CHAPTER 1
INTRODUCTION

1. PLASTICIZERS

1.1. HISTORICAL OVERVIEW

The plasticizing effect of oils, waxes and balsams on brittle natural resins and varnishes was known in antiquity and has been applied for a long time. Success in the search for new materials was first attained over a hundred years ago. Already at that time it was possible to nitrate cotton, polymerize some vinyl compounds and condense phenol and formaldehyde to form resinous materials. However, conversion of this knowledge into large-scale production had to wait until the 20th century when cellulose derivatives, polycondensates and, particularly, vinyl polymers were introduced on an industrial scale giving an unexpected impetus to plastics technology.

In the beginning, the situation with regard to plasticizers was unsatisfactory; manufacturers of celluloid or celluloid lacquers had to make do with natural camphor and castor oil. The discovery of triphenyl phosphate in 1912, later used as a substitute for camphor, was a turning point, the importance of which was not immediately recognized. This discovery ushered in the era of ester plasticizers. The most important resulting product was tricresyl phosphate, which is still in use today. For a time, tributyl phosphate was highly regarded for cellulose derivatives but lost its importance when it was replaced by less volatile products. The same was true of glycerin acetates. From 1920 onwards, the first phthalic acid esters, which had been known since 1908, extended the still small range of plasticizers. Within this group di-butyl phthalate gained a dominant position, which it held for many years and continues to hold today for polyvinyl acetate dispersions.
Di (2-ethylhexyl) phthalate, known since 1930\(^1\), became important decades later. Its commercial development is closely associated with the expansion of polyvinyl chloride production. Today, more plasticizers are consumed in processing PVC than in any other thermoplastic resin and phthalic acid esters dominate the market both in number and production volume.

Pressure for the development of specialty plasticizers came from increased quality requirements, the need for materials with specific characteristics and compatibility problems relating to particular products. Food legislation, industrial safety and commercial aspects played a not inconsiderable role and, over the last 40 years, have led to the development of the vast range of plasticizers currently available.

Initially only a few fatty acid esters, benzoates tartrates, and chlorinated hydrocarbons were available but were soon joined by esters of adipic, azelaic and sebamic acid. The latter immediately attracted interest because they considerably improve the cold fracture temperature of plasticized PVC. There followed numerous polyester plasticizers with high resistance to extraction and migration. Epoxidized fatty acid esters were especially attractive because of their synergetic thermo-stabilizing effect. Ethyl butyric and nonionic acid esters used for the manufacture of polyvinyl butyral films made a contribution to more stringent safety requirements in the automobile industry because they made possible the manufacture of laminated glass windshields. Requirements, mainly from the cable industry, for nonvolatile plasticizers, which could be thermally stressed over long periods of time, were first satisfied with di (isotridecyl) phthalate and later on with the trimellitic acid esters. The lack of light stability shown by the triaryl phosphates was countered by the introduction of alkylated phenols as esterification components. Linear, or predominantly linear, C\(_6\) to C\(_{11}\) alcohols available from new technology, have given further impetus in recent years. Therefore, a large number of high performance
plasticizers can be produced nowadays by systematic etherification with aliphatic or aromatic carboxylic acids available in large-scale production.

1.2. PLASTICIZERS AND PLASTICIZING

A plasticizer is a substance, which is added to a material (usually a plastic, resin or elastomer) to improve its processibility, flexibility and stretch ability. A plasticizer can decrease melt Viscosity, glass transition temperature and the modulus of elasticity of the product without altering the fundamental chemical character of the plasticized material\(^1\). The solvation/desolvation equilibrium and the fact that the plasticizers is bound physically by dipole forces rather than chemically (covalently) are characteristic of all externally plasticized polymers.

There is no stoichiometric upper limit to plasticizer uptake. This enables a processor to adjust the flexibility of the basic polymers (PVC, rubber mixtures, cellulose derivatives) over a wide range. Thus the product properties are tailored to the application, e.g. for use in hot or cold climates, for normal or elevated service temperatures, or for articles in contact with oils or fuels. A disadvantage of external plasticizing is the extract-ability of plasticizers from the plasticized material. This depends on the contact medium but can never be completely avoided.

In general, even small quantities of plasticizer have a noticeable effect and most polymers are plasticized with only a small amount of plasticizer. However, PVC possesses the ability to take up large quantities of plasticizer, so that, as more is added and the brittle point is passed, its mechanical properties gradually change from rigid to soft/gel-like (viscoelastic)\(^4\).

The principle of "internal" plasticizing involves monomers leading to homopolymers with high glass transition temperature being selectively copolymerized with monomers whose homopolymers have a substantially lower glass transition temperature.
The advantage of internally plasticized products lies in the strong chemical combination of "hard" with "soft" segments, which cannot be separated from each other by extraction. However, the technique is limited; every copolymer is only suited to certain flexibility requirements. The mechanical properties of internally plasticized materials show marked temperature dependence and the materials have insufficient dimensional stability at elevated temperature. Of course, internally plasticized polymers can be plasticized externally as well.

The classification of organic substances into primary plasticizers, secondary plasticizers and extenders is useful as a guide. Primary plasticizers must gel polymers in the usual processing temperature range quickly and satisfactorily, be usable alone and not exude from the plasticized material. On the other hand, secondary plasticizers have lower gelling power and limited compatibility with the polymer so that combination with a primary plasticizer is necessary. Least useful alone, extenders gel PVC very poorly, tend to exude strongly if used singly and are only suitable for application in restricted amounts as diluents for primary plasticizers.

1.3. ANTI-PLASTICIZERS AND ANTI-PLASTICIZING

On incorporation of small amounts of a plasticizer into certain plastics there is no increase in elongation and no decrease in tensile strength. On the contrary, the polymers become harder and more brittle. This is termed "anti-plasticizing". In addition to PVC, this effect is found with polycarbonate, polysulfone, polyphenylene ether, polyesters and even with polyamide 66. The brittleness which is brought about in PVC by small quantities of plasticizer should not be confused with the occurrence of stress cracking in molded plastics parts.

Although small amounts (less than 10%) of a plasticizer facilitate the thermoplastic processing of PVC, the end product is extremely brittle and is liable to fatigue failure.
The reasons for this behavior are to be found in the degree of order as a consequence of increased mobility of the PVC molecules the degree of crystallinity rises. At 4 to 15% plasticizer content, the degree of order is at its highest and the mechanical parameters (e.g. tensile strength at break) show maximum or minimum values. Increasing amounts of plasticizer reduce and finally eliminate crystallinity and plasticizing is achieved. Plasticizers with high polarity have especially pronounced anti-plasticizing effects. With these materials, steric hindrance of the forces of attraction between PVC chains, caused by the plasticizer, can also be a contributing factor.

All plasticizers can cause brittleness in PVC; the maximum effect depends on the plasticizer structure (aliphatic/aromatic acids, linear/branched alcohols) and generally occurs at plasticizer content of up to 15%. Emulsion PVC shows a reduced effect compared to suspension PVC.

### 1.5. THEORIES OF PLASTICIZING AND PLASTICIZER EFFECT

#### 1.5.1. LUBRICATION THEORY

In the lubrication theory the plasticizer is viewed as a lubricant, which exhibits no bonding forces with the polymer. Lubricants only lower inter-molecular forces and therefore only cause partial plasticizing. In the early days of plastics technology, relatively ineffective plasticizers have been used in small quantities as processing aids. They decreased melt viscosity thereby facilitating processing while generally affecting the properties of a polymer only insignificantly. In contrast, effective plasticizers lower the glass transition temperatures of polymers and can no longer be described as processing aids.

#### 1.5.2. SOLVATION THEORY

The solvation theory is based on concepts of colloid chemistry. The polymer/plasticizer system is regarded as a lyophilic colloid in which the
plasticizer forms solvation shells around the polymer particles (disperse phase). There is, from the physical point of view, no difference in principle between materials termed solvents and those termed plasticizers\textsuperscript{11}. In both cases there is a non-chemical interaction between the components. Two substances are miscible when the Gibbs free energy of mixing is negative\textsuperscript{12}. Mixing energies can be determined in various ways, e.g. vapor pressure measurements on plasticized PVC, or by DSC\textsuperscript{13}. According to such studies, plasticizers are weak solvents possessing poor to moderate solvation power for polymers. They render a strongly dipolar polymer flexible at room temperature by gel formation with an equilibrium between solvation and desolvation.

The solvating or swelling power of a plasticizer depends on its molecular weight and on its functional groups\textsuperscript{14}. Whether or not a plasticizer is effective as a solvent depends on three intermolecular forces: plasticizer/plasticizer, plasticizer/polymer and polymer/polymer. Plasticizers should have small molecules and possess appropriate forces attractive to the polymer, which must, however, be less than those between the polymer chains. The effectiveness of a plasticizer is improved the lower the plasticizer/plasticizer forces compared with the polymer/polymer forces. This is summarized in the leihlich rule that states that the viscosity of a plasticizer should be as low as possible and have a low temperature coefficient. Judged by these criteria the plasticizers, which are used in practice, seem to be relatively inadequate. This is a demonstration of the fact that commercial products often involve compromises between incompatible demands.

To summarize: A plasticizer must have molecules, which are not too small otherwise it would be too volatile. It should also not be too poor a solvent as it could then only be used in small quantities and the danger of separation and exudation would be too great.

1.5.3. THERMODYNAMIC THEORY
The thermodynamic theory uses solution and swelling as explanations of gelling but views plasticizing as the reduction of brittleness of polymers (alteration of the glass transition temperature). As temperature is increased, polymers undergo successive changes from hard to viscoelastic, viscoliquid, limited elastic and plastic forms. The thermodynamic theory attempts to interpret the intermolecular forces in the plasticizer/polymer system by a model based on the resistance to deformation of a three-dimensional gel. Bonding forces, which are effective along the polymer chains, forms the gel. As an example, in a stiff, brittle polymer the intermolecular separations are small compared with an elastomer and every deformation causes internal stresses, which the molecules cannot accommodate; consequently, elasticity of this polymer is very low (hard rubber). The macro Brownian motion of the chain molecules and the micro Brownian motion of molecular segments are hindered in PVC by strong dipole forces, while a thermoplastic elastomer with only a few intermolecular bonds (coarsely networked) is flexible even without incorporation of a plasticizer (weakly cross-linked rubber).

The effect of a plasticizer is now treated as that of reducing the intermolecular forces (dipole and dispersion forces and hydrogen bonding) as much as possible and loosening the bonding of polymer molecules with each other, i.e. shielding the force centers which hold together the polymer chains. This causes the macromolecules to have fewer points of attachment and the polymer becomes elastic and flexible, although, after cooling, linkages between polymer segments or crystallites can be formed again. The network structure of PVC is explained in this way\textsuperscript{15}.

Plasticizers are only absorbed into the amorphous region of polymers; they do not remain permanently firmly bound (secondary bond formation). It is more likely that there is a continuous exchange of plasticizer molecules. At salvation/desolavation equilibrium, when a certain proportion of the force centers of the polymer chain remain shielded, the gel is stable.
1.5.4. POLARITY THEORY

According to the polarity theory, the intermolecular forces between the plasticizer molecules, the polymer molecules and the polymer/plasticizer molecules must be well balanced to ensure that the gel is stable. Therefore, plasticizers contain one or more of both polar and nonpolar groups, which must match the polarity of the particular polymer. The polarity of a plasticizer molecule depends on the presence of groups containing oxygen, phosphorus and sulfur. Proven plasticizers contain polar ester groups, polarizable phenyl groups and nonpolar alkyl groups as shielding groups. In terms of chemical structure a plasticizer is:

- A polar aromatic compound comprised of polar and nonpolar portions. Examples: di (2-ethylhexyl) adipate, tri (2-ethylhexyl) phosphate;
- A polar aromatic/aliphatic compound comprised of polar, polarizable and nonpolar portions. Examples: benzyl butyl phthalate, diphenyl 2-ethylhexyl phosphate.

The polar, directional and orientating groups of a plasticizer interact with the dipoles of the polymer. The purpose of the aromatic, polarizable parts of the molecule is to conduct further the attractive forces of the dipoles and thereby to promote the polar character of the plasticizer molecule. The aliphatic, nonpolar portions shield the dipoles of the polymer from one another. Substances, which consist of polar groups only, associate and exude.

Pictures taken by electron microscope and small-angle X-ray scattering investigations clearly show changes in the morphology of a polymer after being plasticized. Incorporation of plasticizers as ball-shaped agglomerates in PVC is conceivable.

1.6. CHOICE OF PLASTICIZERS
Processing and properties of plasticized polymers are markedly affected by the type and quantity of plasticizer. The following points must be particularly considered:

I. Volume cost analysis,

II. Compatibility,

III. Processing characteristics,

IV. Thermal, electrical and mechanical properties,

V. Resistance to water, chemicals, weathering, dirt and micro organisms,

VI. Toxicity,

VII. Effect on rheological properties.

The volume cost analysis is based on the fact that the sale of most end products is by meters, square meters etc., that is by "volume". The volume cost analysis gives advantages to plasticizers with low density and low plasticizing activity (e.g. di-isonyonyl phthalate plasticizers PVC less than di-isocyl phthalate). This is, of course, true only as long as the volume cost of PVC is not lower than that of the plasticizer.

The choice of a plasticizer demands experience and the exact definition of the desired properties of the end product. Important parameters for PVC are:

A. The processing method starting either from dry-blends, agglomerates, or granules: extrusion, calendering

B. Injection molding, compression molding; processing as plastisol by coating, dipping, casting or spraying,

C. Special demands on the end product, such as high or low temperature application or resistance to petrol, require specific plasticizers. e.g. low volatility plasticizers, low-temperature plasticizers or polyester plasticizers.
In general, an optimized plasticizer mixture rather than a single plasticizer is used. Furthermore, the cost of a mixture can be reduced by the use of extenders or fillers such as chloroparaffins or calcium carbonate. Plasticizers with low effectiveness, used in large amounts, can also reduce the volume cost of a mixture.

1.7. COMPATIBILITY

The compatibility of a plasticizer with a given polymer is its most important property. High compatibility means that a stable, homogeneous mixture of plasticizer and polymer is produced. Plasticizers may be compatible at the processing temperature but exude from the material on cooling; the reverse can also occur.

Primary plasticizers are highly compatible with PVC in all proportions, and neither exudes as drops or as a surface film, nor do they bloom (form a firm deposit). Substances, which show a certain amount of exudation or blooming, particularly at high concentrations, are termed secondary plasticizers, e.g. the aliphatic dicarboxylic acid esters. The boundary between primary and secondary plasticizers is not clear-cut and depends on concentration and ambient conditions. In PVC, phthalates such as dioctyl phthalate and butyl benzyl phthalate show satisfactory compatibility under almost all service conditions.

Secondary plasticizers, which are incompatible when used alone, are also called extenders. Alkylated aromatic hydrocarbons and chlorinated hydrocarbons have adequate dispersion forces and sufficiently high solubility parameters but are too weak in polarity and in their hydrogen bonding ability to be usable as primary plasticizers.

The compatibility of a plasticizer is also influenced by the presence of other additives, and by pressure, temperature, moisture and light. Plasticized polymers are in dynamic equilibrium at a particular temperature. As soon as the temperature changes, the effectiveness of the forces alters. With more energy added (at elevated temperature) it
becomes easier to break the bond between polymer and plasticizer (favorsing desorption) and the opposite is true at lower temperature. Under normal service conditions diffusion always ensures that there is a certain amount of plasticizer on the surface. This does not mean, however, that the plasticizer is exuding. Exudation means that the surface feels oily and fatty because of separated plasticizer. In this case the dynamic adsorption desorption equilibrium between plasticizer and polymer molecules is disturbed.

The exuded material generally contains all of the liquid components, which were used in the original mixture. Solid deposits are not usually caused by incompatibility of plasticizers.

**Table 1.1: Effect of temperature on Shore hardness A and D) of plasticized PVC with a plasticizer content of 30%.

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Shore A/Shore D hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPB</td>
<td>98/75 97/69 94/58 85/- 71/- 66/- 62/- 60/-</td>
</tr>
<tr>
<td>DOP</td>
<td>98/76 97/71 94/65 90/47 85/- 72/- 66/- 62/-</td>
</tr>
<tr>
<td>DINP</td>
<td>98/82 97/70 90/54 90/45 82/- 73/- 97/- 63/-</td>
</tr>
<tr>
<td>DOA</td>
<td>97/62 91/48 82/- 70/- 64/- 59/-</td>
</tr>
</tbody>
</table>

1.12. TESTING OF PLASTICIZERS

For characterization and control of consistency and of purity a series of characteristic values are determined for plasticizers and plasticized PVC. There are specific standards for molding compounds, individual plasticizers, plasticizer groups and plasticized PVC (DIN 7749 part 1, ISO 2898-1-86). Table 3 lists the purpose for determining a number of characteristic values and test methods for obtaining them (DIN 53400).
<table>
<thead>
<tr>
<th>Property</th>
<th>Purpose, application, assessment</th>
<th>DIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasticizer</td>
<td>Symbols</td>
<td>7723</td>
</tr>
<tr>
<td>Density</td>
<td>Calculation of mass and volume</td>
<td>1306</td>
</tr>
<tr>
<td>Density/temperature dependence</td>
<td>Consistency and purity</td>
<td>51757</td>
</tr>
<tr>
<td>Refractive index n_D^20</td>
<td>Consistency, purity and optical properties</td>
<td>53491</td>
</tr>
<tr>
<td>Flash point</td>
<td>Flammability of vapors</td>
<td>51758</td>
</tr>
<tr>
<td>Ignition temperature</td>
<td>Assignment to hazard classification</td>
<td>51794</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Consistency, purity; plasticizing breaching for plasticizers based on the same acid but different alcohols</td>
<td>51561 51675 53015</td>
</tr>
<tr>
<td>Viscosity/temperature dependence</td>
<td>Storage, transport</td>
<td>See above and 51 563</td>
</tr>
<tr>
<td>Acid number (mg KOH/g)</td>
<td>Consistency, degree of purity</td>
<td>53402</td>
</tr>
<tr>
<td>Saponification number (mg/KOH g)</td>
<td>Consistency, degree of purity</td>
<td>53401</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>Consistency, degree of purity</td>
<td>53240</td>
</tr>
<tr>
<td>Pour point</td>
<td>Thickening at low temperature</td>
<td>51597</td>
</tr>
<tr>
<td>Hazen color</td>
<td></td>
<td>53409</td>
</tr>
<tr>
<td>Ash content</td>
<td></td>
<td>51757</td>
</tr>
<tr>
<td>Bromine content</td>
<td></td>
<td>51774</td>
</tr>
<tr>
<td>Nitrogen content</td>
<td></td>
<td>51772</td>
</tr>
<tr>
<td>Sulfur content</td>
<td>Consistency, degree of purity</td>
<td>51768</td>
</tr>
<tr>
<td>Water content</td>
<td></td>
<td>51777</td>
</tr>
<tr>
<td>Iodine number</td>
<td></td>
<td>55934</td>
</tr>
<tr>
<td>Aniline and mixed aniline points</td>
<td></td>
<td>51775 51787</td>
</tr>
</tbody>
</table>
1.13. TYPES OF PLASTICIZER

In the literature, plasticizers are divided according to different view points into:

I. Internal (copolymers), vulcanizable or cross-linkable plasticizers (in which the plasticizer reacts with the polymer or with itself).

II. Physical mixtures,

III. Primary plasticizers,

IV. Secondary plasticizers, thinners or extenders (plasticizer diluents).

Use of any of these proposed methods for the classification of plasticizers is inadequate because there is always a remainder, which cannot be assigned to any class. The clearest classification is a chemical one:

a) Phthalates,

b) Aliphatic/aromatic monocarboxylic acid esters,

c) Aliphatic dicarboxylic acid esters,

d) Phosphates,

e) Polyester or polymeric plasticizers

f) Special plasticizers,

g) Extenders (hydrocarbons, chlorinated hydrocarbons).

Phthalates are the most common, especially di (2-ethylhexyl) and diisooctyl phthalate and, recently diisononyl and diisodecyl phthalate. Aliphatic dicarboxylic acid esters (adipates, sebacates and azelainates) are used to impart good low-temperature flexibility. Epoxidized plasticizers made from natural oils can be used as primary plasticizers. In general they improve heat and light stability as well as resistance to extraction. Extenders (secondary plasticizers) are used in combination with primary plasticizers as a way of reducing cost. In general they lower heat and light...
stability and show some incompatibility, so that they can be used only in quantities limited to about 20% of that of the primary plasticizer.

Polyester (polymeric) plasticizers are primary plasticizers with very good resistance to extraction by aliphatic hydrocarbons but they reduce low-temperature flexibility of articles containing them. Elastomers, such as nitrile rubber, ethylene/ vinyl acetate copolymers, chlorinated polyethylene, thermoplastic polyurethane etc., can be used for special articles where high demands are made with respect to low volatility as well as to migration and chemical resistance of the plasticizer. They are used in powder form, which can be easily incorporated.

As an example, table 4 shows the distribution of plasticizer production in the USA according to these groupings. The percentages given are probably as a rough approximation applicable worldwide.

Since 80% of plasticizers are used in the manufacture of plasticized PVC, developments required for PVC and plasticized PVC products are decisive in determining the market importance of plasticizers; although use is stagnating in some branches, in others there is actually showing a tendency to increase.

Out of the more than 20000 substances with plasticizing properties described so far, about 200 arcs used in practice with about 40 products having achieved noticeable market significance. About 12 products account for half of the plasticizer production in the Western world\textsuperscript{11}. The most important starting materials are given in table 4.

<table>
<thead>
<tr>
<th>Product Group</th>
<th>Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phthalates</td>
<td>61</td>
</tr>
<tr>
<td>Trimellitates</td>
<td>1</td>
</tr>
<tr>
<td>Phosphates</td>
<td>6</td>
</tr>
<tr>
<td>Adipates</td>
<td>3</td>
</tr>
<tr>
<td>Sebacates</td>
<td>1</td>
</tr>
<tr>
<td>Polyesters</td>
<td>2</td>
</tr>
<tr>
<td>Fatty other esters (oleates, stearates etc)</td>
<td></td>
</tr>
<tr>
<td>Fatty acid esters, epoxidized</td>
<td>5</td>
</tr>
<tr>
<td>All other cyclic plasticizers</td>
<td>13</td>
</tr>
<tr>
<td>All other acyclic plasticizers</td>
<td>6</td>
</tr>
</tbody>
</table>

At present the worldwide production capacity for plasticizers is estimated at around 4 mio-tons per annum and the annual consumption at approx. 3.1 mio-tons. The fourfold increase in production in the years 1960 to 1970 was not maintained between 1970 and 1980 and a lower figure is also likely for the 1980 to 1990 period.

2. INTRODUCTION OF NITRILE RUBBER

The Introduction of acrylonitrile (ACN) into the polymer backbone imparts oil resistance and affects many other properties. Grades that vary in acrylonitrile content from 18 to 50 % are commercial available, the percentages of acrylonitrile present forming the basis of the following grade descriptions:

- Low 18-24 % ACN
- Medium low 26-28 % ACN
- Medium 34 % ACN
- Medium 38-40 % ACN
- High 50 % ACN

Many properties are influenced by the acrylonitrile content:
Properties | Acrylonitrile content
---|---
---------50 % | ←→ 18 %
Oil resistance improvement | ←→
Fuel resistance improvement | ←→
Tensile strength improvement | ←→
Hardness increase | ←→
Abrasion resistance improvement | ←→
Gas impermeability improvement | ←→
Heat resistance improvement | ←→
Low temperature flexibility improvement | ←→
Plasticizer compatibility | ←→

A typical Tg of an 18% CAN co-polymer is -38 °C, and that of a 50% ACN co-polymer -20°C. Carboxylated nitriles, hydrogenated nitrile, liquid nitriles, and blends with polyvinyl chloride (PVC) are also commercially available.

The carboxylated types (XNBR) contain one or more acrylic type of acid as a terpolymer, the resultant chain being similar to nitrile except for the presence of carboxyl groups, which occur about every 100-200 carbon atoms. This modification gives the polymer vastly improved abrasion resistance, higher hardness, higher tensile and tear strength, better low temperature brittleness, and better retention of physical properties after hot oil and airing ageing when compared to ordinary nitrile rubber.

Low molecular weight liquid nitrile grades are available, and these can be used as compatible plasticizers in the compounding of nitrile rubber. Such plasticizer can be partially cross-linked to the main chain during cure; hence they exhibit low extractability.

PVC / NBR poly blends can be produced as colloidal or mechanical blends, the former generally giving superior properties. Commercially available poly
blends have PVC contents ranging from 30 to 55 %. The poly blends have reduced elasticity, which gives improved extrudability, but they also exhibit superior ozone resistance, improved oil swell resistance, and tensile and tear-strength; these properties, however, are achieved at the expense of low temperature flexibility and compression set. The ozone resistance of such polyblends is improved only if the PVC is adequately distributed and fluxed. Failure due to ozone attack can occur if proper distribution and fluxing are not achieved, but this is harder to do in mechanical blends.

Another method by which the ozone resistance of nitrile rubber can be improved is the removal of the double bonds in the main chain of the copolymer by hydrogenation. Hydrogenated nitrile rubbers also exhibit much greater resistance to oxidation and extend the useful service temperature range of nitriles up to 150 °C. Commercially available grades offer different degrees of hydrogenation, with residual double bonds ranging from 0.8 to 6 %. Nitriles have good resistance to oil, aliphatic and aromatic hydrocarbons, and vegetable oils, but polar solvents such as ketones swell them. The unsaturated main chain means that protection against oxygen, ozone, and UV light is required.

In compounding, choice of the correct grade is required if the required balance of oil resistance and low temperature flexibility is to be achieved.

Sulphur, sulphur donor systems and peroxides can cure nitrile rubber. However, the solubility of sulphur in nitrile rubber is much lower than in NR, and a magnesium carbonate coated grade (sulphur MC) is normally used this is adds as early in the mixing cycle as possible. Nitrile rubber requires less sulphur and more accelerator than is commonly used for curing natural rubber. A cadmium oxide/magnesium oxide cure system gives improved heat resistance, but the use of cadmium. A heavy metal will increasingly be restricted.

The hydrogenated nitrile grades that contain the lowest level of residual double bonds can be cross-linked only by the use of peroxides and radiation.
While those with a level of residual double bonds greater than about 3.5% can be cured by sulphur.

In addition to the normal sulphur cure systems, metal oxides can be used to cure the carboxylated nitriles. The low temperature properties of nitriles can be improved by the use of suitable plasticizer (e.g. ester plasticizers).

Nitrile rubber, because of its oil resistance, is widely used in sealing applications, hose liners, roll coverings, conveyor belts, shoe soles, and plant lining. Nitrile rubber is also available as latex.

1. INTRODUCTION OF PVC

Polyvinyl chloride (PVC) is the world’s most versatile thermoplastics with a wide range of applications than any other plastics. Virtually all areas of human activities whether domestic or industrial, leisure or commercial, PVC’s presence is dominating. It plays an important role in every field such as agriculture, electrical, irrigation, house roofs, shoe soles and many other fields.

Vinyl chloride was first synthesized and reported by Reghawl in 1835. Hoffmann published the first report of polyvinyl chloride in 1860. The full-scale commercial production of PVC resin began in 1931 in Germany. In India the manufacturing of PVC began in 1961 when Calico started its plant in Mumbai.

- Presence of chlorine atom causes an increase in inter chain attraction and increase hardness and stiffness of polymer. Hence PVC is ‘hormy material’.
- PVC is polar in nature due to presence of C-Cl dipole, thus having high dielectric constant and power factor.
- Solubility parameter of PVC is 19.4 MPa. Hence polymer is resistant to non-polar solvents, which are having less solubility parameter. Suitable solvents for PVC are Cyclohexanone, Tetrahydrofuran and Xylene.
- Presence of Chlorine atom makes the material ‘flame retardant and self extinguishing’ and also presence of plasticizer reduces rate of burning.
- These polymers are amorphous in mature. Properties of Poly Vinyl Chloride are given in table

3.1. PROPERTIES OF PVC

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td></td>
<td>1.18-1.70</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>5.5-26.2</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>MPa</td>
<td>4.8-12.4</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>MPa</td>
<td>30</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>150-450</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>°C</td>
<td>80-85</td>
</tr>
<tr>
<td>Dielectric Strength</td>
<td>KV/mm</td>
<td>9.9-15.8</td>
</tr>
</tbody>
</table>

3.2. Compounds of PVC

A PVC compound may contain the following ingredients

3.2.1. STABILIZERS

Heating of PVC at temperature above 70 °C has a number of adverse effects on the properties of the polymers. Sufficient degradation may take place during standard processing operations (150-200°C) to make the product useless.

Therefore to avoid degradation ‘stabilizers’ are found useful, so that useful moldings can be obtained.

The most important stabilizer for PVC is ‘basic lead carbonate” (white lead). Tri basic lead sulphate is a good heat stabilizer but due to its heavy cost (when compare to sulphate & carbonate), its use is restricted. ‘Dibasic lead phthalate’ is also used in PVC. Today, only the compounds of Cd, Ba, Ca and Zn are prominent as PVC stabilizers.

3.2.2. PLASTICIZERS

These are found useful,

- For reducing processing temperature of polymer below the decomposition temperature.
- To modify the properties of finished products such as flexibility or extensibility etc.
- To modify processing properties.

All PVC plasticizers have a solubility parameter to that of PVC. Di-iso-octyl phthalate (DIOP) and di-ethyl-hexyl phthalate (DEHP) are most important plasticizers used in PVC.

3.2.3. EXTENDERS

Sometimes plasticizers are not found useful in PVC because of their limited compatibility with the polymer. But when mixed with ‘true plasticizer’ (commercially called extenders), a reasonable compatibility is acquired. Therefore ‘Extenders’ can often replace plasticizers without any adverse effects on the properties of compound.

Commonly used extenders in PC are
- Chlorinated paraffin waxes
- Chlorinated liquid paraffin fraction
- Oil extracts

The solubility parameters of these extenders are generally lowers that of PVC.

3.2.4. LUBRICANTS

In plasticized PVC the main function of a lubricant is to prevent sticking selecting a material of limited compatibility with PVC which will bleed out from melt during processing to from a film between the bulk of the compound and the metal surface of the processing equipment. The additives used for this purpose are known as ‘external lubricants’. Calcium stearate, normal lead stearate, dibasic lead stearate, graphite are employed to improve flow properties.

In unplasticized PVC the internal lubricants are incorporated to improve the flow of the melt and lower the apparent melt viscosity. These materials are reasonably compatible with the polymer. Internal lubricants are wax derivatives and glyceryl esters (glyceryl mono stearate)
3.2.5. FILLERS

Fillers are commonly employed in opaque PVC compounds in order to reduce cost. They may also be incorporated for technical reasons such as to increase the hardness of a flooring compound, to reduce tackiness of highly plasticized compounds, to improve electrical insulation properties and to improve the hot deformation resistance of cables.

For electrical insulation, china clay is commonly employed while various carbonates (ground limestone, Precipitated CaCO₃ and coated CaCO₃) are used for general-purpose work. Occasionally employed fillers are talc, light magnesium carbonate, barium sulphate (barites) and the silica’s and silicates. For flooring applications ‘asbestos’ has been important filler.

3.2.6. PIGMENTS

A large number of pigments are now commercially available which are recommended for use with PVC.

To add a pigment, firstly the following facts are to be considered
- Will it decompose, fade or plate out?
- Will the pigment adversely affect the functioning of stabilizer and lubricant?
- Will it fade, bleached out or will it bleed?
- Will the pigment adversely affect properties that are relevant to his end usage (because many pigments will reduce the volume resistivity of a compound)?