STUDY ON PHYSICO-MECHANICAL PROPERTIES OF RADIATION RESISTANT PVC-NBR COMPOSITES

A thesis submitted in partial fulfillment of the requirements for the Degree of

MASTER OF ENGINEERING
In
POLYMER TECHNOLOGY

Submitted by
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CERTIFICATE

This is to certify that the major project entitled ***“Study on Physico-Mechanical properties of Radiation Resistant PVC-NBR Composites ”*** being submitted by me, is a bonafide record of my own work carried by me under the guidance and supervision Dr.G.L Verma and Dr. R.K Diwan in partial fulfillment of requirements for the award of the Degree of Master of Engineering in Polymer Technology , from University of Delhi, Delhi.

This result contained in this project is original and have not been submitted to any University or Institute for the award of any degree.

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CONTENT

Page no.

LIST OF FIGURES

FIGURE

LIST OF TABLES

TABLE

ABBREVIATIONS

DOP	Dioctyle Pthalate $C_6H_4(COOC_8H_{17})_2$)
DIDP	Diisodecyl Phthalate
ESO	Epoxidised Soya bean Oil
Irganox 1076	Octadecyl 3,5-Di-(tert)-butyl-4-hydroxyhydrocinnamate
PVC	Poly Vinyl Chloride
ASTM	American Society for Testing and Materials
Bis A	Bisphenol A
EDC	Ethylene Dichloride
VCM	Vinyl Chloride Monomer
BIS	Bureau Of Indian Standards

Abstract

Gamma radiation is very important in polymer industry and in polymer applications. It is very harmful for human body to the protection of gamma rays a plasticized PVC sheet has been made which remains stable under the certain amount of gamma radiation dose .

PVC can be converted easily into to a desired shape. Mechanical properties of PVC are very important for the application purpose . It’s properties can be changed easily by giving it the various type of radiation doses , radiation makes it more applicable in various uses. Different compositions were prepared and were exposed to different gamma radiation dose to study different mechanical properties .The plasticized PVC sheets were analyzed before and after radiation for various properties such as density ,tensile strength ,tear strength ,elongation and hardness etc.

CHAPTER 1

INTRODUCTION

Poly Vinyl Chloride (PVC) is one of the most fascinating, interesting, universal thermoplastic which has profound applications in various sectors such as healthcare, general purpose, packaging , construction and strategic applications. The most important property of PVC is that it can be tailor made for various applications . On one hand it is the polymer which comes into contact with a baby's skin only a few minutes after its birth, in many countries the bracelet on which the name and the birthday of the newborn are noted is made of PVC. A lot of other medical items such as oxygen tents and blood bags are also based on PVC because of the chemical and physical properties of PVC which are not offered by other materials. On the other hand many PVC products, for example toys as children or more durable items as U-PVC windows, cladding, electrical insulation on wires and cables, resilient flooring, pipes for land drainage, sewage and drinking water are with us throughout our lives. Even the coffins that we are finally buried in are probably covered in PVC foil or veneer and lined with flexible PVC film.

PVC, is one of the world's leading synthetic polymers. It has many uses, ranging from long-term construction applications, such as pipes used in the transportation of potable water, to short-term uses, such as food packaging. Because of the presence of chlorine, it is a highly polar polymer, which allows a wide range of additives to be incorporated within it. This variety of additives can be incorporated for improvement of properties for the intended applications. This provides the great application of PVC permits a broad range of physical property characteristics; hence there is not one PVC composition but many. This also explains the great diversity of applications in which PVC has been used from the time of its original commercial development in the early 1930s, when a few hundred tones were produced, to its annual global consumption rate of nearly 25 million tones in the year 2000. Thus PVC is indispensable part for the polymer industries from both point of views i.e commercially as well as application wise.

Gamma radiation as such is harmful for mankind .This high energy radiation destroys tissues of our body and causes severe skin burns . Properties of PVC can be changed very easily by blending it with NBR and giving it the different dose of gamma radiation ACN content determines several basic properties such as oil and solvent resistant ,low temperature flexibility ,glass transition temperature and abrasion resistance. PVC-NBR coupled with various additives has been reported as well as used in oil, fuel, chemical and radiation resistant applications. Light weight gamma radiation resistant protective polymeric composition can be used in nuclear power plants to control radiations.

During transportation of nuclear radioactive material in virgin or waste form ,the container has been sealed properly so that no leakage of radioactive material occurs for such applications sealing of container has been done by using imported polymeric material that can resist gamma radiation of 100 M rad.

PVC has been selected as one of the polymeric component for such applications. PVC can be blended with Nitrile rubber in different proportions and compounded with chemicals that can improve its ability to resist high energy radiation .

In this project an attempt has been made to improve the mechanical properties of the PVC SHEET by optimizing dose of gamma radiation .

CHAPTER 2

OBJECTIVE AND SCOPE OF WORK

The main aim of the project is to develop a gamma rays resistant plasticized PVC composition.

- Detail evaluation of developed PVC Compositions before and after radiation by Tensile strength, Hardness, Elongation,Specific gravity, and Tear strength.

- To study the effect of gamma radiation on Physico-Mechanical properties of PVC sheet.

- To prepare plasticized PVC composition using PVC resin,NBR,DOP,lubricants etc. in different proportions

CHAPTER 3

LITERATURE SURVEY

3.1 Vinyl Chloride:

Vinyl Chloride is known as Chloroethene in IUPAC nomenclature , it is a simple vinyl halide. It is an important industrial chemical mainly used to produce its polymer, Polyvinyl Chloride (PVC). At room temperature, Vinyl Chloride is a toxic, colorless gas with a sweet odor.

3.1.2 Vinyl Chlorid Preparation:

Vinyl Chloride, the monomer for PVC , is generally prepared by treating acetylene at 1-1.5 atm pressure with hydrogen chloride at 60-80^{0}C, in the presence of metal chloride as catalyst,

$$\mathbf{CH{\equiv}CH + HCl \rightarrow CH_2{=}CH\text{-}Cl}$$

Acetylene Vinyl Chloride

$$\mathbf{CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl}$$

Vinyl Chloride is also prepared by heating ethylene dichloride to 500 °C at 15–30 atm pressure, then it is decomposed to produce VCM and HCl.

$$\mathbf{ClCH_2CH_2Cl} \rightarrow CH_2{=}CHCl + \mathbf{HCl}$$

3.1.3 Properties of VCM :

Molecular formula : CH_2CHCl
Molar mass : 62.498 g/mol
Appearance : Colorless gas
Density : 0.91 g/ml
Melting point : - 154 °C (119 K)
Boiling point : -13 °C (259 K)
Solubility in water : Insoluble

3.1.4 Applications:

It is used for the production of PVC.

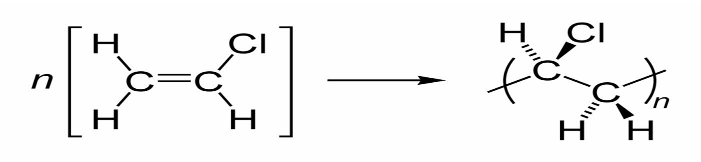
3.2 Polyvinyl Chloride:

History:- Polyvinyl Chloride was discovered in 1835 by Henry Victor Regnault . In the early 20th century, the Russian Chemist Iran Ostromislensky and Fritz Klatte of the German Chemical company, Goieshein-Elektron both attempted to use PVC in commercial products, but faced difficulties in processing the rigid, sometimes brittle polymer blocked their efforts. In 1926, Waldo Semon of B.F. Goodrich developed a method to plasticize PVC by blending it with various additives. The result was a flexible and more easily processed material that soon achieved widespread commercial use.

Polyvinyl Chloride is one of the most widely used plastics in the world . It has a linear structure similar to polyethylene but with a chlorine atom replacing a hydrogen atom on alternate carbon atoms. PVC is a flexible or rigid material that is chemically non reactive. PVC has low thermal stability and high melt viscosity. Therefore, it is combined with a number of additives to vary properties to suit different end-use applications. In terms of revenue generated, it is one of the most valuable products of the chemical industry. Around the world, over 50% of PVC production is consumed in construction. As a building material, PVC is cheap, durable, and easy to assemble. Rigid PVC is easily machined, heat formed, welded, and even solvent cemented. PVC can also be machined using standard metal working tools and finished to close tolerances and finishes without great difficulty. PVC resins are normally mixed with other additives such as impact modifiers and stabilizers, providing hundreds of PVC based materials with a variety of engineering properties .

3.2.1 PVC Preparation:

The major technique of polymerizing vinyl chloride monomer (VCM) to PVC is by suspension polymerization. It is carried out in small droplets of monomer suspended in water. VCM is dispersed in water by agitation, and the droplets are stabilized by the action of a suspending agent such as a protective colloid (often polyvinyl alcohol). The activation for polymerization comes from monomer soluble initiators that generate free radicals upon thermal decomposition. Other additives are also used, such as chain transfer agents, which together with the polymerization temperature, determine the polymer chain length and hence molecular weight.



VCM **PVC**

During the polymerization reaction pressure remains constant until 70 to 75 percent of the monomer has been converted. From this point on , the pressure begins to decrease, since the free monomer has been converted and the remaining monomer is absorbed in the polymer, which reduces the monomer partial pressure. Where a typical batch cycle is seen to be about 6.5 hours. The pressure is usually allowed to drop 3 or 4 bar (40 to 60 psia), which corresponds to a monomer conversion of approximately 90 percent. At this point, the reactor contents are depressurized into the slurry stripper feed tank, where most of the unconverted monomer vaporizes. The vapor stream evolved is directed to the monomer recovery system. The depressurized slurry leaves the slurry stripper feed tank and is pumped to the top of the slurry stripper. At this point, the slurry typically contains 10,000 ppm vinyl chloride.

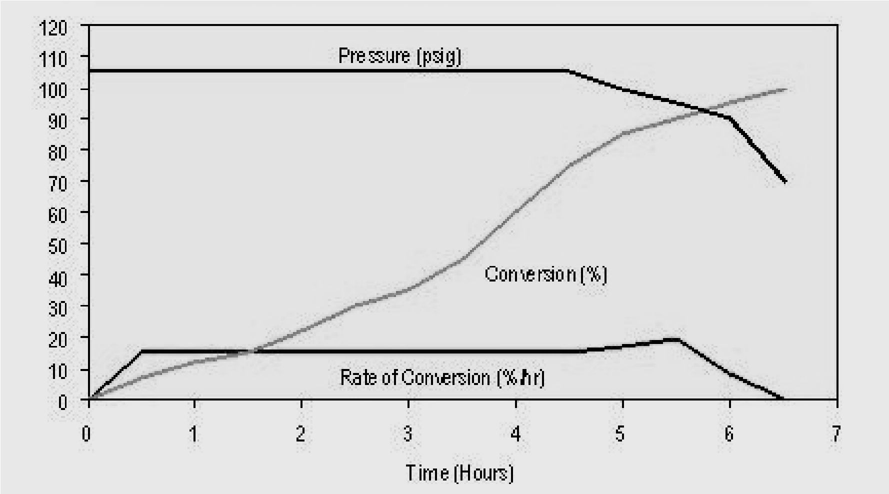


Figure 1: Pressure and Conversion Profiles for PVC Suspension Process.

3.2.2 Properties:

Density : 1380 kg/m^3
Young's modulus : 2900-3300 MPa
Tensile strength : 50-80 MPa
Elongation at break : 20-40%
Notch test : 2-5 kJ/m^2
Glass temperature : 87 °C
Melting point : 212 °C
Specific heat (*c*) : 0.9 kJ/(kg·K)

PVC is insoluble in , alcohols, water and hydrocarbons. Acid and alkalis have practically no effect on PVC. It dissolves in ketones and chlorinated hydrocarbons. A mixture of acetone and carbon disulphide is found to be an excellent solvent for PVC. It possesses flame retardation and self-extinguishing characteristics.

It has high strength, ,good dimensional stability, good weather resistance, high impact strength, clarity, colorability . It is flexible or rigid, economical, chemically inert, ease of fabrication, tasteless, odorless , non-toxic . It is excellent resistance to dilute and concentrated acids, alcohols, bases, aliphatic hydrocarbons and mineral oils.

3.2.3Applications:

Nuts, Filters , Signs ,Tanks , Pipes, Bolts ,Valves, Bushings ,Tank and pool liner, Laboratory equipment, Ducts ,Sprinkler systems , Wall coverings , Pump parts , Fittings System , Pipe, Rod & Bar,,Square Bar, Rectangular Bar, Weld-on Cement and Welding Rod, PVC Hollow, Angle and Hex Bar Stock ,

3.2.4 Technical Importance of PVC :-

Polyvinyl Chloride (PVC) has become worldwide a very important bulk plastic over its almost 70 year history.

PVC is expected to remain important among thermoplastics because of its compatibility with a large number of additives (e. g., plasticizers, impact modifiers), in contrast to other plastics. PVC properties can be adjusted over a wide range, yielding everything from rigid to flexible end products. The thermal stability and toxicological problems which at one time were major obstacles in the manufacture and processing of PVC were solved satisfactorily many years ago.

When PVC was first developed, flexible PVC was dominant, but rigid PVC production has increased continually and is now approximately two-thirds of total consumption in many countries. The low thermal stability of PVC is well known. Despite this fact, processing at elevated temperatures is possible by adding specific heat stabilizers which can stop the damage. This is one of the main reasons PVC has become a major bulk plastic. The development and production of suitable heat stabilizers followed the production of PVC from the beginning, and remains a precondition for processing and application in the future.

3.3 Acrylonitrile Butadiene Rubber:

NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of application areas requiring oil, fuel, and chemical resistance. In the automotive area, NBR is used in fuel and oil handling hose, seals and grommets, and water handling applications. With a temperature range of –40°C to +125°C, NBR materials can withstand all but the most severe automotive applications. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications.

3.3.1 Manufacturing Process:

NBR is produced in an emulsion polymerization system. The water, emulsifier/soap, monomers (butadiene and acrylonitrile), radical generating activator, and other ingredients are introduced into the polymerization vessels. The emulsion process yields a polymer latex that is coagulated using various materials (e.g. calcium chloride, aluminum sulfate) to form crumb rubber that is dried and compressed into bales. Most NBR manufacturers make at least 20 conventional elastomer variations, with one global manufacturer now offering more than 100 grades from which to choose. NBR producers vary polymerization temperatures to make "hot" and "cold" polymers. Acrylonitrile (ACN) and butadiene (BD) ratios are varied for specific oil and fuel resistance and low temperature requirements. Specialty NBR polymers which contain a third monomer (e.g. divinyl benzene, methacrylic acid) are also offered. Some NBR elastomers are hydrogenated to reduce the chemical reactivity of the polymer backbone, significantly improving heat resistance. Each modification contributes uniquely different properties. Figure 2 shows the typical NBR manufacturing process.

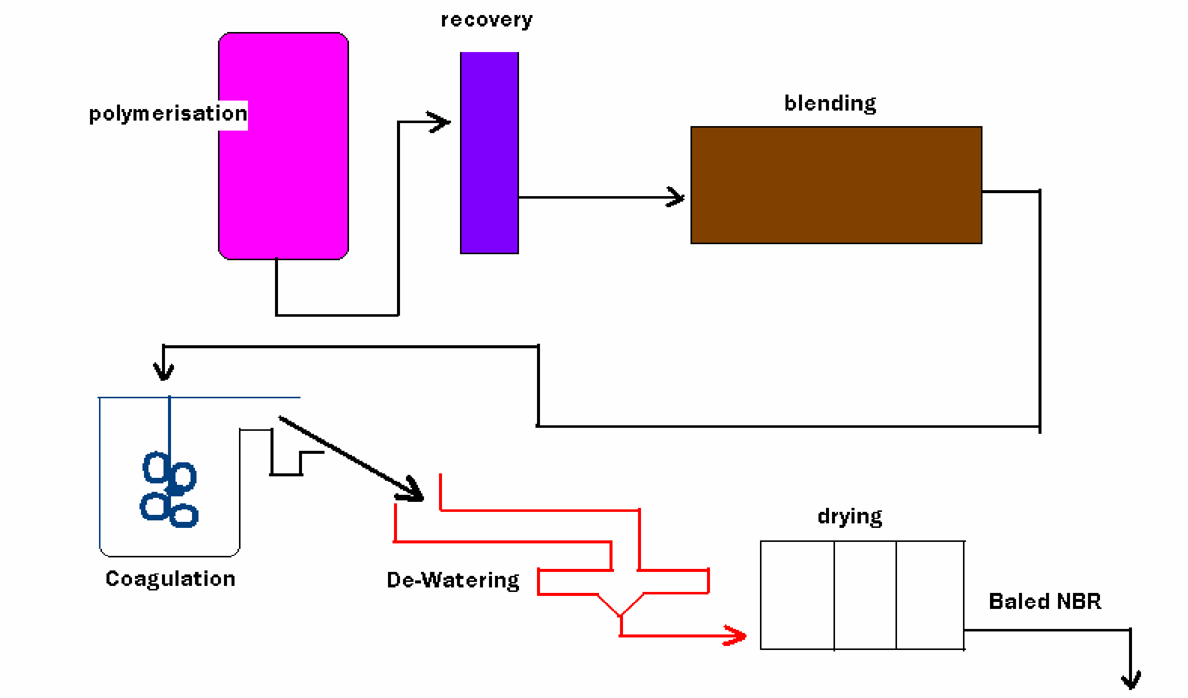


Figure 2: NBR Manufacturing Process

3.3.2 Acrylonitrile (ACN) Content:

The ACN content is one of two primary criteria defining each specific NBR grade. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance, low-temperature flexibility/glass transition temperature, and abrasion resistance. Higher ACN content provides improved solvent, oil and abrasion resistance, along with higher glass transition temperature.

3.4 Electromagnetic Radiation:

Radiation is energy in the form of waves or moving subatomic particles. Electromagnetic (EM) radiation, also called light, even though it is not always visible, is a self-propagating wave in space with electric and magnetic components. These components oscillate at right angles to each other and to the direction of propagation, and are in phase with each other. Electromagnetic radiation is classified according to the frequency of the wave. These include, in order of increasing frequency, radio waves, microwaves, terahertz radiation, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. These are given in table no.1

Table 1 Electromagnetic radiations.

Serial No.	Type	Wavelength Range A^o	Generation	Detection
1.	X-Rays	0.006-1019	Emitted by sudden stopge of fast moving electrons	• Photographic • Phosphorescence • Chemical action • Ionization • Photoelectric action • Diffraction by crystals etc.
2.	Gamma rays	0.001-1.4	Emitted when atomic nuclei disintegrate (Radioactivity)	As for X-Rays but more penetrating
3.	UV-Rays	136-3900	Radiation from very hot bodies and emitted by ionized radiation	Same as X-Rays as reflected refracted by final grating

Serial No.	Type	Wavelength A^0	Generation	Detection
4.	Visible rays	3900-7700	Radiation from hot bodies and emitted by ionized gases	Sensation of light same as ultraviolet
5.	IR-Rays	7700 - $4x10^{6}$	Heat radiation	Heating effect on thermocouple .bolometer etc. Rise in temperature of receiving body .
6.	Solar radiation	2960-53000		Limited wavelength Reaching earth
7.	Radio wave	$1x10^{11}$-$3x10^{14}$	Spark gas discharge Oscillation triode valve	Coherer ,spark across minute gaps in resonant receiving circuit. Reflected ,refracted ,diffraction
8.	Electric waves	$3x10^{14}$-$3.5x10^{16}$	Coil rotating in magnetic field	Mechanical ,Electrical ,Thermal effect of alternating current
9.	Broadcasting band	$2x10^{12}$-$5.5x10^{12}$	Same as radio waves	Same as radio waves

3.4.1 Gamma Rays:

Gamma rays (denoted as γ) are one of the three types of natural radioactivity. They are electromagnetic in nature. The other two types of natural radioactivity are alpha and beta radiation, which are in the form of particles.

Gamma rays are the most energetic form of electromagnetic radiation , they have highest frequency and energy, and also the shortest wavelength less than one-tenth of a nanometer. Gamma radiation is the product of radioactive atoms.

3.4.2 Gamma Production:

A nucleus which is in an excited state may emit one or more photons (packets of electromagnetic radiation) of discrete energies. The emission of gamma rays does not alter the number of protons or neutrons in the nucleus but instead has the effect of moving the nucleus from a higher to a lower energy state (unstable to stable).

Gamma rays are often produced alongside other forms of radiation such as alpha or beta. When a nucleus emits an α or β particle, the daughter nucleus is sometimes left in an excited state. It can then jump down to a lower level by emitting a gamma ray in much the same way that an atomic electron can jump to a lower level by emitting visible light or ultraviolet radiation.

Gamma rays, x-rays, visible light, and radio waves are all forms of electromagnetic radiation. The only difference is the frequency and hence the energy of the photons. Gamma rays are the most energetic. An example of gamma ray production follows.

First ^{60}Co decays to excited ^{60}Ni by β decay:

$$^{60}\mathrm{Co} \rightarrow {}^{60}\mathrm{Ni}\,* + e + V\mathrm{e}$$

Then the ^{60}Ni drops down to the ground state (see nuclear shell model) by emitting two gamma rays in succession:

$$^{60}\mathrm{Ni}^{*} \rightarrow {}^{60}\mathrm{Ni} + \gamma$$

Gamma rays of 1.17 MeV and 1.33 MeV are produced.

3.4.3 Irradiator:

The radiation source is housed in a pool of demineralised water of capacity 25000, lts. In the cell area around the wall of 1.6 meter thick concrete.
An automatic system which conveys the products into the irradiation cell through labyrinth where boxes are exposed to the radiation for a specific time and are brought out automatically.

On Earth gamma rays originate largely from cosmic radiation. One high-activity source of gamma rays is cobalt-60 (^{60}Co). The products to be irradiated are packed in standard corrugated card board cartoons. these cartoons are loaded in carriers ,having five shelves .each carrier travels at a controlled speed on an over head mono rail ,enters the irradiation cell through a labyrinth ,passes each side of the source twice and return through the labyrinth ,passes each side of the source twice ;ensuring exposure of the products to a required dose .

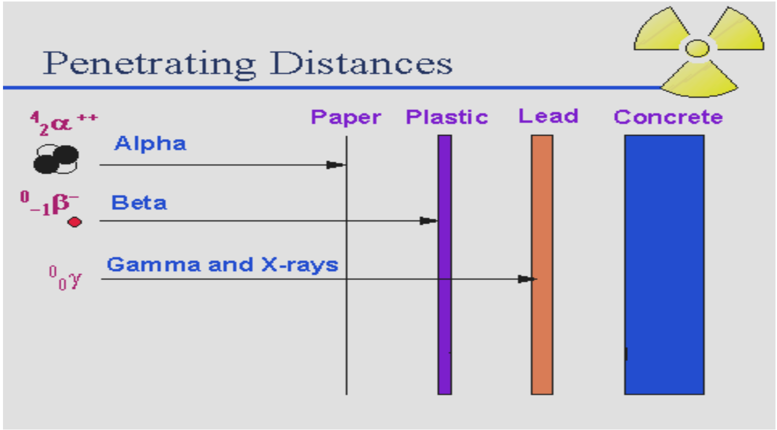


Fig.3 Penetration power of different particles.

3.4.4 EFFECT OF RADIATION ON POLYMERS:

I) Polymer Degradation:

Gamma irradiation of living species induces breaks in the DNA double helix preventing replication and hence sterilization. Damage to polymers is by a similar mechanism. all plastics are affected by radiation. Some effects are favorable or negligible while others are not. A polymer under stress is attacked more by radiation than unstressed material is.

II) Potential Problems:

A potential drawback of gamma processing, however, is that this form of high-energy irradiation can affect both the color and the physical properties of many thermoplastics. For example PVC can develop rancid oil odors from oxidized soybean & linseed oils.

3.4.5 Classes of Reactions:

1 **Recombination** -no change in properties

2 **Crosslinking** -increase in strength & decrease in elongation

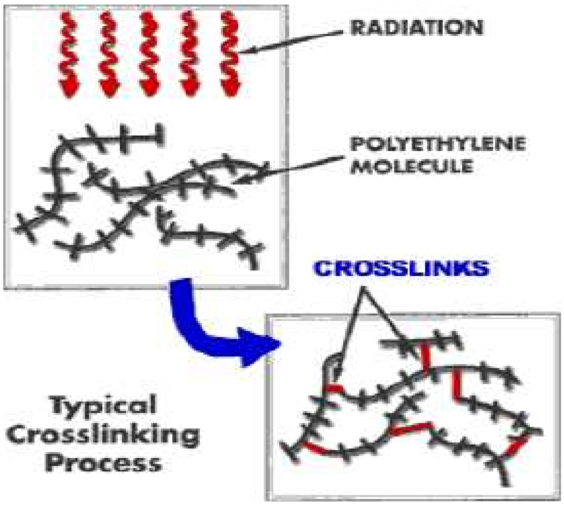


Fig.4 Cross linking in polymers.

Radiation cross linking has effects on the three main characteristics of plastics, depending on the nature of the radiation cross linkable resins which are as fallows.

a) Mechanical behaviour **:**

Radiation cross linking can confer on certain plastics (PA, PE, but not PBT for example) improved mechanical characteristics, without any dimensional change. The following changes can thus be observed in plastics are:

- Increasing hardness.
- Increasing stress at break and increasing modulus.
- Improved impact resistance.
- Improved creep resistance ,improved resistance to stress cracking and to abrasion.

b) Chemical stability on radiation in plastics

Generally, radiation cross linked plastics present an improved resistance to:

- Acid and solvents (for example, acids in the case of polyamids, organic derivates in the case of polyethylene or elastomers)
- Hydrolysis (in the case of TPE or polyamides 6 and 6-6)
- To chemical aggressive agents, like salt haze, grease, oil.
- Oil and grease resistance.

Most thermoplastics (PVC, PC, PS, ABS) experience color shift after exposure to gamma radiation .This shift is most often characterized by a yellowing effect. Phenolic antioxidants contained in most polymers are responsible for gross discoloration .

c) Thermal resistance

Of all properties, the thermal properties are enhanced most strongly after radiation . In particular, significant improvements can be observed in:

- Dimensional stability
- Heat distortion temperature (HDT)
- Creep
- Glow wire resistance
- Flame resistance

Radiation cross-linking is mainly done to improve:

- Heat Deflection Temperature (HDT)
- Tracking Resistance
- Chemical Resistance

3 Chain scission -loss of strength elongation

If chain scission dominates then low molecular weight fragments, gas evolution (odour) and unsaturated bond (colour) may appear. Plastics that crosslink more than they scission generally do better in the radiation environment. Highly crystalline polymers have higher resistance to radiation.

3.4.6 Sensitivity to Radiation:

Only a few plastics cannot be sterilized by radiation:

- Polyacetals (turns to dust)
- Polypropylene
  (unstabilize)
- Teflon (turns to wax)

- PVDF
- Polyethylene is predominantly cross linked but acceptable to irradiation
- LDPE < LLDPE < HDPE < UHMWHDPE
- PE can be stabilized to make it gamma stable

3.4.7 Applications :

It is used as cross linking agent in polymers.

Gamma rays can be used in many different situations. In radiotherapy they are replacing X-rays from expensive X-ray machines in the treatment of cancer. The rapidly growing cells of the diseased tissue which cause cancer are even more affected by radiation than healthy cells.

Medical instruments, bandages, and such like are sterilized (after packing, to prevent contamination and to make handling easier) by brief exposure to gamma rays. This treatment kills any microbiological organisms which may be on the instruments, thus preventing unintentional spreading of disease. No radioactivity is produced in the material irradiated by the gamma rays and thus this is perfectly safe.

A similar procedure is carried out on foods, extending their "life"-time considerably. For example, meat can be made stay fresh for fifteen days instead of three of four days.

CHAPTER 4

MATERIALS AND METHODS

4.1 Compounding of PVC:

Polyvinyl chloride, better known as PVC or vinyl, is an in expensive plastic so versatile it has become completely pervasive in modern society. The list of products made from polyvinyl chloride is exhaustive, ranging from phonograph records to drainage and potable piping, water bottles, cling film, credit cards and toys. More uses include window frames, rain gutters, wall paneling, doors, wallpapers, flooring, garden furniture, binders and even pens. Even imitation leather is a product of polyvinyl chloride. In fact, it's hard to turn anywhere without seeing some form of this plastic.

During the fifty years following the end of World War II, PVC has become the second most widely used plastic in the world. Today more than 20 million tonnes are Manufactured each year. In Europe the total consumption of PVC products was estimated at approximately 7.4 million tonnes in 1998, which corresponds to ca. 5.5 million tonnes of PVC polymer (ECVM). About one third of the total production of PVC polymer is used for the production of flexible PVC products, the remaining two thirds fall into the category of rigid PVC products.

Virgin PVC is thermally and photochemically unstable and depending on requirements and desired characteristics of the application, a number of additives are applied to reduce these problems prior to manufacture of PVC products. The quantitatively important classes of additives are heat stabilizers, plasticisers, and inert fillers, the latter generally added to reduce cost and get more volume for a given amount of polymer Other classes of additives for specific applications include pigments, impact modifiers, lubricants, fillers, UV stabilizers, biocides (to prevent fungal growth on flexible PVC) and antistatic agents.

In the following sections an overview is provided of the main application areas of PVC and the most important classes of additives. The average quantities of these components used in PVC products are given wherever possible. It has to be borne in mind that a wide range of applications and substances are added to different PVC products, accordingly, a more detailed and quantified inventory of components applied to PVC is hardly possible within the scope of this study.

PVC products with long and extra long service life are predominately used in the building and automotive sector, while PVC products for packaging purposes have a short service life. Except for cables, flexible PVC has a rather short to medium-term service life and the majority of rigid PVC products is in use for a long time period. PVC products with very long life-span are presently still retained in the use phase. Thus, the present PVC waste stream is not directly correlated with the current production, in particular PVC products with a comparatively long life-span used in large quantities in the building sector are just beginning to appear in the waste stream and will certainly effect future PVC waste stream composition.

All PVC products contain at the minimum a PVC polymer, a stabilizer and a lubricant. Various other components are incorporated in PVC, sometimes in large quantities with regard to the polymer. Generally, the percentage of additives varies between 10 and 25 % in weight of the resin, in the case of rigid products. Flexible PVC can contain plasticizers up to 60 % of the weight, the average content is about 30%. Although the composition of PVC products is broadly known, the actual formulation of a product differs depending on the year of production and on compounding specifics of different PVC converters, thus even in the same application (e.g. window profiles, pipes, films) the composition of the PVC material varies. In the following sections the most commonly used additives are described in brief. The effect of additives on the properties and characteristics of the product is summarised in the following overview:

4.2 Process diagram

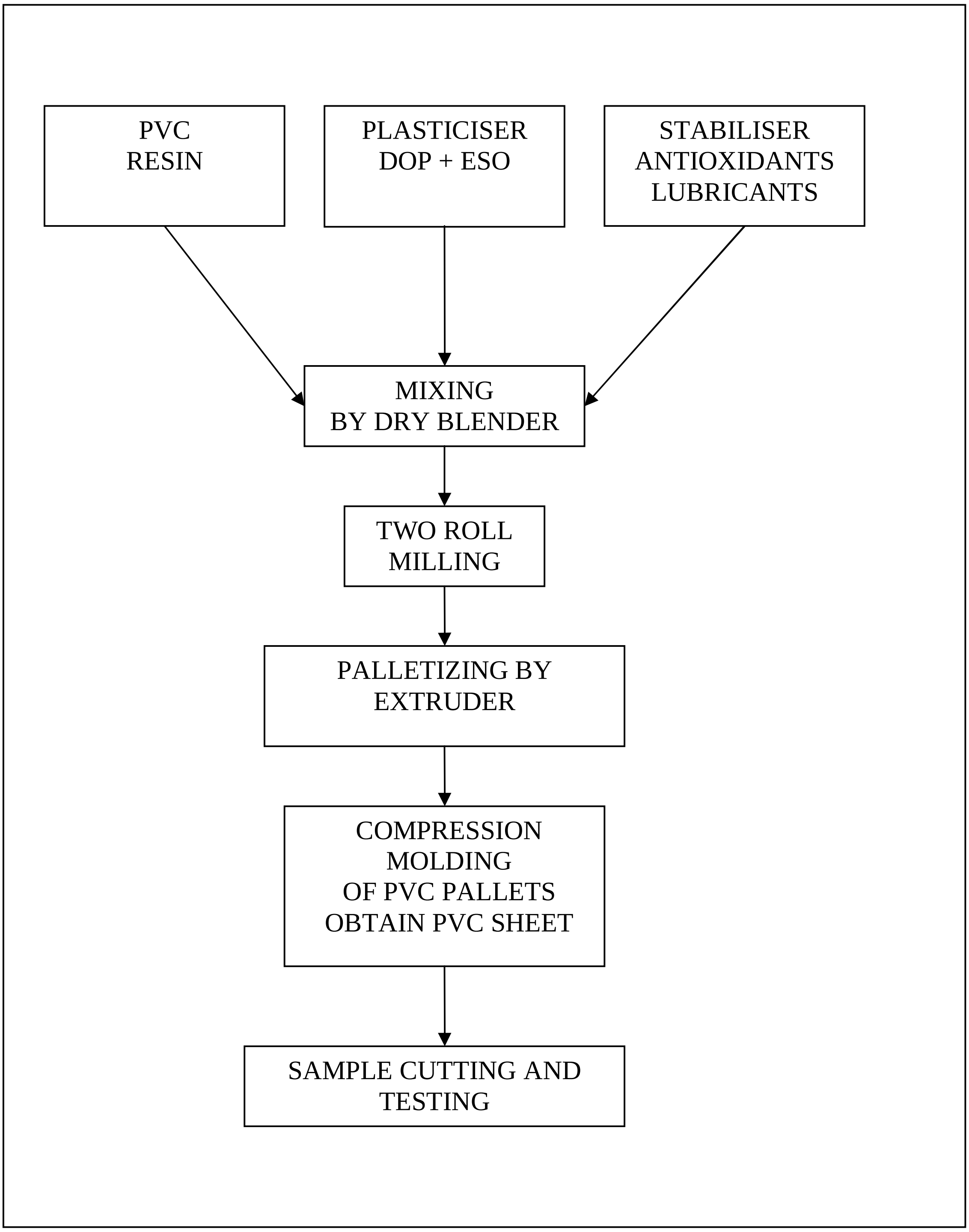


Fig. no.5 Process diagram.

4.3 Methodology Adopted:

- Detail literature survey on various aspects of the project through internet, journals chemical abstracts, Encyclopedia of Chemical Technology etc.
- Procurement of necessary raw material such as polymer resin ,PVC resin ,plasticizer ,antioxidant stabilizer etc for experimental work.
- Design and develop gamma resistant PVC formulation by incorporation of suitable compounds,plasticizers ,lubricants ,processing aid ,additives into PVC composition.
- Development and optimization of the process for making light weight gamma ray resistant PVC sheet by compression molding technique .
- Evaluation of developed gamma ray resistant PVC sheet for physical mechanical properties.

4.4 PVC Additives and their uses .

Additives	*Properties Imparted*
Anti-oxidants & other stabilizers	Slow down the rate at which the polymer will be degraded by oxygen, heat, visible light or UV radiation
Compatiblizers	Enable PVC to be mixed with other plastics and helps plastic recycling
Flame retardants	Reduce flammability of plastic
Pigments	To color the plastic
Plasticizers	To produce flexible and manageable plastic
Impact modifiers	To absorb shock without damage
Fillers	Inexpensive, inert materials that simply add bulk to the plastic

Table no. 2 PVC Additives and their uses .

Stabilizers are ingredients that are generally added to the PVC polymer in order to prevent thermal degradation and hydrogen chloride evolution during processing. And to give the finished article optimum properties like heat and UV stability. Approximately 1-8 % stabilizer may be added to PVC formulation depending on other components and the final application. The most important group of stabilizers are metal salts (i.e. calcium and zinc stearates, basic lead sulphate and lead phosphite), Organo metals (i.e. mono- and diorganotin, tin thioglycolate) ,Organo phosphites (i.e. trialkyl-phosphites),Epoxy compounds (i.e. epoxidised soya bean oil, sunflower oil and linseed oil) Antioxidants, polyols (i.e. BHT, pentaerythritol) .

Tinuvin P has been used as Ultraviolet stabilizer

Plasticizers:

Phthalates are the most widely used plasticisers, primarily to make soft and flexible polyvinyl chloride (PVC) for the applications in the industry of automotive, building & construction material, cable, flooring, medical device and toys. Phthalates make the long polyvinyl molecules to slide against one another commonly used plasticizers are DOP , DIDP, ESO**.** DIDP has properties of volatility resistance, heat stability and electric insulation . The typical content of DIDP in flexible PVC products is between 25 and 50%. **ESO** is used to keep plastics and rubber soft and pliable. The epoxy functionality provides excellent heat and light stability. They are replacing for DOP (dioctyl phthalate) due to its biodegradability over traditional phthalate plasticizers

Lubricants:

These are used in amounts of 1 – 4 weight %, they are added to prevent the plastic from adhering to the metal walls of the molding machines, and to modify the properties of mixtures. Examples of such lubricants are waxes, fatty acids (stearic acid etc), and fatty alcohols, etc.

Fillers:

These are added to improve certain properties, i.e. mechanical and electrical resistance, and may comprise 50% of a PVC formulation. In rigid PVC for building applications, no more than 5 % fillers are added. The main fillers are of mineral origin: calcium carbonate (limestone), talc, chalks etc.

These are mainly organic pigments and coloring agents and mineral pigments (titanium oxide, iron oxide, chromium oxide, cadmium oxide, etc). Typical amounts are 0.1 weight%, but up to 15% may be used in extraordinary cases.

In many applications, the presence of chlorine in PVC provides satisfactory fire performance, but the addition of flame retardants is used in particular in some flexible PVC building materials in relatively high concentrations – up to 10 – 20 weight %. Flexible PVC has a lower chlorine-content than rigid PVC and is therefore more flammable.

Flame-retardants:

The chlorinated paraffins used are almost exclusively of medium chain length or longer Chlorinated paraffins also have plasticising properties and therefore are also used as secondary plasticizer for PVC products such as floorings, cable insulation, garden hoses, coatings, and shoes.

Other additives:

These are added for specific purposes, such as biocides or fungicides. Impact modifiers are used in concentrations of up to 15 weight % to improve the impact resistance of rigid PVC.

In its massive form , PVC is a hard, horny, rigid material with a characteristic tendency to stick to metallic surfaces at elevated temperatures, and therefore difficult to process. However, PVC can be conveniently processed to rigid items if only it is compounded with various ingredients such as fillers, plasticizers extenders and other process aids.

All flexible applications of PVC depend on significant use of plasticizers. Depending on plasticizer percentage, fully rigid to highly flexible finished products can be obtained. Chlorinated paraffin and the phosphate plasticizers are used in fire retardant compounds.

Compounded PVC is converted into moulded objects by melt processing or by processing of PVC pastes and lattices. Widespread processing techniques included injection moulding, extrusion, calendaring, blow moulding and thermoforming.

4.5 PVC Processing :

4.5.1 Dry Blending :

Dry blends of PVC formulations for gamma radiation were prepared by a sequential blending process . PVC resin and thermal stabilizer were first charged to steam heated jacketed ribbon blender at 80 ^{0}C and allowed to mix for 10 minutes .the required amount of plasticizer, lubricants, antioxidants .etc were then added and allowed to blend with PVC for 30 minutes till free flowing powder blend was obtained .the resulting dry blend was than discharged from the ribbon blender.

4.5.2 Two roll mill:

It is the process to convert the reduced size lumps of the semi gelled dry blend powder into homogenous PVC sheet by milling. lumps are fed between the two anticlockwise rotating heated steel cylinders at 120-125 ^{0}C for about 5-10 min. By this we get perfect mixing.

4.5.3 Extrusion Processes:

Extrusion is the process where a solid plastic usually in the form of beads or pellets, is continuously fed to a heated chamber and carried along by a feedscrew within. The feed screw is driven via drive/motor and tight speed and torque control is critical to product quality. As it is conveyed it is compressed, melted, and forced out of the chamber at a steady rate through a die. The immediate cooling of the melt results in re-solidification of that plastic into a continually drawn piece whose cross section matches the die pattern. This die has been engineered and machined to ensure that the melt flows in a precise desired shape.

Plastic pellets or beads (also referred to as resin) are fed from the hopper along a feed screw through a barrel chamber. As the resin travels along the barrel, it is subject tom friction, compression, and heated zones.

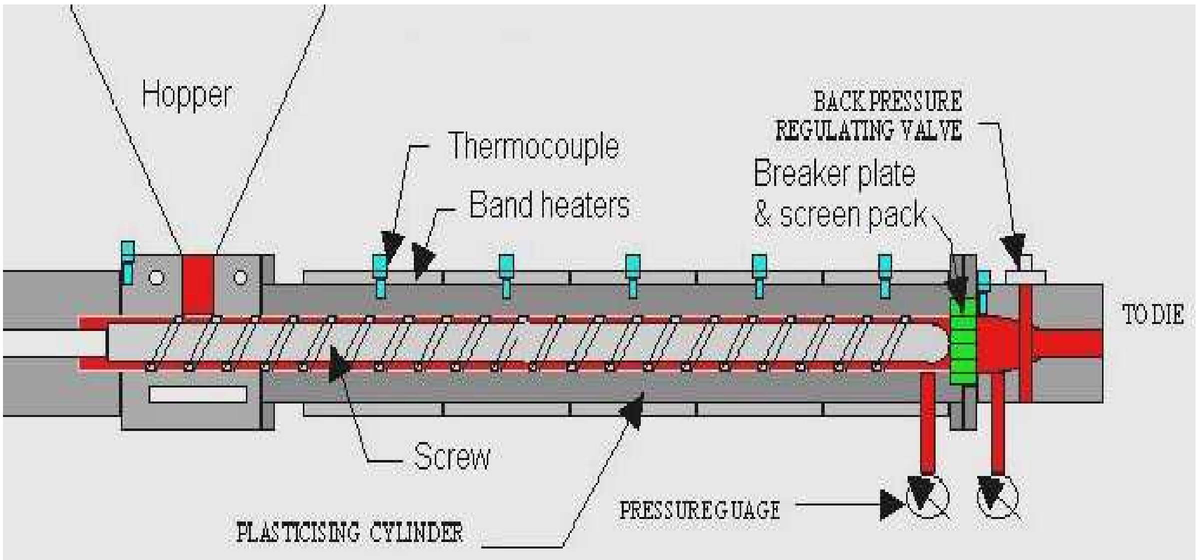


Fig.6 Extruder screw.

The result is that the resin melts and further travel at the exit end of the screw serves to mix the melt homogeneously. The melt enters a chamber designed to ensure an evenly distributed flow to the die. In many machines, a melt pump is used to prevent any pressure surges. Also, breaker plates serve to prevent any solid particles or foreign objects from passing through the die. The die is a precisely machined part with a patterned opening such that the extruded plastic takes that die pattern for its cross sectional area. With products such as extruded sheet, there are adjustments to the die to allow for a variety of sheet thicknesses with one die. Shapes are varied, and typically are holes for filament, annular rings for pipe and tube. All die surfaces must be free from defects otherwise unwanted patterns will appear on the extruded product. Product from the die solidifies quickly. Depending on the end

4.5.3.1 Various zones of the screw:

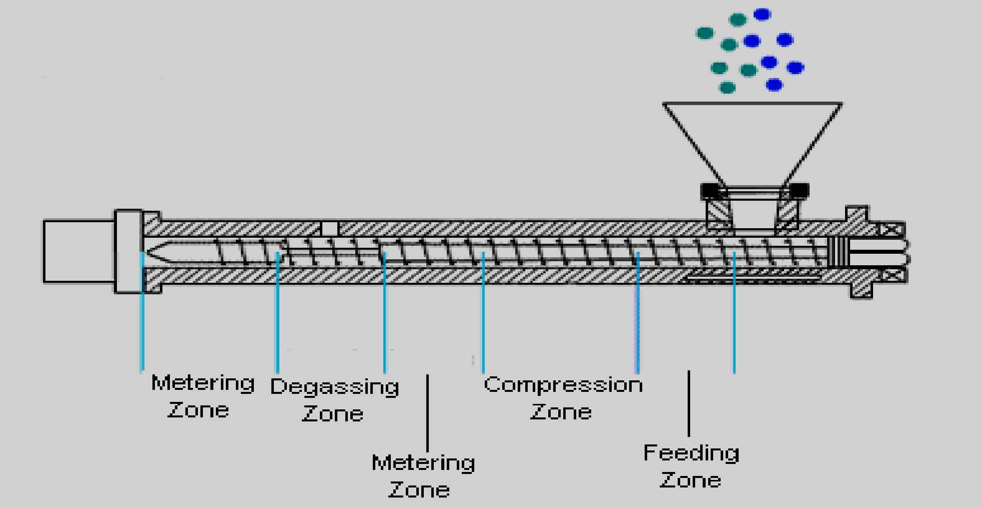


Fig.7 Various zones of the screw.

Feed zone :

The feed zone takes resin from the hopper and conveys it along. During the journey, resin pellets encounter friction from feed screw surfaces, barrel surfaces, and each other. so it is critical that the drive equipment to turn the screw have the HP capabilities to overcome friction and turn the feed screw at a steady and controlled rate. Some extruders can continue to plasticate materials long after their external heat sources are shut down.

Compression zone:

The compression zone is next. Here, the channel depth between screw flights diminishes and the result is to pressurize the now melting resin. Friction, barrel heating, and compression in this stage should complete the melting process. Two important design parameters are associated with this zone.

(a) The compression ratio is measured as the channel depth at the end of this zone divided by the channel depth in the feed zone. Different compounds or operating pressures require different compression ratios.

(b) The length of the compression zone affects the rate of compression. These two parameters will be different for different compounds.

Metering zone:

The metering zone has a constant channel depth and primarily exists to further mix molten resin. The end result is a smooth consistent melt with uniform temperature.

De-gassing zone :

In some processes, a de-gassing or de-volatizing section is required. This is a shorter zone that immediately follows the compression zone (See figure.3) . Channel depth is suddenly increased, and the resulting pressure drop causes a release of any gas, which can be vented or drawn off via vacuum pump. The remaining melt is re-compressed and meter

4.5.4 Compression molding :

In this technique, small pieces of PVC sheets were placed between the gaps of a highly polished steel mould, which was then pressed between two halves of the compression molding machine. The mould was then heated by electric heaters, fitted with two halves (upper & lower) of the molding machine. The PVC material was molten and acquired the space in the mould. The mould was then allowed to cool by switching off the heaters and circulating water into the machine. The machine was then opened and the mould was removed. The PVC sheet was released from the mould.

In order to obtain a satisfactory molding, a slight excess of the molding material (PVC) was placed in the mould so that a thin skin of material, i.e., flash was extruded from the mould. Finally, a uniform molded PVC sheet was obtained.

Fig. no.7 Compression molding machine.

The conditions employed for compression molding were:

- Molding temperature =(150 -155 ^{0}C)
- Molding pressure = Sequential increase up to 30 tons
- Total time for molding =20 min + cooling time (25 min)
- Sheet dimension = 8’ X 8’ X 3mm

In compression molding there are 4 important considerations that have to bear in an engineer mind :

a) Selection of proper amount of the materials.

c) Determination of minimum time required to heat the compound as well as the appropriate heating techniques.
d) The prediction of required force to make sure that every volume of the melt has the desired shape.
e) Temperature of the molds should decrease rapidly during the cooling process.

4.6 Tensile Strength (ASTM D 638)

Tensile tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. The data is often used to specify a material, to design parts to withstand application force and as a quality control check of materials.

Specimens are placed in the grips of the Instron at a specified grip separation and pulled until failure. For ASTM D638 the test speed is determined by the material specification. For ISO 527 the test speed is typically 5 or 50mm/min for measuring strength and elongation and 1mm/min for measuring modulus. An extensometer is used to determine elongation and tensile modulus.

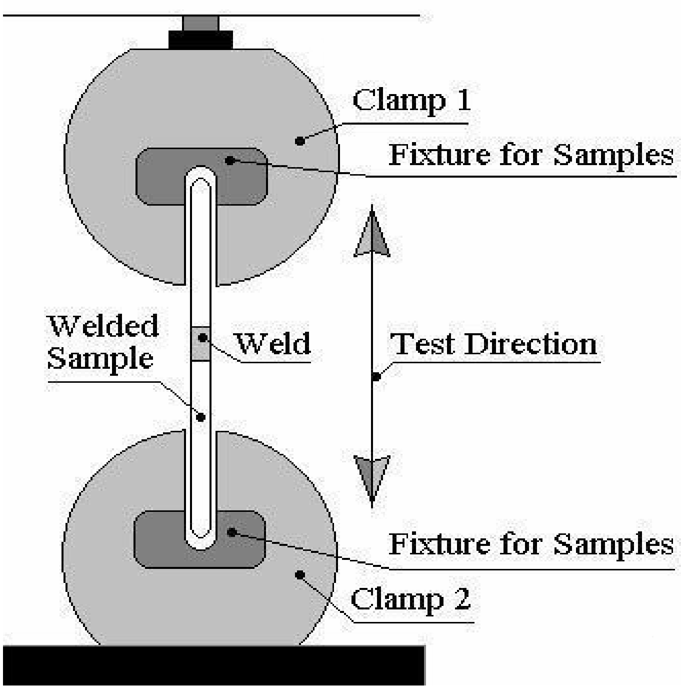


Fig.9 Tensile testing diagram

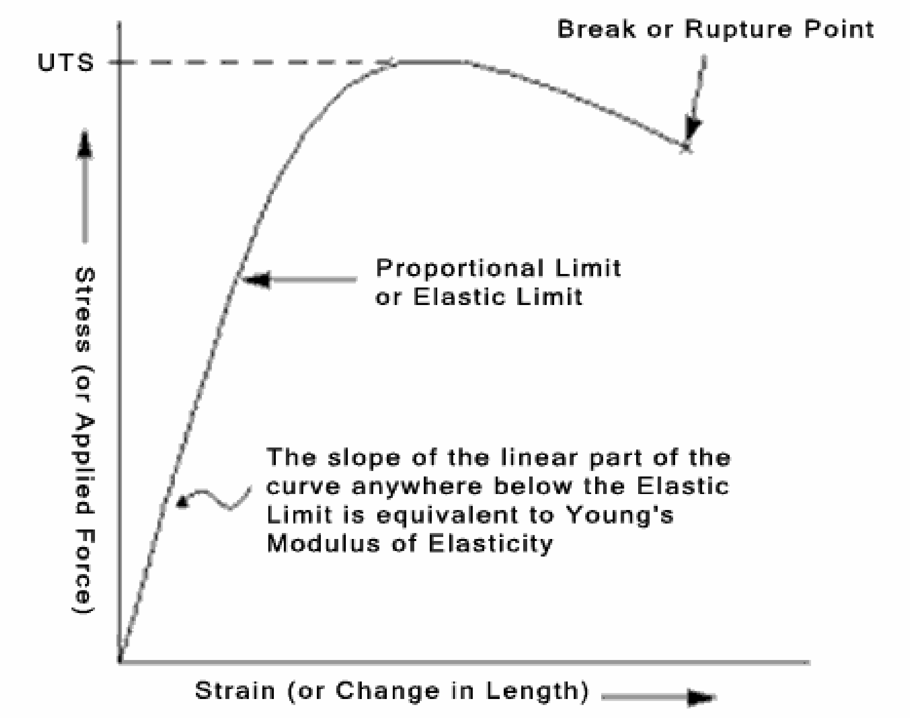


Fig.10 Stress strain curve for tensile testing

4.7 Density :

Density of PVC material is determined by water displacement method.

The density of a solid is a property that can be measured conveniently to identify a material, to follow physical change in a sample, to indicate degree of uniformity among different sampling units or specimens, or to indicate the average density of a large item. Density was determined as per ASTM D 792.

The specimen was weighed in air. The specimen was then tied with a fine wire and suspended from the balance head into the immersion vessel (filled with distilled water) placed so on a support. Sufficient care was taken such that the specimen and the wire did not touch the vessel and there were no bubbles adhering to the specimen, wire or vessel. The suspended specimen was then weighed.

Density of the specimen was calculated as follows:

$$\textbf{Density} = \frac{\textbf{Wt. of specimen in air}}{\textbf{Wt. loss in water}} \times \textbf{Sp. gravity of water at } 23^{0}\text{C}$$

4.8 Tear Strength (ASTM D 624)

Tear Strength is the force required to rip a sample of plastic film, sheeting or rubber product. An unnicked 90-degree angle specimen is used to measure the tear resistance .

Calculation:

Calculate the resistance to tear from the maximum force registered by the testing machine and the thickness of the specimen, and express as the force in newtons (or kilogram, pounds-force) required to tear a specimen 1 m (or 1cm, 1 inch) in thickness.

Tear Strength = F / t

where:
F = force, N (kg, lbf).
t = specimen thickness, m (cm, inch).

4.9 Hardness Shore A (ASTM D 2240)

Durometer Hardness is used to determine the relative hardness of soft materials, usually plastic or rubber. The test measures the penetration of a specified indentor into the material under specified conditions of force and time. The hardness value is often used to identify or specify a particular hardness of elastomers or as a quality control measure on lots of material. Shore A hardness of plastic sheet before and after radiation were determined as per ASTM D 2240.

The specimen is first placed on a hard flat surface. The indentor for the instrument is then pressed into the specimen making sure that it is parallel to the surface. The hardness is read within one second (or as specified by the customer) of firm contact with the specimen.

Specimen size:
The test specimens are generally 6.4mm (¼ in) thick. It is possible to pile several specimens to achieve the 6.4mm thickness, but one specimen is preferred.

Data:
The hardness numbers are derived from a scale. Shore A and Shore D hardness

scales are common, with the A scale being used for softer and the D scale being used for harder materials.

CHAPTER 5

RESULTS AND DISCUSSION

Different batches of the ingredients were prepared by taking different quantity of the ingredients. The composition of each batch is shown below in the table.

S.N	INGRADIENTS	BATCH (1) Phr	BATCH (2) Phr	BATCH (3) Phr	BATCH (4) Phr	BATCH (5) Phr
1	PVC	100	100	100	100	100
2	DOP	40	40	45	45	45
3	DIDP	10	10	10	10	20
4	NBR	---	5	---	5	10
5	ESO	7	7	7	7	7
6	OTM	3	3	3	3	3
7	Steric Acid	0.5	0.5	0.5	0.5	0.5
8	Calcium sterate	0.5	0.5	0.5	0.5	0.5
9	Bisphenol A	2	2	2	2	2
10	TNPP	0.4	0.4	0.4	0.4	0.5
11	Uvitex OB	0.2	0.2	0.2	0.2	0.2

Table.3 Plasticized PVC compositions

S.N	INGRADIENTS	BATCH (6) Phr	BATCH (7) Phr	BATCH (8) Phr
1	PVC	100	100	100
2	DOP	10	60	60
3	DIDP	10	10	10
4	NBR	3	5	20
5	ESO	5	7	5
6	OTM	3	3	3
7	Steric Acid	1	0.5	0.5
8	Calcium sterate	--	0.5	0.5
9	Bisphenol A	2	2	2
10	TNPP	0.4	0.4	0.4
11	Uvitex OB	0.2	0.2	0.2

Table 4 Plasticized PVC compositions

The compositions of all of these batches were processed through different operations to prepare the samples for testing of different mechanical properties.

All samples prepared from these batches were tested and the mechanical properties of these samples are arranged in the tables as shown below

BATCH 1

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	130	119	107	98	100
Elongation %	170	138	122	109	103
Hardness Shore A	80	78	77	71	69
Tear Strength (Kg/cm)	67	59	51	32	28
Specific Gravity	1.215	1.212	1.209	1.207	1.205

Table 5 Properties profile of gamma irradiated PVC Composition Batch 1

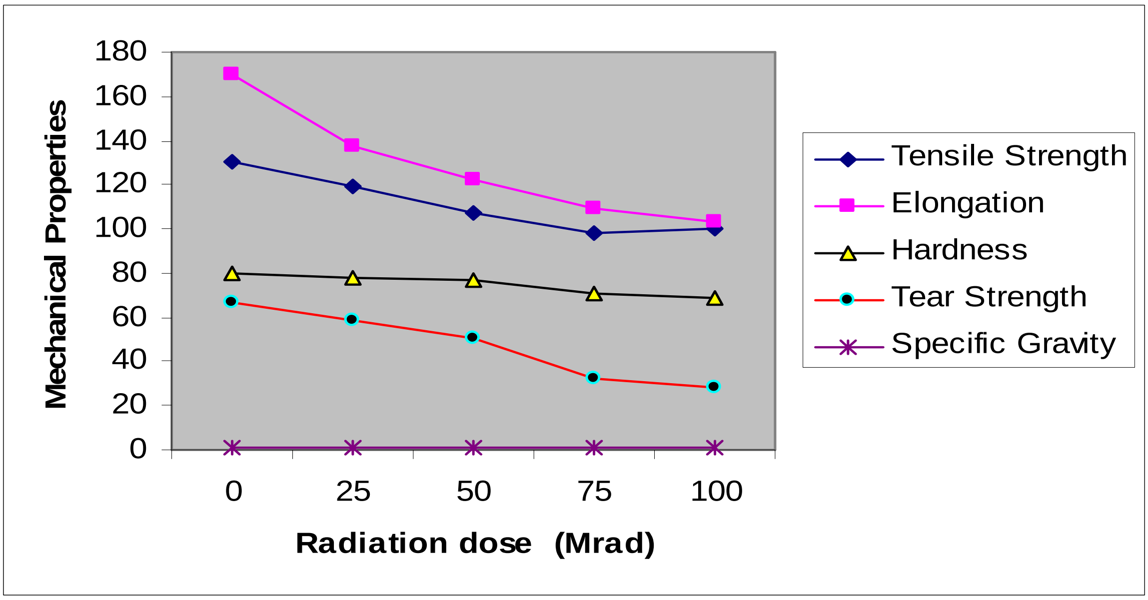


Fig.11 Effect of Radiation dose on properties of PVC Batch 1

BATCH 2

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	150	131	123	114	102
Elongation %	255	203	181	145	114
Hardness Shore A	78	77	75	74	73
Tear Strength (Kg/cm)	51	34	28	27	23
Specific Gravity	1.195	1.195	1.194	1.195	1.194

Table 6 Properties profile of gamma irradiated PVC Composition Batch 2

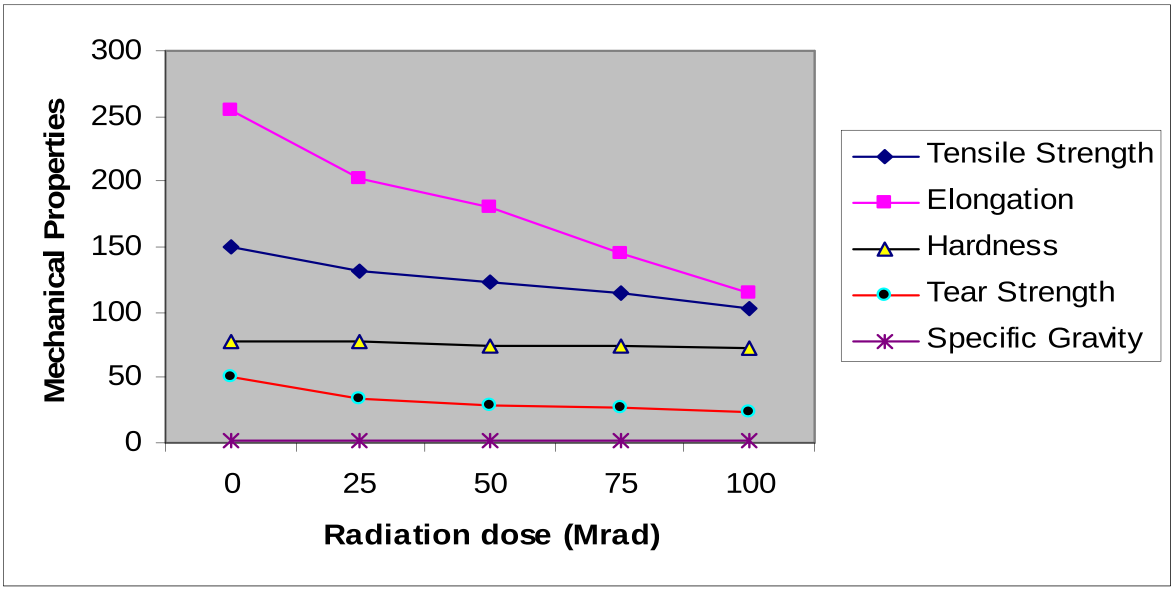


Fig.12 Effect of Radiation dose on properties of PVC Batch 2

BATCH 3

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	140	123	111	110	107
Elongation %	220	172	153	146	139
Hardness Shore A	77	76	76	75	75
Tear Strength (Kg/cm)	56	54	51	47	48
Specific Gravity	1.202	1.201	1.20	1.20	1.20

Table 7 Properties profile of gamma irradiated PVC Composition Batch 3

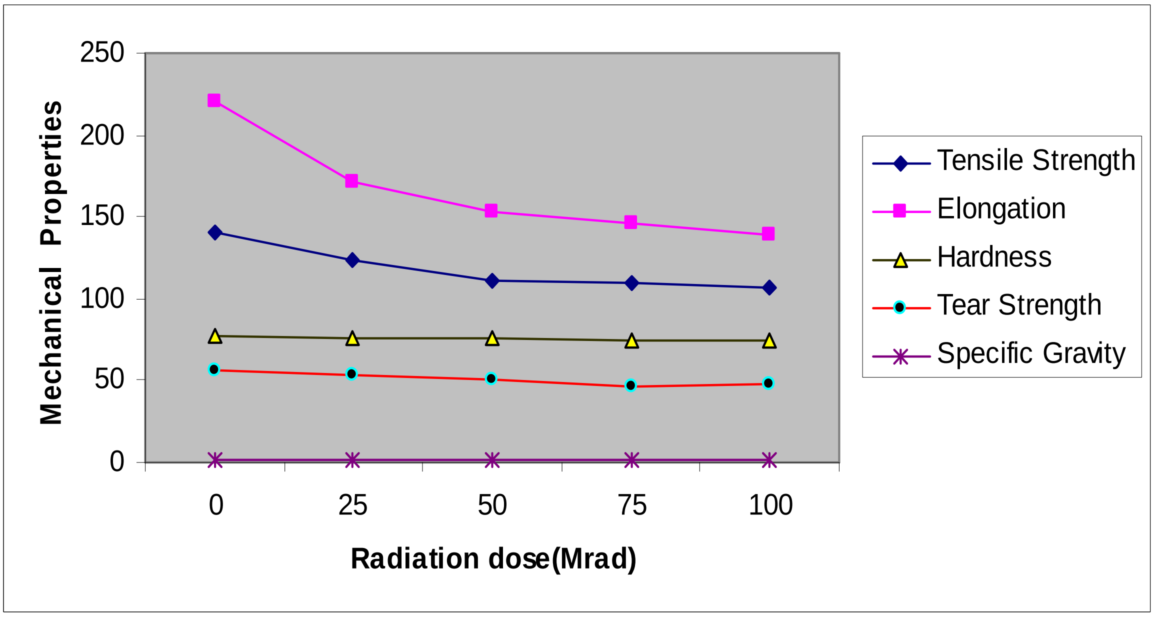


Fig.13 Effect of Radiation dose on properties of PVC Batch 3

BATCH 4

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	150	133	121	114	109
Elongation %	271	210	170	127	95
Hardness Shore A	76	74	74	73	72
Tear Strength (Kg/cm)	49	43	39	34	31
Specific Gravity	1.195	1.93	1.190	1.190	1.190

Table 8 Properties profile of gamma irradiated PVC Composition Batch 4

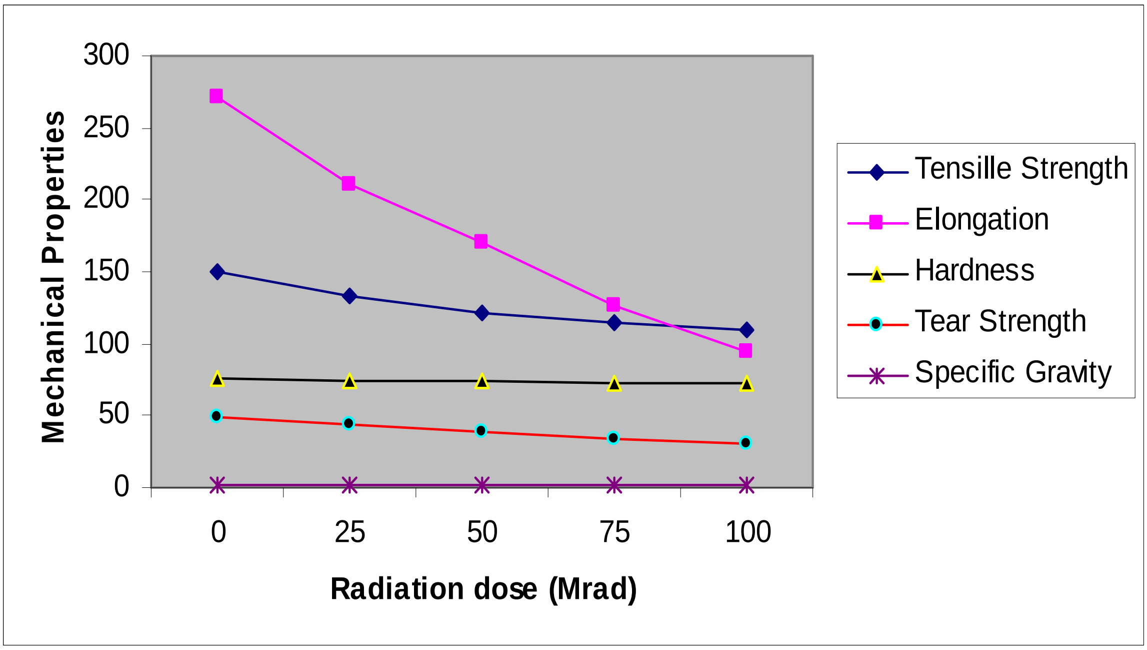


Fig.14 Effect of Radiation dose on properties of PVC Batch 4

BATCH 5

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	140	110	110	100	90
Elongation %	280	160	115	81	40
Hardness Shore A	74	78	81	83	84
Tear Strength (Kg/cm)	82	40	31	27	25
Specific Gravity	1.75	1.42	1.31	1.27	1.2

Table 9 Properties profile of gamma irradiated PVC Composition Batch 5

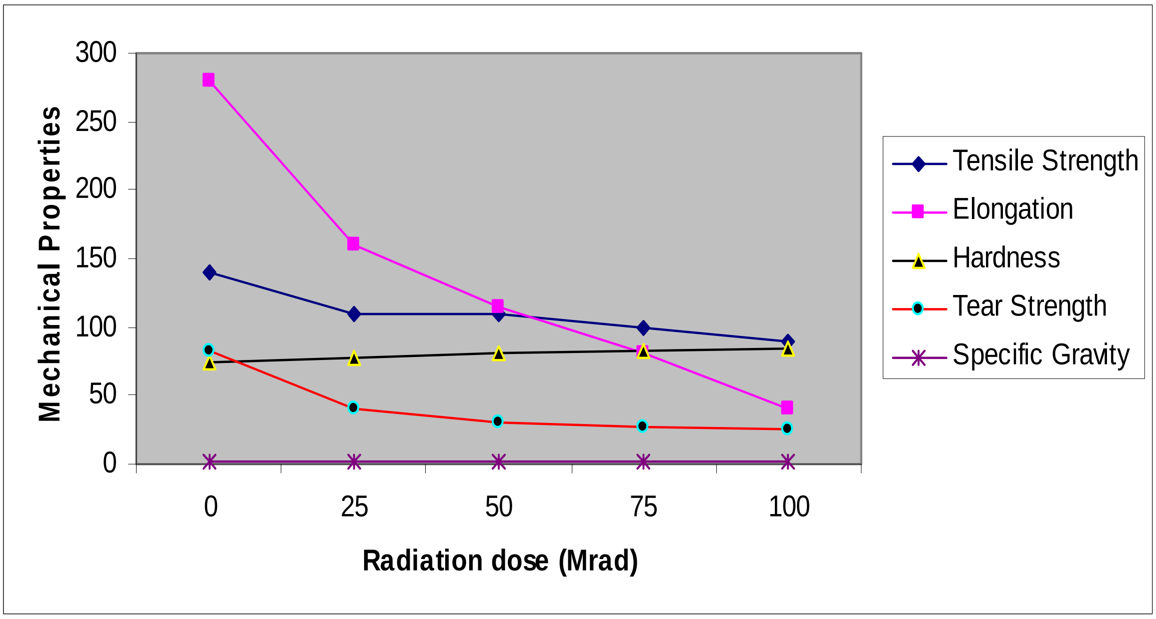


Fig.15 Effect of Radiation dose on properties of PVC Batch 5

BATCH 6

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	118	121	124	127	128
Elongation %	255	183	171	166	100
Hardness Shore A	85	74	73	73	73
Tear Strength (Kg/cm)	41	33	27	24	24
Specific Gravity	1.273	1.247	1.258	1.233	1.220

Table 10 Properties profile of gamma irradiated PVC Composition Batch 6

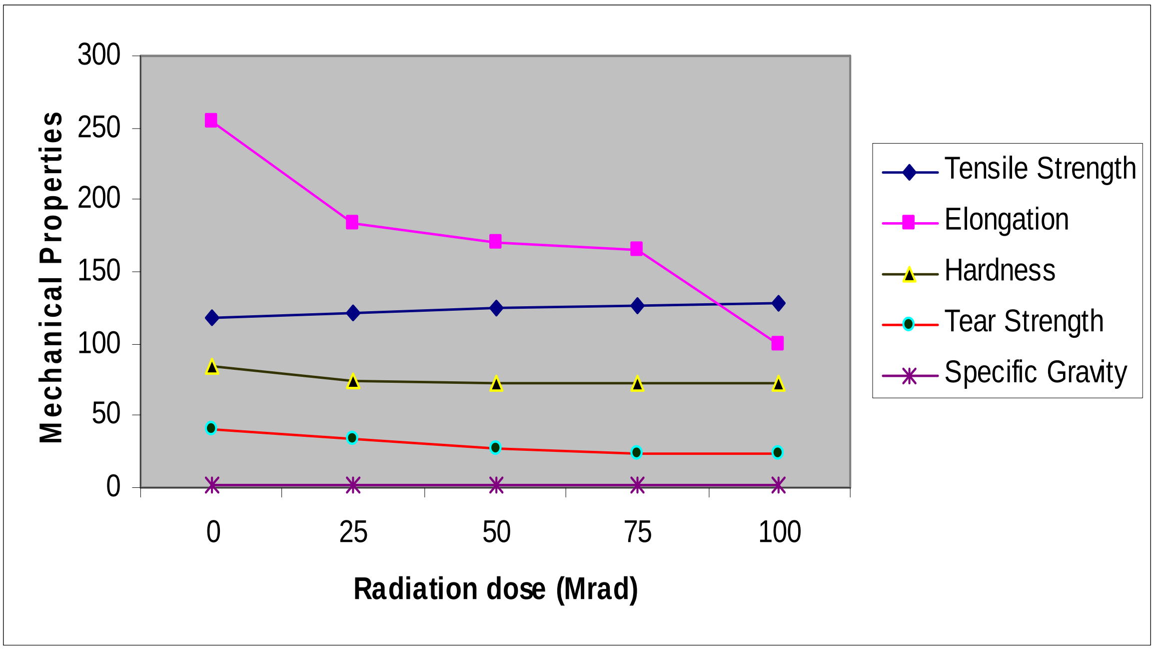


Fig.16 Effect of Radiation dose on properties of PVC Batch 6

BATCH 7

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	140	100	90	80	80
Elongation %	360	209	193	191	187
Hardness Shore A	71	74	72	70	66
Tear Strength (Kg/cm)	73	53	47	44	43
Specific Gravity	2.08	1.82	1.71	1.43	1.21

Table 11 Properties profile of gamma irradiated PVC Composition Batch 7

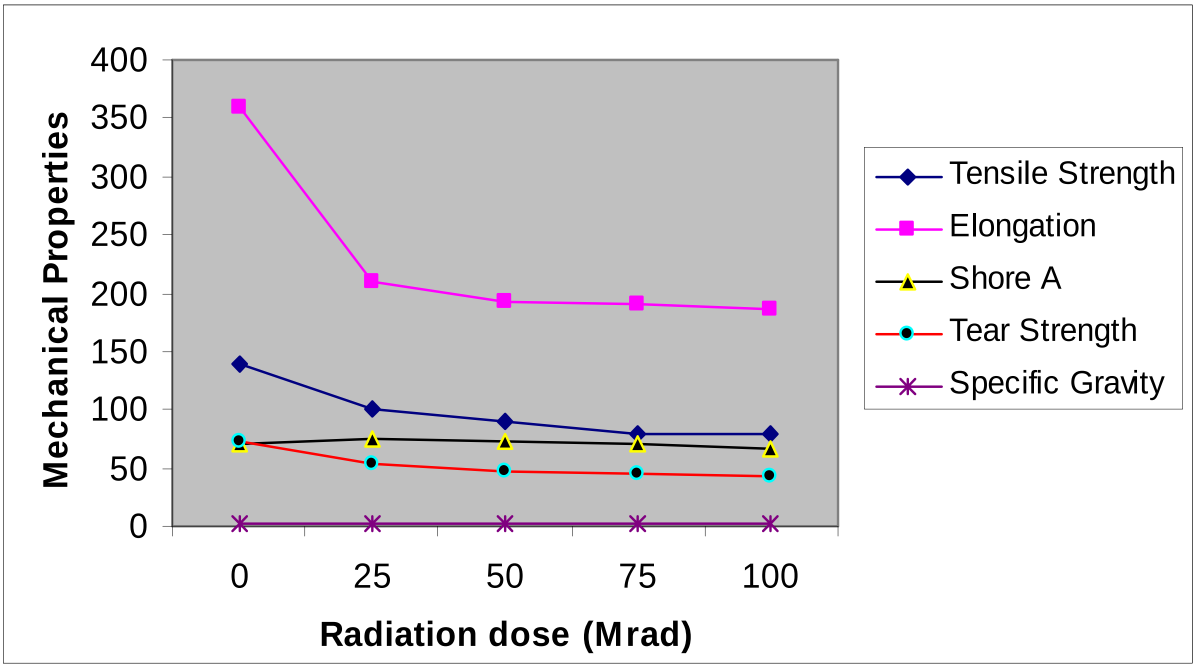


Fig.17 Effect of Radiation dose on properties of PVC Batch 7

BATCH 8

Properties	Before Radiation	After Radiation			
	0 Mrad	25 Mrad	50 Mrad	75 Mrad	100 Mrad
Tensile Strength (Kg/cm^2)	120	100	90	80	80
Elongation %	345	263	251	203	179
Hardness Shore A	72	81	70	72	70
Tear Strength (Kg/cm)	73	53	45	39	23
Specific Gravity	1.75	1.53	1.47	1.33	1.21

Table 12 Properties profile of gamma irradiated PVC Composition Batch 8

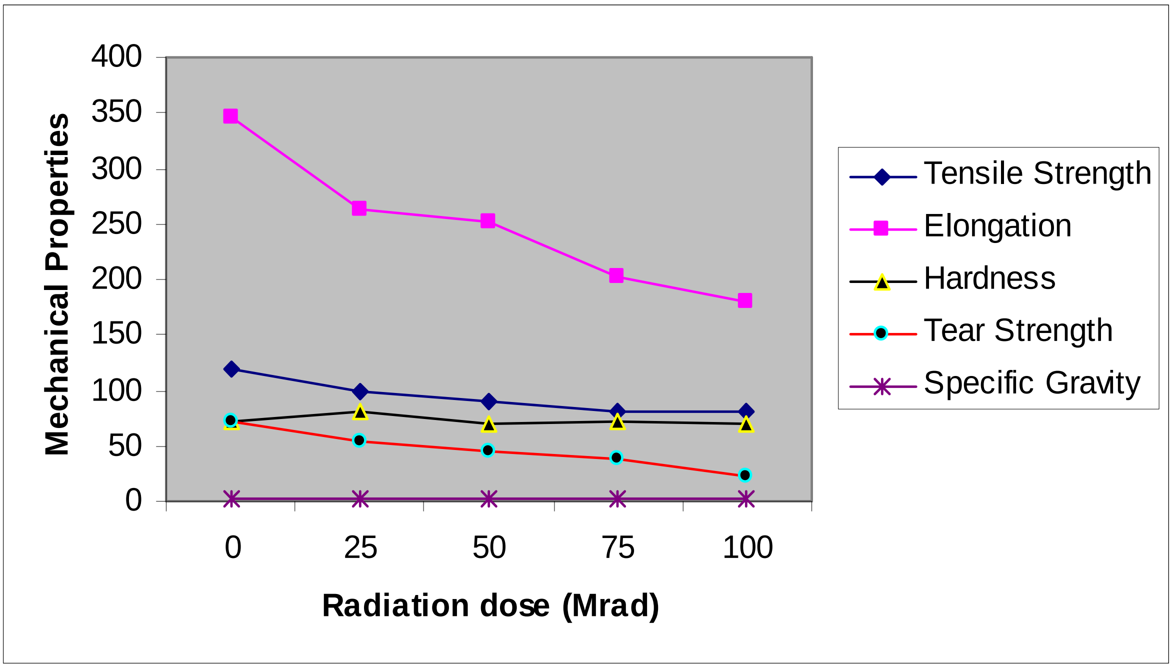


Fig.18 Effect of Radiation dose on properties of PVC Batch 8

Conclusion

The outcome of the research work are as fallows:

The results of Tensile Strength ,Tear Srength Hardness ,Elongation % at break of different samples before and after radiation depicts the effect of various doses of gamma radiation ranging 25-100 M.rad . Mechanical properties of the plasticized PVC sheet can be easily changed with gamma radiation. With plasticizer Tear Strength decreases, and with increasing radiation tear further decreases. Tensile and Elongation increases with plasticizer as well as NBR but decreases with radiation dose strength . On the surface hardness it is observed that the hardness values of pure PVC is higher than the corresponding hardness values of the irradiated specimens .This clearly indicates as we increases the dose the hardness of PVC decreases due to degradation of PVC. Density also decreases with radiation dose.

Color changes in irradiated polymers are very strongly depended upon the dose of radiation.PVC turns black under heavy irradiation as do most organic chemicals but the range of dose in which discoloration varies widely depends on the chemical structure of the polymer . color changes occurs when various plastics containing dyes or pigments are subjected to radiation .color of plasticized PVC sheet changes from light yellow to dark black at 100 Mrad.

Thus by applying different strength radiation dose we can develop a PVC sheet which can remain stable under certain extent of radiation.

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