elastomers based on gel-containing PVC are being marketed by Sumitomo Bakelite K K.

Miscibility of PVC blends was first observed with NBR/PVC systems among PVC-related manufacturer, these blends probably have been the most widely studied system due to their significant commercial interest. They have been described as miscible, partially miscible and even heterogeneous, based on the different experimental techniques and copolymer compositions. Miscible blends are widely used as flexible compositions with the NBR acting as a permanent plasticizer. In order to discuss the miscibility of NBR/PVC blends, the system must be characterized. The methods of characterization vary in effectiveness depending on which composition between the NBR/PVC and the acrylonitrile contents in elastomer is involved.

NBR, of certain compositions, exhibits compatibility with PVC which is unusual among polymers [39-47]. In well-mixed blends of most polymer pairs, the presence of two phases had been reported as was evidenced by two glass transitions [40], [46], [48]. In contrast, blends of NBR and PVC have a single broad glass transition over a glass temperature range between the T_g 's of the unblended components [39], [41], [44], [45], [47].

The temperature dependence of the dynamic storage modulus (E') and the dynamic loss modulus (E'') for the PVC/PBD blend and the NBR/PVC system as a function of composition is shown in Fig 2.4 [45]. As is evidenced in Fig 2.4 (a), the T_g for the minor component, polybutadiene (PBD) in the PVC/PBD blend, is observed at temperatures in the region of -100°C .

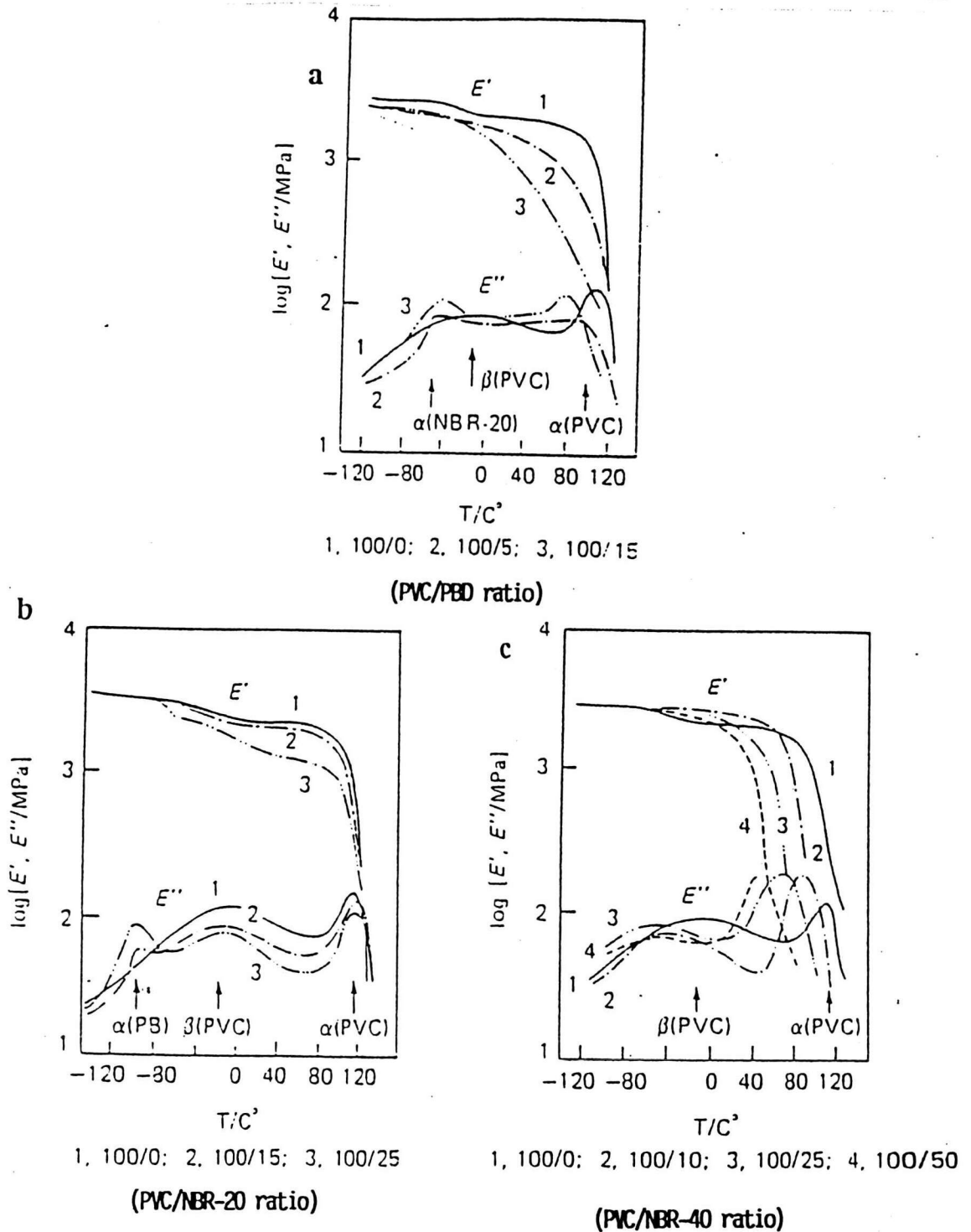


Fig 2.4: Temperature dependence of the dynamic modulus (E') and dynamic loss modulus (E'') for (a) PVC/PBD blend, (b) PVC/NBR-20 blend and (c) PVC/NBR-40 blend.

While only a slight decrease in the E' is observed in this glass transition temperature range, the E'' exhibits distinct peaks when PBD is present. At $+86^{\circ}\text{C}$ the continuous phase, PVC, undergoes its glass transition, resulting in a larger change in the E' as the material transforms from a rigid to a viscoelastic mass. E'' exhibits a separate loss peak. Similarly, in the blend of PVC and NBR-20, as seen in the Fig 2.2 (b), the presence of an E'' peak corresponding to the glass transition temperature of the blends of PVC/NBR-20 at -40°C is evident. However, its upper tail overlaps with that of the PVC in this semi-compatible system, the interaction between the two phases is marked. The value E'' does not exhibit two glass transition; instead the glass transition is broadened and shifted lower in temperature. The PVC/NBR-40 system shows a third distinct type of behaviour, somewhat reminiscent of that of the random copolymer compositions for the NBR-40 assumes a sharpness characteristic of homopolymers or random copolymers. It is clear from Fig 2.2 (b) and (c) that an increase in the AN content of NBR results in an increased compatibility with PVC.

Numerous studies [49], [50], [51] have been carried out on thermoplastic NBR/PVC blends for the purpose of answering two questions. The first question is whether the blend is one phase or multiphase. The second one is how the change of the acrylonitrile and the content of the elastomer component affects the properties of the blends. The answer to the first question appears to be that some blends contain only one phase while others are multiphase. The one phase blends have been found to contain regions of microheterogeneity in some instances.

An important factor controlling the number of phase present is the acrylonitrile content of the nitrile elastomer in the blend.

Rezenikova and coworkers [49], [50] studied the effects on the properties of thermoplastic NBR/PVC blends with varying acrylonitrile content of the nitrile elastomer and the amount of nitrile elastomer in the blends. Nitrile elastomers containing 12-50% of acrylonitrile were mill mixed with PVC over a range of 0-100% PVC. Nitrile elastomers containing 28% or less acrylonitrile had poor compatibility with PVC. Hence, they tend to give PVC compounds which were cloudy, weak and had poor elasticity. Lel'chuk and Sedlis [51] studied NBR/PVC blends prepared by latex blending followed by coagulation and then milling at 130-140°C. Nitrile elastomers containing 19-40% acrylonitrile were employed. The effects of varying the molecular weight from 40,000 to 390,000 of a 35% acrylonitrile elastomer were investigated. Nitrile elastomer containing 35-40% acrylonitrile with a low molecular weight gave the best processibility and properties. The compatibility of the NBR/PVC mixtures was studied by several methods [51], [52].

Dynamic mechanical test measurements have been a popular method of investigating the compatibility of NBR/PVC blends. In the NBR/PVC blends, Nielsen [53], Breuers [54] and coworkers found that a single maximum in damping occurs at a temperature between the corresponding temperatures of the pure components. They reasoned that the polymer were soluble in each other. Nielsen [55] concluded that the broad damping peak found for an NBR/PVC blend indicated that the two polymer were soluble in each other, but the intermolecular attraction is so weak that

considerable association of like segments is taking place in the soluble mixture. Nielsen also pointed out that in plasticized PVC crystallites act as crosslinks, preventing the rubbery material from flowing under a load even though it is not crosslinked by a chemical reaction as is vulcanized rubber. The presence of three-dimensional network structure in plasticized PVC in which the tie points are PVC crystallites were elucidated by Alfrey et al [56].

Takayanagi et al [57], [58], [59], [60] measured the dynamic viscoelastic behaviour of NBR/PVC blends prepared in solution and recovered by evaporation of the solvent. They concluded that even though the two polymers mix molecularly, there is some evidence of microheterogeneity due to the different segmental environments. Matsuo and coworkers [61], [62] examined mill-mixed blends of PVC with nitrile elastomers containing 8-40% acrylonitrile. The results of dynamic viscosity measurements were interpreted to indicate that 20% acrylonitrile elastomer gave two phase blends for PVC whereas 40% acrylonitrile elastomer gave almost homogeneous blends. Electron microscope pictures were interpreted to indicate that microheterogeneity existed even in the blends with the 40% acrylonitrile elastomer. Using differential thermal analysis, Oganosov and coworkers [63] investigated the homogeneity of mill-mixed blends of PVC with nitrile elastomer containing 40% acrylonitrile. They concluded that the blends can be single or two phase depending upon the polymer ratio. Feldman [64] and Rusu [65] examined the compatibility of PVC with nitrile elastomer containing 40% acrylonitrile by viscometric measurements of solutions in cyclohexane. They concluded that the polymers were compatible. Krause [66], in her

review of polymer compatibility, lists the combination of PVC and butadiene-acrylonitrile copolymer as compatible.

Using differential thermal analysis and dynamic mechanical measurement, Jorgensen and coworkers [67] demonstrated the presence of two glass transition temperatures in commercial non-crosslinked nitrile elastomers of less than 35% acrylonitrile content. The two glass transition temperatures were attributed to the presence of two separate phases of different acrylonitrile content. They concluded that for NBR/PVC blends containing 70% NBR, the PVC acts as selective solvent for only that portion of the NBR which is highest in acrylonitrile content. Zerkzewski [68] used phase contrast microscopy, differential scanning calorimeter and torsion pendulum analysis to examine the compatibility of mill-mixed NBR/PVC blends. He concluded that nitrile elastomers containing 23-45% acrylonitrile are compatible with PVC at all PVC levels.

Landi [69] reviewed previous studies on the compatibility of NBR/PVC blends and employed a differential scanning calorimetry to measure the glass transition of the blends. When a 29% acrylonitrile elastomer with two glass transitions was mixed with PVC, only a higher glass transition was affected. A single glass transition nitrile elastomer containing 34% acrylonitrile had a single glass transition in its PVC blends. Randy and his students [70], [71] examined the properties of mill-mixed blends of PVC with elastomer containing 22-24% acrylonitrile using light scattering, gas permeability, density and dynamic mechanical measurements. They found that an increased amount of acrylonitrile in the elastomers resulted in increased compatibility with the PVC.

Wang and Cooper [72] investigated the morphology and the properties of NBR/PVC blends spincast from tetrahydrofuran. Their studies were carried out at various temperatures using a differential scanning calorimetry, dynamic mechanical analyzer, stress-strain behaviour tester, transmission electron microscopy, and infrared dichroism techniques. Nitrile elastomer containing 44% acrylonitrile was found to be incompatible with the PVC employed under the conditions of their blend preparation. Nitrile elastomer containing 31% acrylonitrile was found to be compatible with the PVC with some indication of heterogeneity in the form of microdomains which were rich in either PVC or nitrile elastomer.

The morphological behaviour of NBR/PVC blends is complex. There appears to be a window of compatibility, the boundaries of this window are not clearly defined. The center of the window appears to lie in the region 30-40% acrylonitrile content in the nitrile elastomer. Jogensen [67] has shown that all commercial non-crosslinked butadiene-acrylonitrile elastomers with less than 35% acrylonitrile have two glass transition temperatures. These are correlative with the fraction of different acrylonitrile content. In blends with these copolymer, PVC tends to solubilize the higher acrylonitrile content fraction.

Even in the region near the center of the window, microheterogeneity has been reported in NBR/PVC blends [61], [62], [72]. The occurrence of microheterogeneity in this region may be due to the multi-phase nature of the NBR, and to the crystallites and residual "primary particles" of PVC discussed by Terselius and Ranby [73].

A number of reviews have been published covering thermoplastic NBR/PVC blends. Pedley [32] published a description of the history, preparation and properties of the NBR/PVC blends.