

**STUDIES ON SOME GAMMA RADIATION RESISTANT
PVC-PLASTISOL FORMULATIONS**

A Major Project Report submitted in partial fulfillment for the award of the degree

of

MASTER OF TECHNOLOGY

in

POLYMER TECHNOLOGY

by

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(2010/PST/11)**

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CERTIFICATE

This is to certify that the M.Tech major project entitled “**Studies on some Gamma Radiation Resistant PVC-Plastisol Formulations**” has been submitted by **Ms R. Mrudhula**, for the award of the degree of Master of Technology in Polymer Technology is a record of bonafide work carried out by her. Ms R. Mrudhula has worked under our guidance and supervision and has fulfilled the requirements for the submission of the dissertation. The project work has been carried out during the session 2012-2013.

To the best of our knowledge and belief, the contents therein is her own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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ACKNOWLEDGEMENT

I would like to acknowledge my deep gratitude to all those who have been kind enough to extend their help and support to me in various ways, directly or indirectly, throughout my project and have seen its materialization in the form of this thesis.

I would like to thank my Institutional guide Dr. Saurabh Mehta (Assistant Professor, Department of Applied Chemistry & Polymer Technology, Delhi Technological University, Delhi) for his care and guidance throughout my M.Tech course.

I would also like to thank the management of Shriram Institute for Industrial Research, Delhi, for giving me this opportunity to carry out this project work in their esteemed MSD. I would like to express my gratitude to my external guide Dr. R. K. Diwan (Sr. Asst. Director & Chief (MSD) for giving me an opportunity to complete my M.Tech. project work under his selfless guidance. He not only proposed this project but also obliged me with his valuable suggestions at every step of the project. For me it was a privilege to work with his research team at the Shriram Institute for Industrial Research, Delhi.

I am very much grateful to the authorities of Shriram Institute for Industrial Research, Delhi especially Sh. K. M. Chacko, Director and Sh. U. K. Niyogi, Jt. Director for permitting me and enabling me to pursue my research work.

I would like to thank Sh. Vinay Kumar Tyagi, Sh. Parveen Gogia, Sh. Bhuvaneshwar Rai and Ms. Mayuri Gupta of Shriram Institute for Industrial Research for their continuous guidance, advice encouragement and most importantly for their patience. I also would like to thank Sh. Aman Verma of Delhi Technological University. Without their consistent support this work would not have been a success.

I wish to appreciate my husband Dr. B. Madhusudhana Reddy for his constant encouragement throughout the period of this work. I thank my children B. Nivedit Reddy and B. Charuhas Reddy for their continuous encouragement, cooperation and support. I thank one and all, who helped me directly or indirectly for completing this research work.

Lastly, I desire to record here my sincere thanks to my colleagues for their friendly co-operation and co-ordination and also to all those whose names I forget to mention but who in different ways have helped and encouraged me.

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ABBREVIATIONS USED

1.	ASTM	:	American Society for Testing and Materials
2.	cP	:	Centipoise
3.	Cs-137	:	Cesium 137
4.	Co-60	:	Cobalt 60
5.	DONP	:	Di iso nonyl phthalate
6.	DOP	:	Di Octyl phthalate
7.	DOA	:	Di-2-ethyl hexyl adipate
8.	DIDP	:	Di-iso decyl phthalate
8	ESO	:	Epoxydised Soyabean oil
9	EVA	:	Ethylene vinyl acetate
10	γ	:	Gamma
11	T _g	:	Glass transition temperature
12.	g/l	:	grams per litre
13.	g/cm ²	:	Grams per square centimeter
14.	Hz	:	Hertz
15.	MPa	:	Mega pascal
16.	Mrad	:	Mega rad
17.	μ	:	Micron
18.	mg/l	:	milligrams per litre
19.	mm	:	millimeter
20.	N/mm	:	Newton per millimeter
21.	phr	:	Parts per hundred resin
22.	pm	:	Pico meter = 10 ⁻¹² m
23.	PVA	:	Poly vinyl acetate
24.	PVC	:	Polyvinyl chloride
25.	SEM	:	Scanning Electron Microscope
26.	m ² /g	:	square metre per gram
27.	m ² /kg	:	square metre per Kilogram
28.	TMA	:	Tri millitic anhydride
29.	TMPTMA	:	Trimethyl propane tri methacrylate
30.	UV	:	Ultra Violet rays
31.	UTM	:	Universal testing Machine
32.	VCM	:	Vinyl chloride monomer

ABSTRACT

An attempt is made to develop the radiation resistant PVC sheets for making aprons for the personnel working in the areas contaminated with radiation in the oncology departments in the hospitals and also to protect from accidental exposure of high radiation dose during medical examinations. This includes development of radiation resistant PVC plastisol formulation and making of sheets from it, study of physico-mechanical and thermal stability properties of developed compositions, study the effect of radiation on the physico-mechanical properties of developed compositions and weatherability study of developed compositions.

DOP concentration was changed apart from changing crosslinking agents and exposed to various doses of gamma radiation. Results show that PVC plastisol with 3 phr of TMPTMA have shown good/improved mechanical properties up to 25 Mrad gamma radiation exposure. Thermal stability and artificial weatherability of the developed formulation was also observed to be good. The developed compositions may find applications for making radiation protection apron.

AIM AND OBJECTIVE

The main objective of the present work is to develop the radiation resistant PVC plastisol materials using the cross linking agent, and preparation of PVC sheets which can be used for making aprons for the personnel working in the areas contaminated with radiation.

Objectives

- To develop radiation resistant PVC plastisol formulations.
- To study physico-mechanical and thermal stability properties of developed compositions.
- To study the effect of radiation on the physico-mechanical properties of developed compositions.
- Weatherability study of developed compositions.

CHAPTER-1

INTRODUCTION

1.1 General: Radiation is the emission and propagation of emissions energy through space and material medium in the form of waves or by extensive corpuscular emissions such as alpha or beta particles. This is emitted due to the instability of the nucleus of certain atoms, in this process spontaneous emission of alpha, beta and gamma particle radiations is accompanied.

Particle radiation consists of a stream of charged or neutral particles, both charged ions and subatomic elementary particles. This include solar wind, cosmic radiation, and neutron flux in nuclear reactors.

Electromagnetic radiation consists of emissions of electromagnetic waves, the properties of which depend on the wavelength. This includes X-rays, Gamma Radiation, and UV-radiation.

Out of the above two types of radiation, electromagnetic radiations are the most useful radiation sources which are being widely used in polymer industries for structural modification, crosslinking, functionalization of the polymer surface as well as for characterization of material (viz. FTIR, UV, XRD, SEM, TEM), sterilization of medical and hygienic products, treatment of patients suffering with various disease (viz. cancer) and medical diagnosis (viz. X-ray, MRI, CT scan).

Gamma radiation has a very short wavelength and high energy. Gamma radiation is the most penetrating form of radiation. It travels great distances through air (500 meters). A gamma emitter is protected by thick sheets of lead or concrete. Gamma (γ) radiation consists of photons with a wavelength less than 3×10^{-11} meters (greater than 10^{19} Hz). Gamma radiation emission is a nuclear process that occurs to rid of the decaying nucleus of excess energy after it has emitted either alpha or beta radiation. Both

alpha and beta particles have an electric charge and mass, and thus are quite likely to interact with other atoms in their path. Gamma radiation penetrates much further through matter than either alpha or beta radiation as there is no charge in them.

Gamma rays can be stopped by a sufficiently thick layer of material, where the stopping power of the material per given area depends mostly on the total mass of the barrier along the path of the radiation, regardless of whether the material is of high or low density. However, as is the case with X-rays, materials with high atomic number such as lead or depleted uranium add a modest (typically 20% to 30%) amount of stopping power over an equal mass of less dense and lower atomic weight materials (such as water or concrete).

Gamma radiation is often used to kill living organisms, in a process called irradiation. Applications of this include sterilizing medical equipment (as an alternative to autoclaves or chemical means), removing decay-causing bacteria from many foods or preventing fruit and vegetables from sprouting to maintain freshness and flavour. Despite their cancer-causing properties, gamma rays are also used to treat some types of cancer, since the rays kill cancer cells also.

Gamma rays are also used for diagnostic purposes in nuclear medicine in imaging techniques. The most common gamma emitter used in medical applications is the nuclear isomer technetium-99m which emits gamma rays in the same energy range as diagnostic X-rays.

The use of gamma radiations presents a significant health hazard and shows harmful effect (viz. skin burn, damage to eyes, cancer) to the people working in the respective fields and also contaminates the surrounding environment. That's why it is necessary to protect the people and the environment from the harmful effects of ionizing

radiation, which includes both particle radiation and high energy electromagnetic radiation. The effect of gamma radiation on living tissues is related to the amount of energy deposited rather than the charge. This is called absorbed dose which is the amount of radiation required to deposit one joule of energy in one kilogram of any kind of matter. In SI units, it is expressed as gray (Gy) and in CGS system, it is deprecated as rad. One rad is equivalent to 0.01 Gy.

Radiation protection can be classified as

- a) Occupational radiation protection, which is the protection of workers,
- b) Medical radiation protection, which is the protection of patients, and
- c) Public radiation protection, which is protection of individual members of the public, and of the population as a whole.

Following are the three factors which control the exposure of the persons and environment from the radiation at the radio-active source and the radiation exposure can be managed by a combination of these factors:

Time:

Reducing the time of an exposure reduces the effective radiation proportionally. An example of reducing radiation doses by reducing the time of exposures might be improving operator training to reduce the time they take to handle a source.

Distance:

Increasing distance reduces dose due to the inverse square law. Distance can be as simple as handling a source with forceps rather than fingers.

Shielding:

The term 'biological shield' refers to a mass of absorbing material placed around a reactor, or other radioactive source, to reduce the radiation to a level safe for humans. The effectiveness of a material as a biological shield is related to its cross section for

scattering and absorption, and to a first approximation is proportional to the total mass of material per unit area interposed along the line of sight between the radiation source and the region to be protected. Hence, shielding strength or "thickness" is conventionally measured in units of g/cm^2 .

Protection of the environment can be achieved through shielding the radiation source by constructing a thick wall around the radiation source whereas the protection to the people working in the radiation environment can be achieved by providing protective equipment such as aprons, thyroid collars and glasses.

Protective equipment

At present, thick lead plates are being used as a liner in the aprons, thyroid collars and gloves for protection of the personnel from the radiation. The patients and personnel working in the medical field are being exposed to radiation during treatment and medical examination must have to wear a protective apron of at least 0.25 mm lead equivalent, gloves of at least 0.35 mm lead equivalent.

But the Lead plates which are being used as liners are very heavy and hard to shape which are uncomfortable to wear and handle. The lead is also toxic for human beings and for environment. Literature on the protection from radiation shows that polymers after modification or compounding can be used for radiation protection very effectively and also proved to be very cost effective.

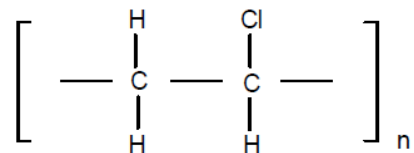
1.2 Poly vinyl chloride (PVC)

Polyvinyl chloride (PVC) has large and broad uses in commerce. It is second in volume only to polyethylene which can be attributed to several unique properties. Vinyl compounds usually contain close to 50% chlorine. The chlorine present inhibits combustion in the gas phase, providing the vinyl with a very high level of combustion

resistance, useful in many building applications as well as many electrical housings and electrical insulation applications.

PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds, materials that are virtually unbreakable with a notched Izod impact greater than 0.5 J/mm at -40°C , materials that are weatherable with good property retention for over 30 years, compounds that have stiff melts and little elastic recovery for outstanding dimensional control in profile extrusion, or low viscosity melts for thin walled injection moulding.

It is produced by free radical polymerization, PVC has the following structure:



The degree of polymerization, n , ranges from 500 to 3500. For commercial PVC the molecular weight is characterized by inherent viscosity or K- value. The K- value of 56 is used for injection moulding, pipe fittings whereas the material with a K value of 70 is used in medical tubing and automotive moulding applications. History on development of PVC is given in the Table 1.1.

Table 1.1 History of development of PVC^[9]

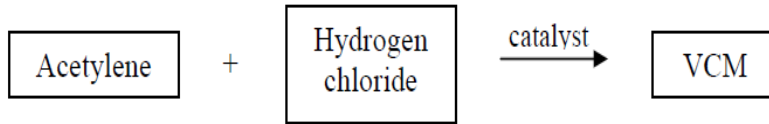
Year	History
1835	VCM was first prepared by Regnault.
1872	Baumann discussed the reaction of vinyl halides and acetylene in a sealed tube.
1921	Plausen discovered how to polymerize PVC from dry acetylene which made PVC more than a laboratory curiosity.
1928-1930	Patent disclosures of VC/VAC copolymers and polyvinyl halides. Introducing of emulsion polymerization to prepared vinyl chloride.
1930	Plasticisation of PVC by phthalate ester. Introduction in non-rigid vinyl chloride plastics. Suspension polymerization of vinyl chloride in England and Germany. Technical production of chlorinated PVC polymer and fibres. Commercial production of PVC polymers in Germany and USA.
1942-1943	Commercial production of PVC polymers in England.

1.2.1 Chemistry and Manufacturing

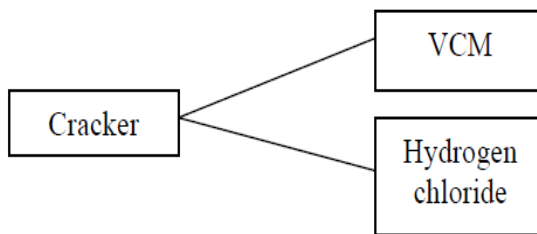
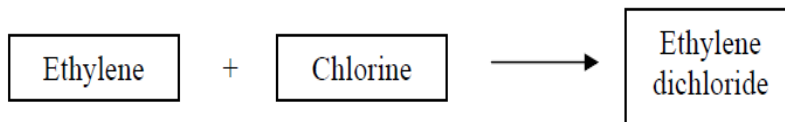
Vinyl Chloride Monomer (VCM)

Acetylene, ethylene, chlorine and oxygen feedstocks are necessary to manufacture vinyl chloride monomer. The process by which feedstock is converted to VCM is shown in Figure 1.1. In the early days of VCM production, acetylene was the dominant method; today, only 7 % of the VCM is so manufactured. The remainder is produced by oxychlorination which is given in Figure 1.2.

Acetylene Process



Ethylene Process



Balanced Process

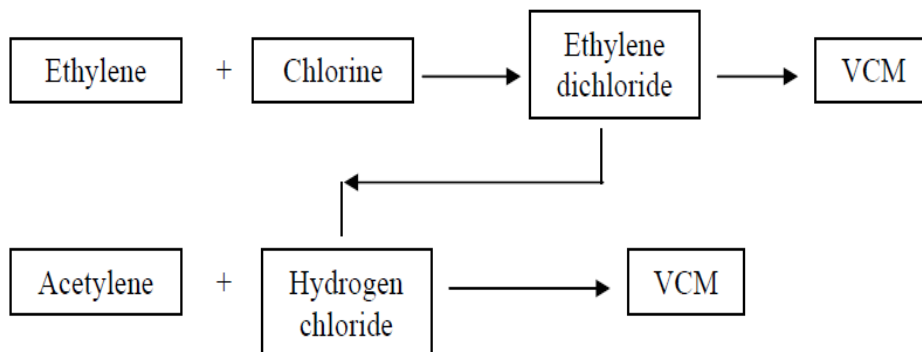


Figure1.1 Feedstock conversion to vinyl chloride

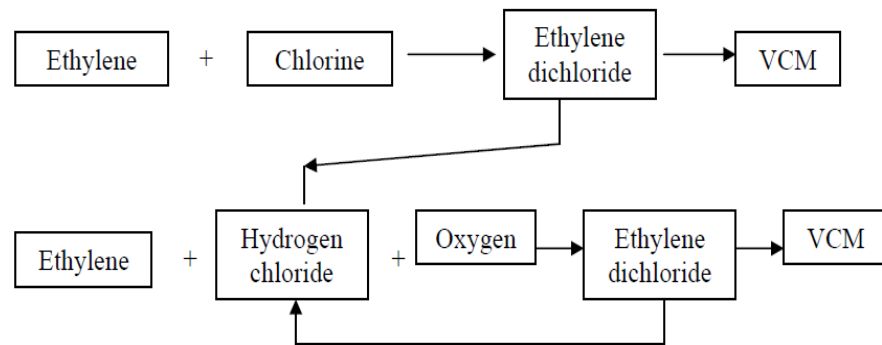
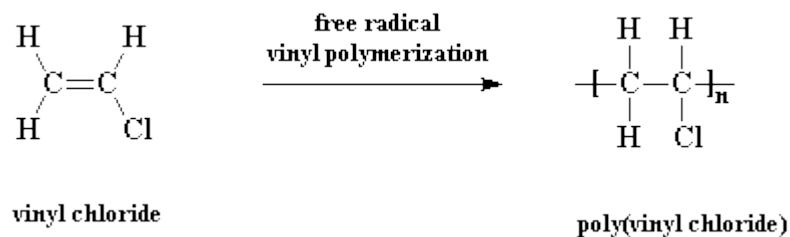


Figure 1.2 Oxychlorination process

1.2.2 PVC resin manufacturing processes: The major type of polymerization of PVC is the suspension polymerization route which accounts for an estimated 85% of the production. It is also produced by emulsion, solution and bulk or mass polymerization techniques. The morphology formed during polymerization strongly influences the processability and physical properties. Mass polymerized PVC has a similar morphology as compared to suspension PVC.



1.2.2.1 Suspension polymerisation: It is also known as pearl or granular polymerization in which monomer is dispersed in another dispersing liquid phase in which both the monomer and polymer are insoluble. The monomer is first finely dispersed in water by vigorous agitation. Suspension stabilizers act to minimize coalescence of droplets by forming a coating at the monomer-water interface. The hydrophobic-hydrophilic properties of the suspension stabilizers are key to resin properties and grain agglomeration. In the suspension polymerization of PVC, droplets of monomer 30 – 150

mm in diameter are dispersed in water by agitation. Suspending agents like PVA, Gelatine, Maleic Anhydride, Vinyl Acetate Copolymers are generally used.

1.2.2.2 Mass polymerization: Mass or bulk polymerization of PVC is normally difficult. At high conversions, the mixture becomes extremely viscous, impeding agitation and heat removal, causing a high polymerization temperature and broad molecular weight distribution.

While the mass process saves drying energy, it has remained a minor process when compared to the suspension process. Mass polymerized PVC also has a skin of compacted PVC primary particles very similar in thickness and appearance to the suspension polymerized PVC skin.

1.2.2.3 Emulsion polymerisation: Emulsion polymerization takes place in a soap micelle where a small amount of monomer dissolves in the micelle. The initiator is water soluble. Polymerization takes place when the radical enters the monomer swollen micelle. Additional monomer is supplied by diffusion through the water phase. Termination takes place in the growing micelle by the usual radical-radical interactions.

The average number of radicals per particle is low, 0.0005 to 0.1. The high solubility of vinyl chloride in water, 0.6 weight %, accounts for a strong deviation from true emulsion behaviour. Also PVC's insolubility in its own monomer accounts for some behaviour such as a rate dependence on conversion. Schematic diagram of conventional emulsion polymerisation is given in Figure 1.3.^[9]

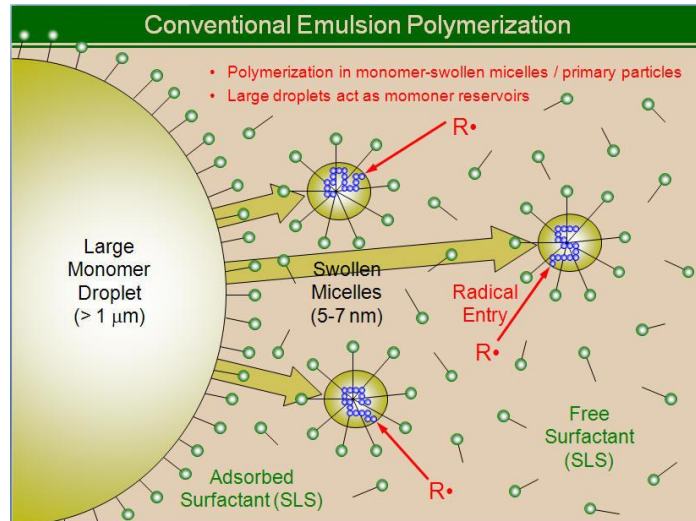


Figure 1.3 Conventional emulsion polymerisation

Emulsions of up to 0.2 mm diameter are sold in liquid form for water based paints, printing inks, and finishes for paper and fabric. Other versions, 0.3 to 10 mm diameter and dried by spray drying or coagulation, are used as plastisol resins. Plastisols are dispersions of PVC in plasticizer. Heat allows fast diffusion of plasticizer into the PVC particle followed by fusion (gelation) to produce a physically cross linked elastomer, where the physical crosslink's are PVC crystallites.

1.2.3 Physical Properties: Physical properties of commercial PVC are given in Table 1.2

Table 1.2 Physical properties of PVC*

Sl.No	Property	Value
1	Crystallographic data Commercial PVC	Orthorhombic 1.06 0.54 0.51 nm
2	Percent crystallinity As polymerized from the melt	19% 4.9%
3	Density (uncompounded) Whole Crystallites	1.39 gms/cc 1.53 gms/cc
4	Refractive Index	1.54
5	Glass Transition Temp. Tg	83 °C
6	Coefficient of linear thermal expansion (unplasticised)	$7 \times 10^{-5} / ^\circ\text{C}$
7	Specific Heat of rigid PVC at 23°C Plasticised (50 phr DOP)	0.22 cal per gram °C 0.37 cal per gram °C
8	Thermal Conductivity (Unplasticised)	4.2×10^{-4} cals per cm sec °C
9	Dielectric strength	20 kvolts per mm
10	Solubility parameter	9.75 cal per m ³

* PVC Handbook^[9]

1.3 Compounding: The additives found in PVC help make it one of the most versatile, cost-efficient materials in the world. Without additives, literally hundreds of commonly used PVC products would not exist. Many materials are useless until they undergo a similar modification process. Steel, for instance, contains among other things, chromium, nickel and molybdenum. PVCs are tailored to the requirements using sophisticated additives technology.

A PVC compound generally contains the following ingredients:

Plasticisers	Stabilisers	Lubricants
Fillers	Extenders	Pigments
Polymeric processing aids	Impact modifiers	

1.3.1 Plasticisers: Plasticizer as a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product. Boyer^[9] defines plasticizer as a material which when added to a polymer decreases the accumulation of intermolecular forces along the chain. For a plasticizer to be effective, it must be thoroughly mixed and incorporated into the PVC polymer matrix. The plasticized material is then moulded or shaped into the useful product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting mechanical and physical properties of the flexible product.

Several theories have been developed to account for the observed characteristics of the plasticization process. Plasticization is described by three primary theories, with some modifications.

According to the Lubricating Theory of plasticization,^[9] as the system is heated, the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions (Vander Waals' forces). Here, the plasticizer molecules act as shields to reduce polymer-polymer interactive forces and prevent the formation of a rigid network. This lowers the PVC T_g and allows the polymer chains to move rapidly, resulting in increased flexibility, softness, and elongation.

The Gel Theory considers the plasticized polymer to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak

secondary bonding forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free Volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement.

The plasticizer must not be a powerful solvent for all the PVC parts, but must be selective in entering the amorphous PVC part and must not enter and destroy the crystalline part of PVC. For a plasticizer to be effective and useful in PVC, it must contain two types of structural components, polar and nonpolar. The polar portion of the molecule must be able to bind reversibly with the PVC polymer, thus softening the PVC, while the non-polar portion of the molecule allows the PVC interaction to be controlled so it is not so powerful a solvator as to destroy the PVC crystallinity.

1.3.1.1 Types of Plasticisers: Plasticizers may be classified as either monomeric or polymeric plasticizers, depending on their synthesis steps, which relates in part to their molecular weight. It is preferred to categorize plasticizers on the basis of their chemical structure and associated performance when employed in PVC. The key performance properties are influenced by plasticizer level (phr) as well as the chemical type.

An orderly comparison of plasticizers is facilitated by separating all plasticizers types into three subgroups relating to their performance characteristics in PVC:

General Purpose (GP): plasticizers providing the desired flexibility to PVC along with an overall balance of optimum properties at the lowest cost. These are dialkyl phthalates ranging from diisooheptyl (DIHP) to diisodecyl (DIDP), along with low cost oils called “extenders”.

Performance Plasticizers (PP): contribute secondary performance properties desired in flexible PVC beyond the GP type, while imposing somewhat higher costs. Table 1.3 identifies these key performance criteria as “Strong solvaters”, “Low temperature” and “Low volatility”. These include specific phthalates and other types of plasticizers. Strong solvaters have higher polarity and/or aromaticity. Conversely, low temperature types, such as aliphatic dibasic esters, are less solvating and have higher diffusivity. Low volatility requires high molecular weight plasticizers, such as trimellitates and polyesters.

Specialty Plasticizers: provide properties beyond those typically associated with flexible PVC designed for general purpose or specialty characteristics. These exceptional characteristics are typically a function of specific chemical plasticizer families and may vary as a function of isomeric structure and/or homologues. Such properties are shown in Table 1.3 as “Low diffusivity”, “Stability”, and “Flame resistance”. Few phthalates meet these special requirements. Polyester plasticizers provide low volatility and low diffusivity, along with low smoke (in the absence of aromaticity) under fire conditions. Epoxy plasticizers provide adjuvant thermal stability to PVC; phosphates and halogenated plasticizers provide fire retardant properties. Specialty plasticizers impose even higher costs than PP grade plasticizers.

Table 1.3 Plasticizer Family/Performance Grid

Family	General purpose	Performance plasticisers			Speciality plasticisers		
		Strong Solvent volatility	Low temp	Low	Low Flame Diffusion resistance	Stability	
Phthalates	P	S	S	S	S		S
Trimellitates			S	P	S		
Aliphatic dibasic esters			P				
Epoxydes				P	P		
Phosphates			S	S		P	
Extenders		S	S				P
Miscellaneous		P		P	P		

P = Primary performance function

S = Secondary performance function

1.3.1.2 Phthalates: Phthalates are the most widely used class of plasticisers in PVC. They contribute the most complete array of required performance properties in flexible PVC. They are prepared by the esterification of two moles of a monohydric alcohol with one mole of phthalic anhydride. The main phthalates used as plasticisers in PVC are the di(2-ethylhexyl) phthalate (DOP), the diisodecyl phthalate (DIDP), and the diisononyl phthalate (DINP). DOP is the dominant plasticizer used in PVC due to its low cost and it has been used worldwide in applications such as blood bags, saline solutions, meat wraps and other highly credible usage.

1.3.1.3 Trimellitates: They are the product of three moles of monohydric alcohols and trimellitic anhydride (TMA). The third alkyl group, compared to phthalates, contributes higher molecular weight; the third ester group contributes sufficient polarity to maintain PVC compatibility. They have many advantages like low volatility, good low temperature properties, resistance to extraction and low viscosity.

1.3.1.4 Aliphatic dibasic esters: The entire family of *aliphatic dibasic esters* contributes exceptional low temperature properties. They are prepared by the esterification of one mole of dibasic carboxylic acid, such as adipic or azelaic acid, with two moles of monohydric alcohols. Lower molecular weight alcohols are used with higher molecular weight acids, and vice versa, such that the total carbon content per molecule ranges between C₁₈ and C₂₆. This maintains the apolar/polar ratio required to provide PVC compatibility along with low temperature properties. Di-2-ethylhexyl adipate (DOA) is the standard and most widely used plasticizer in this class. Di-2-ethylhexyl azelate (DOZ), di-2-ethylhexyl sebacate (DOS), and diisononyl adipate (DINA) are used for low temperature applications requiring lower plasticizer volatility.

1.3.1.5 Polyesters: Polymeric plasticizers are typically polyesters, with a molecular weight range from 1,000 to 8,000. Polyethylene copolymers (EVA's, VAE's, etc.) and

terpolymers can range up to > 500,000. Polyesters are prepared by the esterification of propylene glycol or butylene glycol with aliphatic dibasic acids. The greater the plasticizer viscosity, or molecular weight, the greater is its permanence.

1.3.1.6 Epoxy plasticizers: They enhance thermal and UV stability of PVC. They are the only class of plasticizers that undergo a chemical grafting onto the PVC polymer at the site of labile chlorides in the presence of mixed metal stabilizers. This chemical family is composed of essentially two types of epoxidized natural products. Epoxidized oils, such as soybean oil (ESO) and linseed oil (ELSO) are prepared by the use of per acetic acid, which adds the oxirane structure at unsaturated double bond sites.

Depending upon their ability to solvate and compatibility plasticisers are classified as primary and secondary plasticisers. Primary plasticisers have the ability to solvate PVC and will retain compatibility on aging. Primary plasticisers are principal additives responsible for flexibilising PVC. These are classified as monomeric, polymeric, epoxy and speciality flame retardant plasticisers. Secondary plasticisers are low volatility liquids whose compatibility with PVC is such that they can be used along with primary plasticisers as part of the plasticizer system but which exude if used as a sole plasticizer. Chlorinated paraffin is a common example.

1.3.2 Stabilisers: PVC resin is heat sensitive and will degrade if it exposed to a source of energy such as heat, light, pressure and shear forces. It tends to cause chemical changes in the polymers that result in noticeable unwanted changes in their properties. PVC at temperatures above 70°C has adverse properties. Processing temperatures of about 150 to 200°C makes it degrade. The first physical appearance of degradation is a change in colour. Oxygen is known to accelerate the rate of degradation which is accelerated by UV light. Hence, heat stabilizers, antioxidants and UV stabilizers are the important ones which must be used while processing when the temperatures exceed 70°C. To have good

stabilization of PVC with good early color and long term stability, the two types of stabilizers should be combined appropriately for each particular PVC formulation. Stabilization is complicated by the fact that primary stabilizers become strong Lewis acids by reacting with the HCl that catalyzes the initiation and propagation of PVC degradation. To avoid this, secondary stabilizers should react efficiently with HCl to protect the primary stabilizers. Another possibility is to include compounds called co stabilizers in the system. Co stabilizers form relatively stable complexes with the chloro derivatives of primary stabilizers (the Lewis acids) and suppress their degradative effect.

1.3.2.1 Thermal Stabilisers: Thermal stabilizers of PVC possess one or more of the following features in addition to capacity for absorption and neutralization of HCl evolved by PVC during degradation:

1. An ability to replace or displace active, labile substituent groups, such as tertiary and allylic chlorine atoms.
2. A capacity to render pro-degradant substances e.g. heavy metal chlorides inactive.
3. An ability to modify chain reactions, by interrupting conjugated polyene formation and inhibiting the elimination of HCl.

Mono and diorganotin are used extensively as heat stabilizers for processing polyvinyl chloride (PVC). The primary purpose of these tin stabilizers is to reduce the polymer backbone degradation of the PVC. They do this by scavenging the HCl lost during processing at high temperatures and stabilizing the unstable chloride sites in the PVC molecule.

Tin mercaptide stabilizers are some of the most effective PVC stabilizers available. They contain both tin and sulfur. Tin, acting as a base, reacts with the HCl initially released during PVC processing. The strength of this base is critical so it will not extract HCl from the PVC, but only react with the HCl that is already released. The

mercaptan, a weak sulfur-containing acid, reacts with the unstable chloride sites on PVC to heal the polymer and reduce further decomposition. The high molecular weights and ester function in the mercaptan ligands also promote solubility of the stabilizer in PVC and provide lubrication during polymer processing.

There are three major types of tin stabilizers. They are distinguished by their respective alkyl groups: octyl, butyl, and methyl. Octyl tin stabilizers have the lowest tin content and are somewhat less efficient. However, they are approved for food contact applications by most regulatory authorities worldwide.

1.3.2.2 UV Stabilisers: The UV absorbers dissipate the absorbed light energy from UV rays as heat by reversible intramolecular proton transfer. This reduces the absorption of UV rays by the polymer matrix and hence reduces the rate of weathering. Typical UV-absorbers are benzophenones for PVC, benzotriazoles and hydroxyphenyltriazines for polycarbonate.

1.3.2.3 Anti Oxidants: Antioxidants are used to terminate the oxidation reactions taking place due to different weathering conditions and reduce the degradation of organic materials. For example, synthetic polymers react with atmospheric oxygen. Weathering of polymers is caused by absorption of UV lights, which results in, radical initiated auto-oxidation. Antioxidants inhibit the formation of the free radicals thereby enhancing the stability of polymers against light and heat.

1.3.3 Impact modifiers: In the early days of plastics, many unplasticized PVC products were used to be brittle. This gave plastics a cheap reputation. It was therefore quite desirable to develop technology to produce tough plastics. Rubbery particles act as stress concentrators or multiple weak points, leading to crazing or shear-banding under impact load. This can result in cavitations and/or cold drawing, thus allowing the PVC to absorb large amounts of energy. Impact modifiers increase the durability of moulded or extruded

plastics, particularly those subject to impact forces or cold weather service. Impact modifiers generally used are acrylonitrile butadiene styrene ABS, ethylene vinylacetate EVA, methyl methacrylate butadiene styrene MBS etc.

1.3.4 Processing aids: PVC often flows as billion molecule primary particles. Processing aids glue these particles together before the PVC melts, thus acting as a fusion promoter. Processing aids modify melt rheology by increasing melt elasticity and die swell, or, some reduce melt viscosity, and they reduce melt fracture. Some processing aids lubricate to reduce PVC sticking to metal. And processing aids affect dispersion of fillers, impact modifiers, and pigments. The most common processing aids are high molecular weight acrylics based primarily on polymethylmethacrylate copolymers.

1.3.5 Lubricants: A lubricant is a substance that, when added in small quantities, provides a disproportionate decrease in resistance to movement of chains or segments of polymer of at least partly amorphous structure, without disproportionate change in observable properties. Lubricants are added to prevent the sticking of the compound to processing equipment. They are classified as “internal” or “external”. Internal lubricants were considered to be soluble in PVC, or considered to have little effect on fusion, or they reduce melt viscosity; external lubricants were considered to retard fusion or to promote metal release. Internal lubricants are more compatible with PVC which lowers the T_g of the composition, lower Vicat softening point and HDT. Generally used internal lubricants are calcium stearate, paraffin wax, glycol, glycerol monostearate, butyl stearate etc. External lubricants are sufficiently incompatible with PVC compositions at processing temperatures but they reduce the friction during the gelation process. Some of the external lubricants generally used are lead stearate, stearic acid, 12-hydroxy stearic acid etc.

1.3.6 Fillers: Fillers are used to improve strength and stiffness, to lower cost, and to control gloss. The most common filler is calcium carbonate. It ranges in size from 0.07 to

well over 50 mm. Some forms are treated with a stearic acid coating. Clay fillers, such as calcined clay, improve electrical properties. Glass fibers, talc, and mica improve tensile strength and stiffness, but at a loss in ductility.

1.3.7 Pigments: A variety of pigments are added to PVC to give colour, including titanium dioxide and carbon black.

1.4 Processing

The first step in processing is usually powder mixing in a high speed, intensive mixer. PVC resin, stabilizers, plasticizers, lubricants, processing aids, fillers, and pigments are added to the powder blend for distributive mixing. For both suspension and mass PVC resins, intensive mixing above the glass transition temperature, results in a progressive increase in apparent bulk density with higher mixing temperatures.

In plasticized PVC, liquid plasticizers first fill the voids or pores in the PVC grains fairly rapidly during powder mixing. If a large amount of plasticizer is added, the excess plasticizer beyond the capacity of the pores initially remains on the surface of the grains making the powder somewhat wet and sticky. Continued heating increases the diffusion rate of plasticizer into the PVC mass where the excess liquid is eventually absorbed and the powder dries.

Flexible PVC products may be made through two distinctly different routes. One is to use resins made through suspension polymerization. The resin is a porous powder of approximately 100 μm size. The powder may absorb a large quantity of liquid plasticizer and yet remain free-flowing; or the resin-plasticizer mixture may be compounded and pelletized. The other route uses resins made through emulsion polymerization. The resulting emulsion of PVC is spray-dried; the dried powder contains the primary particles of about 1 μm and smaller as well as the agglomerated particles, which are ground to the size smaller than 20 μm . The proportion of the primary particles and the agglomerated

particles may be for example 85 to 15. The powder is mixed with a plasticizer in approximately equal volume to prepare a paste called “plastisol”.

1.4.1 Plastisol: A Plastisol is defined as a suspension of a resin in a non-aqueous liquid. The liquid phase does not readily dissolve or solvate the resin at room temperatures. Generally, PVC resins, homo polymers are used for the polymer phase. They are stable, pourable, cream like dispersions of resin powders in plasticizer. Special PVC resin called paste resins or dispersion resins are formulated so that the plasticizer wets the resin particles at room temperature but only very slowly penetrates and solvates the resin. In plastisol, particle size and particle size distribution affect viscosity characteristics and stability. Smaller particle size produces higher plastisol viscosity due to the presence of greater surface area. Hence, commercial resins of particle size ranging from 0.5 to 2 microns are generally used. The plastisol may be coated on a substrate with high speeds, such as fabric coating, it may be made into films and sheets. Dip coating may be used to make complex shapes like boots and surgical gloves and the rotational moulding and slush-moulding may be used to make hollow objects. Use of relatively inexpensive mould is another advantage of plastisol.

After plastisol is coated on the substrate, it is heated in an oven to gel and fuse. In the gelation stage the resin particles become swollen with plasticizer and in fusion stage they fuse to become a uniform mass. In this process the system changes from a pasty liquid to viscoelastic melt. The development of modulus is important in some processes, e.g. foaming, where the generation of the desired cell structure is intimately related to the viscoelastic properties of the system.

Rheological property is one of the most important criteria for selecting the resin grade and plasticizer type for a given formulation. The rheological requirements may be divided into two areas; one is the rheology at room temperature, where the coating

operation is performed. The other area is the development of modulus during gelation and fusion as mentioned already.

1.5 Crosslinking agents: The use of poly functional monomers as additives are shown to enhance significantly the copolymerization yields of PVC films under certain radiation conditions. Additives that increase the yield in the radiation grafting of monomers are Poly functional acrylates, methacrylates, triallylcyanurate and Trimethylolpropane trimethacrylate (TMPTMA) are the most widely used monomers for this purpose. Functional acrylic monomers are low viscosity liquid monomers with acrylate or methacrylate end groups. Methacrylate monomers are commonly used as coagents with PVC plastisols, due to better stability and lower toxicity. Higher functionality monomers generally exhibit higher cross-link densities, or are functionality materials. Within a given functional group, the molecular weight of the monomer has an effect on the cross-link density because of the distance between the reactive end groups (lower M.W. > higher M.W.). Lower molecular weight monomers yield higher crosslink densities than higher molecular weight monomers.

1.6 Necessity for radiation resistant PVC: In spite of the fact that PVC has occupied the most important position among the general purpose plastics, its industrial applications are limited due to its inferior thermal stability and mechanical properties. Many studies have been conducted to remedy these disadvantages of which the following four methods are conceivable:

- a. Improving PVC itself through polymerization during its production process.
- b. Improving PVC itself through chemical modifications during its production process.
- c. Improving the blending technology to develop new chemical ingredients of PVC.
- d. Improving the processing machinery.

The industrial advances on a) and d) above have almost attained saturation. The industrial interest has shifted more and more to the applications on b) and c) above.

Cross linking can be accomplished chemically or by irradiation. Chemical cross linking with rubber material is called Vulcanization. It is accomplished by a heat induced reaction between the polymers and a cross linking agent. For wire and cable insulations, chemical cross linking is performed by passing the wire through a long pressurized steam tube, called a continuous vulcanizing (C.V.) machine.

Cross-Linking Provides:

1. Higher tensile strength
2. Improved fluid resistance
3. Improved abrasion/cut through
4. Slightly better flame resistance
5. Better crush resistance
6. No change of electricals
7. Solder iron resistance
8. Negligible change in thermal stability
9. Better over load characteristics
10. Decrease in flexibility
11. Resistance to stress cracking
12. Improved high temperature mechanicals

Polymers may also be cross linked by means of electron irradiation. During the irradiation process, high energy electrons bombard the insulation system. Figure 1.4 illustrates two random polyethylene molecules being subject to irradiation. The energy of irradiation ejects a hydrogen atom which then removes a neighbouring hydrogen atom,

forming molecular hydrogen gas (H_2). The vacant sites on the adjacent polymer chain then combine to create a crosslink bond.

For most plastic materials, equivalent properties may be obtained by the use of either C.V. or irradiation cross linking, but irradiation may have the following advantages:

1. Irradiation has no lower limit on physical size, smaller conductor sizes, and thin insulation walls may be provided.
2. Irradiation does not use high temperature or pressure. Separator tapes are not required to prevent thin wall insulations from being forced into the conductor strand surface.
3. Irradiation offers the insulation compounder design freedom. Compound additives may be chosen without regard to their reaction to high temperatures and to moisture.

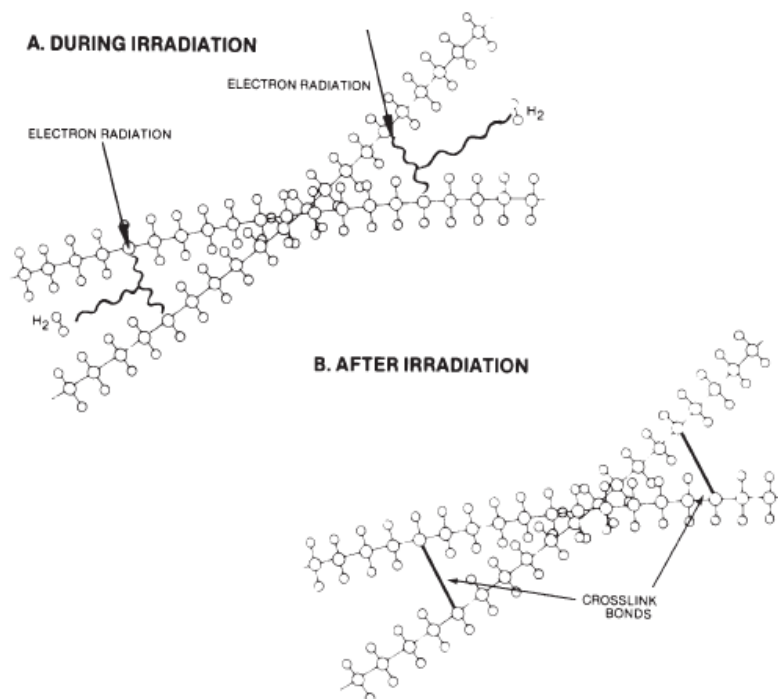


Figure 1.4 PVC molecules being subjected to irradiation

For the cross-linking of industrial polymer products, accelerators are available supplying electron beams in the energy range between 150 keV and 10 MeV and sources of the radio-nuclides Co-60 and Cs-137 emitting gamma rays 1.17/1.33 and 0.662 MeV respectively. The general differences are:

The whole energy of high-energy electrons of EB is deposited in relatively thin layers of material. The total dose for cross-linking a polymer is delivered in real irradiation times ranging from fraction of a second to a few seconds. The irradiation of reeled products such as tubes and wires is thus possible with speeds up to several hundred meters per minute.

The Cobalt-60 emitted gamma rays, on the other hand, loses only 50% of the initial energy after penetrating material with surface density of 25 g/cm² (0.25 density), dose rates are thus 4–5 orders of magnitude lower as compared to EB. Residence time in case of gamma facility is at least several hours. This is however well compensated in gamma facilities by the ability to irradiate large volumes, usually between 10 and 50 m³ at same time. Gamma irradiation is therefore particularly applicable to bulky products and even single pieces measuring a few m³ are routinely irradiated. In case of gamma irradiation, the long residence time enable the continuous diffusion of oxygen into the polymer.

1.7 Proposed work

The main objective of the present work is to develop the radiation resistant PVC plastisols using the cross linking agent for the personnel working in the areas contaminated with radiation in the oncology department and also to protect from accidental exposure of high radiation dose during medical examination. This includes following scope of work:

- To develop radiation resistant PVC plastisol formulation.

- To study physico-mechanical and thermal stability properties of developed compositions.
- To study the effect of radiation on the physico-mechanical properties of developed compositions.
- Weatherability study of developed compositions.

CHAPTER-2

LITERATURE REVIEW

Ang C.H, Garnett J.L et al (1992) used Divinylbenzene (DVB) and trimethylolpropane triacrylate (TMPTA) as representative polyfunctional monomers for the enhancement effect.^[3] When polypropylene was used as backbone polymer, the inclusion of DVB significantly enhanced the radiation grafting of styrene in methanol at all monomer concentrations studied above 35%. At certain monomer concentrations (50%, 60%), the yield of graft copolymer was almost doubled by the addition of DVB.

Tornasella E, V. Labed et al (1995) in order to check the durability of radioactive materials barriers, PVC samples have been subjected to different accelerated ageing processes by exposure to ultra-violet (UV) radiations or gamma rays.^[33] They have determined the effect of such radiation of the samples using two approaches:- demonstration of structural changes using analytical method (Infra-red with Fourier Transform or IRTF),- study of variations in the radon permeation factor. In the first analysis, it seems that the UV irradiation, causes structural changes in the PVC as a function of the irradiation length of time. This leads first to an increase in the efficiency of the polymer as a “radon barrier”. i.e. a reduction in its permeation factor ($2.41 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ for a non exposed membrane, against $3.30 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ for a membrane exposed during 284 hours, with an exposure rate of 62.5 W.m^{-2} , thus a reduction by a factor IO of the radon emission) then to a long-term weakness. The gamma irradiation (dose rate: 1.05 kGy.h^{-1} , dose: 0.71 MGy) also caused a reduction in the permeation factor of PVC, but only by a factor 2.7.

Bataille P, I. Ulkem et al (1995) had prepared PVC compounds containing CaCO₃, filler and plasticizers with or without a trifunctional acrylic crosslinking agent and irradiated by ⁶⁰Co gamma rays under air or nitrogen atmosphere.^[6] The samples without

crosslinking agent did not respond to irradiation. The mechanical properties of the other samples such as tensile strength, yield strength and % elongation showed a great sensitivity to irradiation. Lower values of Young's modulus were observed for samples irradiated in air compared with samples irradiated in nitrogen indicating the effect of atmosphere in the range of irradiation studied.

Klein D, E. Tomasella et al (1997) had studied Polyvinyl Chloride (PVC) and Ethylene Vinyl Acetate (EVA) membranes after gamma exposures.^[20] They evaluated the effects of the gamma radiations on the radon permeation coefficient, and the degradation of these polymers due to this exposure. The second objective of this study was to evaluate the modifications of the polymer surface by cold plasma. Poly Ethylene (PE) and Poly Propylene (PP) membranes were studied. They observed that the exposure of a polymer to a plasma created reactive sites on the polymer's surface. Different modifications in the surface composition (chemical composition, molecular weight, etc.) can be obtained. The advantage of the plasma process is that it acts within seconds and does not produce any noticeable effects on the bulk properties. The obtained results showed that this treatment increases the polymer's efficiency as a radon barrier.

Woo L, Michael T.K. Ling et al (1998) undertaken a study on the thermal oxidative stability of several medical polymers as measured by the oxidative induction time (OIT) on radiation exposures.^[38] It was found that, in selected cases with polyolefins, active antioxidants can be completely consumed during the sterilization process, leaving the polymer unprotected for the required shelf life. In addition, comparison between gamma and electron-beam irradiation sources revealed major differences on OIT reduction, primarily due to the dose rate effect.

Fumio Yoshii, Adujat Sudradjat et al (1998) added compatibilizer to PP to reduce its degradation.^[14] They have observed that the compatibilizers, such as hydrogenated

styrene (10 mol%)/butadiene rubber (CPB-2) and ethylene/propylene rubber grafted with maleic anhydride, retarded remarkably the degradation of PP. The compatibilizer concentration required for enhancing the radiation resistance of PP depends on the radiation resistance before addition of the compatibilizer. Poor radiation-resistant PP of a lower molecular weight (Melt flow index, 10) required a higher concentration, above 10% of CPB-2 to impart radiation resistance, but high-molecular-weight PP (Melt flow index, 1.0) and copolypropylene (CPP) with an ethylene content of 2.5% required CPB-2 of 5% and 10% to induce sufficient radiation resistance. Furthermore, CPB-2 was effective for improvement of transparency besides its contribution to radiation resistance of PP. The CPB-2 lead to lower crystallinity to retard the crystallization of PP and CPP and also may result in a mixed monoclinic and smectic structure giving radiation resistance.

Varada Rajulu A, R. Lakshminarayana Reddy et al (1999) had prepared the films of polymethyl methacrylate/ polyvinyl chloride blends of diferent compositions.^[34] They have been irradiated with a ²⁸Si ion beam of 120 MeV in the fluence range of 1011±1013 ions/cm². The infrared spectra of these samples have been recorded before and after irradiation and based on the spectral information, some structural changes in the films have been found. Naimian F (1999) studied Gamma stabilization of PVC at sterilizing doses in the presence of various mixtures of non-toxic stabilizers. Plasticized PVC containing three different stabilizers like; calcium stearate, zinc stearate and epoxidized soya bean oil, were irradiated by 60-cobalt gamma ray at doses of 25±100 kGy and the effect of irradiation on the structural changes has been investigated up to 2 yr after irradiation.^[25] In the presence of this stabilizing system unstable allylic chlorine units were converted to stable allylic structures thus retarding the development of polyene sequences. This was detected by the changes in UV absorbance at 290 nm. The changes of carbonyl index which has been studied by FTIR spectra, also showed the effectiveness

of this stabilizing system up to 2 yr after irradiation. Measurement of Cl concentration has also confirmed the spectrophotometry results. Finally the most effective stabilizing system was added to the Iranian PVC and its behaviour was compared with the Solvay PVC for 6 months period after irradiation.

Clough R L (2001) reviewed commercial processes and emerging applications of high energy radiation and polymers.^[11] Ionising radiation has been found to be widely applicable in modifying the structure and properties of polymers and can be used to tailor the performance of either the bulk materials or surfaces. This paper provides a survey of radiation processing methods of industrial interest, ranging from technologies already commercially well established, through innovations in the active R & D stage which show exceptional promise for future commercial use. The author discussed the radiation processing technologies under various categories such as crosslinking of plastics and rubbers, curing of coatings and inks, heat shrink products, fibre matrix composites, chain scission for processing control, surface modification, sterilisation, grafting etc.

Jian- Xiong Li and Chi-Ming Chan (2001) experimented by mixing NBR with different acrylonitrile contents.^[17] The morphology of the blends was examined with Transmission Electron Microscopy (TEM). The samples were also exposed to electron beam and the chlorine loss upon electron irradiation was monitored with electron dispersion X-ray analyser (EDX). TEM results indicated that all samples blended with different NBR, including NBR-33 and NBR-41, were heterogenous but the dispersion of NBR-33 was the finest. The results of chlorine loss study showed that the radiation sensitivity of the PVC was improved by the addition of NBR and the extent of improvement was strongly related to the miscibility.

Semsarzadeh M.A et al (2002) in their study established that the mixing of polyvinyl chloride (PVC) with dioctyl phthalate (DOP) shows two stages of gelation and

fusion, but the homogeneity of each stage is influenced by the thermal stability of PVC and its rheological behaviour.^[29] A torque rheometer has been used to gather almost all critical data related to the plasticized PVC in the epoxidized soya bean oil (ESBO). This study shows that, rheological data reflects the effects of DOP and epoxidization levels of SBO, in a DOP plasticized PVC-ESBO. The DOP plasticizer forms a thermodynamically miscible solution with ESBO; that reduces the rate of fusion and torque at balance of PVC. The storage modulus and $\tan \delta$ of the plasticized PVC-ESBO have been used to show the extent of the homogeneity; but the dynamic mechanical behaviour of PVC-ESBO is strongly influenced by DOP and the epoxidization level of SBO. The glass transition temperatures and dynamic properties of DOP plasticized PVC-ESBO were also reported and discussed in terms of the thermal stability and homogeneity of PVC.

Basfar A.A (2002) had prepared various formulations of radiation cross-linked poly (vinyl chloride) (PVC) to improve the flame retardancy for wire and cable insulation applications.^[5] Limiting oxygen index (LOI) was used to characterize the flammability of the developed formulations. The effect of different plasticizers, dioctyl phthalate (DOP), di-isodecyl phthalate (DIDP) and tri-2-ethylhexyl trimellitate (TOTM) and different flame-retardant fillers, Sb_2O_3 , zinc borate, $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ on the mechanical properties and flammability was investigated. The influence of radiation dose on the mechanical properties was minimal both at room temperature and after thermal aging for 168 h at 136 deg C. The highest LOI was 39% for PVC formulations containing DOP as a plasticizer and TMPTA at absorbed doses of 90 and 120 kGy. Both DTG peak maxima and temperature for loss of 50% mass decreased with increasing irradiation dose. No influence of plasticizer type or flame-retardant filler on the thermal properties was observed.

Abdel-Fattah A. A et al (2002) had studied the changes in the optical absorption spectra of unplasticized poly(vinyl chloride),UPVC films, irradiated with high-energy proton beam in the range 25–37 MeV and at a fluence 2.25×10^9 ions cm^{-2} have been studied.^[2] However,at the beam energy 25 MeV and with increasing the beam fluence up to 10^{15} cm^{-2} ,the experiment was performed again upon another series of films, where the films became darken. The dependence of the optical absorption on the beam fluence was investigated in the fluence range of 10^{11} – 10^{15} ions cm^{-2} . The changes in the band structure of the irradiated films were also measured spectrophotometrically using UV/VIS spectrophotometer. The results showed that the tail width of the localized states in the band gap was decreased as the beam fluence increased which led to a decrease in the optical energy gap of the irradiated UPVC films. ESR and FTIR measurements for the samples were also undertaken. The results suggested the possible use of UPVC film as a dosimeter for H^+ ion beam in the fluence range of this study (10^{11} – 10^{15} ions cm^{-2}) by means of visible spectrophotometry and ESR techniques.

Thai Hoang and Neil Varshney (2003) presented the results of study on crosslinking of rigid poly(vinyl chloride) (PVC) by 1,1-di-(t-amylperoxy) cyclohexane (DAPC) in the presence of trimethylolpropane trimethacrylate (TMPTMA).^[31] Gel content of the PVC samples is increased with increasing concentration of TMPTMA and peroxide DAPC. Ultimate tensile strength (UTS) of the PVC samples is rised with increasing concentration of TMPTMA. Maximum UTS of the PVC samples is achieved with 0.4 phr peroxide DAPC for every investigated concentration of TMPTMA. Formation of TMPTMA network, crosslinking and grafting of PVC chain radicals on to TMPTMA network are able to improve the gel content, UTS at low - and elevated temperatures and modulus of rigid PVC material.

Baccaro S et al (2003) have studied the effect of gamma radiation on poly (vinyl chloride).^[4] Radicals produced by irradiation were investigated by EPR measurements at room temperature and the formation of conjugated double bonds was probed by UV–VIS absorbance measurements; samples were also submitted to infrared measurements to be analysed in terms of oxidation products. At 25 and 50 kGy oxygen appears to saturate all radicals and the EPR spectrum shows only one component, associated with peroxy radicals. At the 100 and 150 kGy irradiation doses the EPR spectrum shows more structure and it comprises overlapping signals from the peroxy and polyenyl radicals not yet oxidised. The IR oxidation peak was found in a different region with respect to that expected for the simple ketone C=O bond, because of the inductive influence exerted by the chlorine atom.

Placek V et al (2003) in their work, the effect of dose rate on the degradation rate has been studied.^[27] Three types of NPP cables (with jacket/insulation combinations PVC/PVC, PVC/PE, XPE/XPE) were irradiated at room temperature using ⁶⁰Co gamma ray source at average dose rates of 7, 30 and 100 Gy/h with the doses up to 590 kGy. The irradiated samples were tested for their mechanical properties, thermo-oxidative stability (using differential scanning calorimetry, DSC), and density. In the case of PVC and PE samples, the tested properties have shown evident dose rate effects, while the XPE material has shown no noticeable ones. The values of elongation at break and the thermo-oxidative stability decrease with the advanced degradation, density tends to increase with the absorbed dose. For XPE samples this effect was partially explained by the increase of crystallinity. It was tested by the DSC determination of the crystalline phase amount.

Gloria Maria Vinhas et al (2003) in their work they studied the properties of PVC/plasticizer systems submitted to different doses of gamma radiation.^[15] They have used four commercial plasticizers amongst them di(2-ethylhexyl) phthalate, DEHP, which

is present in a great number of commercial applications. The PVC/plasticizer systems were studied as films made by the solvent evaporation technique. Irradiated and non-irradiated films were characterized by viscosimetric analysis, mechanical essays and infrared spectroscopy. The results have shown that the rigid, non plasticized, PVC film presented the greatest degradation index, while among the plasticized films the one which presented the larger degradation index due to chain scission was the DEHP plasticized PVC.

Cleland M.R et al (2003) in their study established through their work that the physical and chemical properties of polymeric materials can be modified by treatment with ionizing radiation in the form of gamma rays, X-rays and energetic electrons.^[10] High-energy electron beams are especially useful in this regard. Polymerizing (curing), grafting, crosslinking and chain scissioning reactions can be initiated by irradiation. The results of such reactions can enhance the utility and value of commercial products. Brief reviews of a variety of successful applications are given in this paper. Additional information is provided about reaction yields (G-values), temperature rises during treatment and the radiation stability of common polymers.

Wang G.J et al (2004) had prepared heterogeneous latices of acrylic core-shell polymers and prepared via a two-stage seeded emulsion polymerization for plastisol-gel of automotive underbody coatings and body sealers.^[36] 1,6-Hexanediol diacrylate (HDDA) was introduced to the rubbery core and/or the glassy shell with interpenetrating polymer network (IPN). The latices were characterized by submicron particle sizer, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The properties of plastisol-gels prepared by mixing the core-shell polymers and DOP/TCP plasticizers were investigated by testing the storage stability of plastisols and the mechanical properties of plastigels. These novel core-shell polymers represent a highly

positive innovation and a wide application in automotive industry instead of the hazardous material PVC plastisol.

Thai Hoang and Neil Varshney (2004) presented some thermomechanical characteristics of crosslinked poly(vinyl chloride) (PVC) samples such as glass transition temperature (T_g), softening point (T_s), and linear thermal expansion coefficient (α).^[32] Probe load of 0.05 N is most suitable to evaluate expansion, softening and contraction of the crosslinked PVC samples. T_g , T_s and α of the crosslinked PVC samples are higher than those of the uncrosslinked samples. The highest T_g is observed in the PVC sample containing 0.4 phr of 1,1-di-(*t*-amylperoxy) cyclohexane (DAPC) and 10 phr of trimethylolpropane trimethacrylate (TMPTMA). Among the crosslinked PVC samples, the sample with 0.2 phr of DAPC and 15 phr of TMPTMA has the least T_s . The highest α appeared in the PVC sample containing 0.4 phr of DAPC and 5 phr of TMPTMA.

Vinhas G.M et al (2004) examined the gamma radiation effects on PVC plasticized with di(2-ethylhexyl)phthalate (DEHP), diisobutyl phthalate, trioctyl trimellitate and Viernol, as well as its effect on PVC plasticized with DEHP and stabilized with Tinuvin P.^[35] The PVC samples were analysed, before and after irradiation at different doses, by UV spectroscopy, viscometry and mechanical testing. A multivariate statistical analysis was carried out on five properties: tensile strength, percent elongation, number of scissions per chain, viscosity-average molecular weight and UV-visible absorbance. The scores from a principal component analysis (PCA) of the nonstabilized samples showed that the PVC/DEHP samples were the most degraded by chain scission upon irradiation, especially at the 25 and 60 kGy dosages, while the 400 nm absorbance, associated with film yellowing, remained relatively unchanged for these samples. For the other three systems, degradation by chain scission was smaller, and the UV absorbance was more dependent on radiation dosage. For the PVC/DEHP samples,

the addition of Tinuvin P significantly decreased the number of scissions per chain, especially at 25 and 60 kGy irradiation doses.

Gloria M. Vinhas et al (2004) studied to minimize the degradation of this polymer by adding Stabilizing additives.^[16] These additives act by substituting irregular structures such as the allylic chloride atom in the PVC by stable structures, thus retarding the radiolytic degradation of the polymer. In this study they looked at the radiolytic degradation in films of PVC plasticized with DEHP and stabilized with Tinuvin P, by viscometry, mechanical properties and ultraviolet-visible absorption spectroscopy. The variation of the number of scissions per chain, studied by viscometry showed efficiency in the stabilized polymer. The results showed an excellent protection of scission degradation of the chain attributed to the stabilizer, with a maximum protection of 90% at a concentration of 0.5% Tinuvin P, as well as the improvement of the mechanical properties when the polymer was subjected to different doses of radiation.

Benavides R et al in their work we have added 3 transfer agents to PVC formulations (mercaptoethanol-ME, dodecylmercaptane-DDM, benzyltriphenyl phosphonium chloride-CBF) in order to reduce TMPTMA homopolymerization reaction, enhancing crosslinking density of the PVC network.^[7] Gel percentage and crosslinking densities were reported for PVC formulations, as well as Mechanical (DMA) and spectroscopic (FTIR) evaluations. Stability was evaluated by HCl evolution and Activation energies (E_a) for dehydrochlorination measured by a TGA-Arrhenius method.

Sophie Rouif (2005) presented a paper with a purpose to review the innovative and recent applications of radiation cross-linking of polymers that reinforces their dimensional stability in chemically aggressive and high temperature conditions.^[30] Radiation cross-linking can be applied to a great number of plastics: thermoplastics, elastomers and thermoplastic elastomers (TPE). Some of them can cross-link on their

own, some others need to be formulated with a cross-linking agent (promoter) or to be modified during their polymerization. Some results of chemical and thermomechanical characterizations of radiation cross-linked plastics based on engineering polymers was described, and their advantages were emphasized in relation with their applications in various sectors: pipes and cables, packaging, automotive, electrical engineering and electronics, including connectors, surface mounted devices, integrated circuits, 3D-MID technology, etc. The paper concluded with a short review of the industrial irradiation facilities (EB facilities and gamma plants) adapted to the treatment of such various products.

Juliette Colombani et al (2006) found that the room temperature gamma irradiation at medium (1e100 kGy) or high (0.9e25 MGy) doses induced different radicals into pure or industrial poly(vinyl chloride) (PVC); the various ESR signals differ by their shapes and/or values of their g-factors and/or peak-to-peak widths but do not give precise information on the chemical structures of the different radicals as the spectra are only poorly resolved.^[18] However, looking at the ESR parameters of the different signals and their evolution during natural ageing of the samples, allows us to make correlations between the radio induced lines in industrial PVC and the ones induced in pure PVC or in PVC additives.

Pedro Miguel Romero Tendero et al (2006) employed soft PVC for the manufacturing of a wide range of products with different properties and a relatively low cost.^[26] The utilization of soft PVC is restricted by the poor thermal, chemical and mechanical resistance properties. Also, plasticizer migration can modify the properties or can make useless the materials for some applications because of toxicity or a general loss of properties. PVC crosslinking is the most effective way to improve mechanical and transport properties of rigid or flexible PVC at high temperatures, but at the same time the

thermal stability of PVC may be significantly reduced. In this work, the crosslinking reaction of plasticized poly(vinyl chloride) (PVC) through difunctional amines was studied. The mechanisms involved in the crosslinking reaction were explained by Fourier transform infrared (FTIR) analysis. The thermal activated crosslinking reaction was studied by cone and plate rheometry, analyzing the evolution of viscoelastic properties of the suspension as a function of time and temperature. The effect of the addition of crosslinking agents on the thermal stability of the polymer was studied by thermogravimetric analysis (TGA), which revealed that crosslinking reactions promote thermal degradation phenomena in the polymer matrix. This is attributed to the formation of HCl and other species promoting polymer degradation during crosslinking, thus leading to higher weight loss during thermal treatment with respect to unmodified PVC plastisols. This was also confirmed by an evident yellowing after crosslinking, especially at higher temperatures.

Juliette Colombani et al (2007) investigated anaerobic and aerobic radiolysis mechanisms of poly(vinyl chloride) using electron spin resonance (ESR), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). PVC samples have been irradiated by γ rays (^{60}Co) at high doses (up to 4 MGy) and at room temperature.^[19] High dose anaerobic radiolysis of PVC induced several modifications in polymer. Alkyl radicals are formed, and then these radicals induced the formation of polyenic radicals. ^{13}C NMR spectra have also shown the formation of polyenic sequences and crosslinking reactions. The modifications induced in PVC irradiated under aerobic condition are different. ESR spectra have shown that peroxy radicals are formed. Propagating reactions from peroxy radicals are mainly composed by β -scission reactions. These β -scission reactions involved the decrease of average molecular weight and the formation of aldehydes, acids chloride and/or

carboxylic acids. From all these results, anaerobic and aerobic mechanisms of degradation by PVC radiolysis are proposed.

Zaki Ajji (2007) irradiated ternary mixtures of poly(vinyl pyrrolidone) (PVP), citric acid (CA) and water at various gamma ray doses.^[39] Copolymer swelling and gelation% were determined with respect to the irradiation dose and PVP/CA composition. He has observed that the gelation % increases with increasing the irradiation dose, but decreases with increasing the CA content in the graft copolymer. The swelling% of the prepared hydrogels decreases with increasing the irradiation dose and CA content in the copolymer, as a result of an increase in the crosslink density and the hydrogen bonds, respectively. It was also observed that the ion exchange capacity and the uptake of uranyl ions increase with increasing the CA content in the graft copolymer.

McCaffrey J. P et al (2007) had studied the attenuating properties of several types of lead (Pb)-based and non-Pb radiation shielding materials were studied and a correlation was made of radiation attenuation, materials properties, calculated spectra and ambient dose equivalent.^[22] Utilizing the well-characterized x-ray and gamma ray beams at the National Research Council of Canada, air kerma measurements were used to compare a variety of commercial and pre-commercial radiation shielding materials over mean energy ranges from 39 to 205 keV. The EGSnrc Monte Carlo user code cavity.cpp was extended to provide computed spectra for a variety of elements that have been used as a replacement for Pb in radiation shielding garments. Computed air kerma values were compared with experimental values and with the SRS-30 catalogue of diagnostic spectra available through the Institute of Physics and Engineering in Medicine Report 78. In addition to garment materials, measurements also included pure Pb sheets, allowing direct comparisons to the common industry standards of 0.25 and 0.5 mm “lead equivalent.” The parameter “lead equivalent” is misleading, since photon attenuation properties for all

materials (including Pb) vary significantly over the energy spectrum, with the largest variations occurring in the diagnostic imaging range. Furthermore, air kerma measurements are typically made to determine attenuation properties without reference to the measures of biological damage such as ambient dose equivalent, which also vary significantly with air kerma over the diagnostic imaging energy range. A single material or combination cannot provide optimum shielding for all energy ranges. However, appropriate choice of materials for a particular energy range can offer significantly improved shielding per unit mass over traditional Pb-based materials.

Flavio Ferreira da Silva et al (2008) has studied Commercial polystyrene (PS) as a modifier for commercial poly(vinyl chloride) (PVC) when it was submitted to gamma irradiation.^[13] PVC/PS blends were prepared with 100/0, 95/05 and 90/10 compositions. Results for gamma-irradiated (⁶⁰Co) blends were reported and changes in viscosity-average molar mass (M_v) were analyzed. The study showed that the addition of PS into PVC decreased by 73% (95/05) and 79% (90/10) the number of scissions/100 eV in the dose range of 25–100 kGy. Viscosity analyses by the Pan et al. criterion and analyses of FT-IR spectra in the C–Cl vibration region showed negligible intermolecular interactions between the components of PVC/PS blends. However when the films of blends were irradiated to 50 kGy, certain intermolecular interactions were observed by the viscosity method. The addition of PS to PVC and the main scission effect induced by gamma irradiation decreased crosslink density of blends causing changes in the elongation at break and Young's modulus.

Abbas Behjat and Djafar Gheysari (2008) carried out irradiation of plasticized PVC (PPVC) compound containing a cross-linking monomer by a 10 MeV electron beam.^[1] This compound mainly was used as insulation in the wire and cable industry. The cross-linking monomers EHPTM and TAC at different ratio of 3, 6, and 9 phr were used.

The dose range was varied from 50 to 150 kGy. The effects of monomers and radiation dose on radiation cross-linking were studied by hot-set testing and gel content measurements. In the absence of EHPTM and TAC, cross-linking did not take place by high energy electron beam at any dose and samples had very large elongation in a hot-set apparatus. But in the presence of these monomers, gel content augmented with an increase in radiation dose and EHPTM level. The highest value of approximately 76% gel content was obtained. In this case the lowest hot-set value was about 12%. Also, tensile strength, elongation at break, modulus, volume resistivity, dielectric strength, and limiting oxygen index of samples were examined. It was found that the mechanical properties of samples containing EHPTM and TAC improved significantly with increasing radiation dose. But for PPVC samples loaded with EHPTM, tensile strength values were higher than those of the loaded ones with TAC at all radiation doses. From the hot-set data it was concluded that the samples loaded with EHPTM had a low thermal expansion compared with samples loaded with TAC. The results indicated that EHPTM is a more effective cross-linking agent for PPVC compound compared with TAC.

Carole Laine et al (2008) studied kinetics of free radical in-situ polymerization of glycidyl methacrylate (GMA), in a complex evolutionary system: poly(vinyl chloride) (PVC) plastisols.^[8] A predictive model of conversion-time profile based on free radical mechanism was proposed and structure of the modified PVC system developed was investigated by NMR analyses. In order to elucidate the mechanism of the reaction, model molecules for PVC were used with NMR and MALDI-TOF characterization. It was found that in-situ polymerization of GMA in PVC plastisols leads to both homopolymerization and grafting of GMA onto PVC backbone by hydrogen abstraction. For 33 wt% GMA loaded, grafting efficiency is 67% with an amount of grafted polyglycidyl methacrylate (pGMA) equals to 22 wt%. Thus, this article discloses a new type

of PVC plastisols called reactive plastisols where, in addition to usual plasticizers, PVC is modified by polymerizable GMA monomer.

Roach N et al (2009) in their paper described an approach to the study of the influence of the nature and the composition on the performance properties of wood flour/poly(vinyl chloride)(PVC) composites.^[28] The raw materials were mixed on a two-roll mill. The final composites were obtained by controlled press moulding. The results indicate that properties such as surface tension and flexibility do not change significantly with the composition in the chosen composition range. The colour is easily controlled by variation in the content and the type of wood flour. A thermal and morphological study has been performed on the raw materials and on the composites to assess the effect of wood flour on the stability of the composites. The inclusion of wood flour into PVC leads to poorer tensile properties. This effect is related to the lack of association between the wood flour and the PVC.

Moulay S (2010) in his paper, an account of many of the chemical modifications of PVC based on reports over the last decade is delineated, along with related applications.^[24] These modifications are presented according to the bond formed (CPVC–X) between the PVC carbon CPVC and the atom X (X=N, O, S, Hal) of the modifying molecule.

Mei Chan Sin and Irene Kit Ping Tan (2012) with the aim to improve the physical properties of PVC, biopolyesters were investigated for the plasticizing and thermal effects in PVC.^[23] In this study, polymeric medium-chain-length poly(3-hydroxyalkanoates) (mcl-PHA) were produced by *Pseudomonas putida* PGA1 using renewable carbon substrates and oligomeric mcl-PHA were generated by partial thermal degradation of the polymers. The effects of blending these biopolyesters with PVC were investigated in terms of thermal behaviour and thermodegradation kinetics. The PVC/PHA blends

showed a single T_g with lower values than PVC, indicating that mcl-PHA was compatible with PVC. T_g from DSC analysis agreed well with theoretical T_g predicted from Gordon Taylor equation. The apparent activation energy (E_d) and pre-exponential factor (A) for the thermodegradation of PVC and its blends were determined using Kissinger method. Change in entropy of activation (DS) for the thermodegradation was also determined. All PVC/PHA blends had lower E_d , A and DS than PVC. Higher reduction of E_d , A and DS was observed when the proportion of PHA was increased in the blend; and when oligomeric PHA was used as the plasticizer instead of polymeric PHA. The dependence of E_d on the extent of conversion (α) for the thermodegradation process of PVC and PVC/PHA was determined by Flynn-Wall-Ozawa method and results showed that E_d is an increasing function of α . This indicated that the thermal decomposition of PVC and its blends display complex reaction mechanism(s).

Federica Chiellini et al (2013) in their review outlined recent scientific approaches for preventing DEHP contamination of humans by P-PVC medical devices, highlighting the impact of the proposed alternative materials on human health and strategies for implementing them.^[12]

Williams B. da Silva et al (2013) have investigated the samples of commercial PVC containing a salt mixture of CuCl_2/KI (PVC-salt).^[37] The samples were irradiated with gamma radiation (^{60}Co) at dose 25 kGy. PVC and PVC-salt system showed a decrease in viscosity molar mass values on irradiated samples reflecting the main chain random scissions effect. However the PVC-salt at 0.5 wt% concentration showed no significant degradation index value. This result suggests that salt keeps the good radiolytic stabilization behavior of gamma-irradiated PVC. The CuCl_2/KI mixture at 0.5 wt% in the PVC matrix also influenced the thermal behavior of the polymer increasing the maximum thermal degradation temperature in 42 deg C. In addition, the salt mixture

influences significantly the Young's Modulus of PVC increasing the rigidity of polymer. Specific interactions between PVC and CuCl₂/KI mixture were observed in the FT-IR spectra.

Lorena Garcia-Uriostegui et al (2013) had studied the effects of gamma radiation on pristine poly(vinyl chloride) in the presence of the antirads 2-vinylnaphthalene and 4-vinylbiphenyl.^[21] External protection derived from the addition of antirads at 3 and 5% wt concentration in the PVC film and internal protection from grafted antitrades was evaluated. The grafted antirads were obtained through irradiation with a Co⁶⁰ gamma source at a dose rate of 10.5 kGy h⁻¹. Doses ranged from 10 to 40 kGy. Radiation resistance of the modified and pristine PVC (PVCeg-antirads and blends) was evaluated in the range of 600e3000 kGy at a dose rate of 10 kGy h⁻¹. The radiation resistance was characterized from crosslinking measurement, infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry.

CHAPTER-3

EXPERIMENTAL SECTION

During the course of this project, various experimental methods/techniques were used for the preparation, characterization & studies of the PVC-Plastisol compositions. All the testing and analysis were carried out as per the ASTM or available international standards.

3.1 Raw materials: Various raw materials used in the present experimentation are given in detail in the ensuing subsections.

3.1.1 Poly Vinyl Chloride: Polyvinyl Chloride (PVC) from M/s Chemplast India of Grade 124 has been used. It is of paste grade resin of medium molecular weight best suited for making leather cloth and for PVC plastisols. Dispersion resin has a very fine particle size, very high surface area and little or no porosity. Specifications of the said material are given in Table 3.1.

Table 3.1 Product specifications of PVC *

Property	Value
Bulk Density gm/cc	0.57
Inherent viscosity cP	1.60
K value	87
Particle size (microns)	130-180
Porosity cc/gm	0.46
Retention % through 40 mesh	45%

* Grade 124 of M/s Chemplast

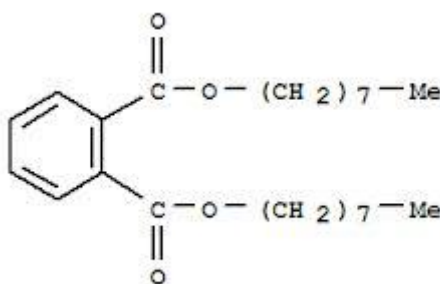
3.1.2 Plasticizers

The main primary plasticizer DOP (Di-octyl Phthalate) is used and epoxidised soyabean oil (ESO) is used as the secondary plasticizer.

3.1.2.1 DOP: Di-octyl phthalate also known as 2-diethyl hexyl phthalate is largely used in PVC compositions. It is a polar aromatic plasticizer whose particles behave like dipolar molecules and forms a link between chlorine atoms belonging to two polymer chains. It can be easily introduced in the polymer matrix. In our formulations, DOP of M/s KLJ polymers was used and product specifications are given in the Table 3.2.

Formula: $C_6H_4(COOC_8H_{17})_2$

Molecular Weight: 390.56



Structural Formula of DOP

Table 3.2 Specifications of DOP*

S.No	Property	Unit	Value
1	Appearance	Visual	Water white clear liquid
2	Colour	Max Haxen unit	30
3	Heat Stability at 180°C for 2 hrs	Visual description	No change in colour
4	Sp. Gravity at 27°C	g/cm ²	0.983 ± 0.003
5	Refractive Index at 27°C	-	1.486 ± 0.002
6	Ester value	(mg KOH /mg)	287 ± 3
7	Ester content (min)	% by weight	99
8	Viscosity at 20°C	CPS	82 ± 2
9	Boiling temperature	Deg Celsius	386
10	Relative fusion temperature	Deg Celsius	84

* KLJ Chemicals

3.1.2.2 Epoxidised Soyabean Oil (ESO):

ESO has a high molecular weight and provides plasticizing cum stabilizing action against degradation by heat and light in PVC compositions. It has excellent resistance to extraction by soapy water and provides resistance to extraction by oil and gasoline. It improves durability of PVC compounds towards UV light. ESO has been used in PVC compositions as secondary plasticizer. The specifications of the ESO are given in the Table 3.3. Structural formula of the said chemical is given below.

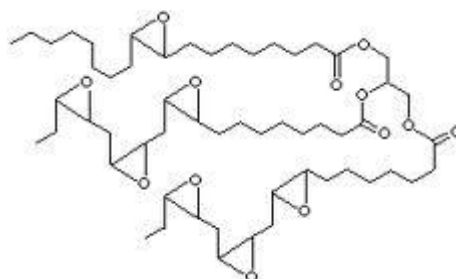


Table 3.3 Specifications of ESO*

S.No	Property	Value
1	Appearance	Light yellow viscous liquid
2	Density	0.994 gm/cm ³
3	Melting point	0°C
4	Solubility in water	Insoluble
5	Flash point	227°C
6	Molecular weight	1000
7	Viscosity in stokes	4.2
8	Refractive Index at 25°C	1.472
9	Fire point	315°C

* Vikoflex 7170

3.1.3 Thermal Stabilisers

Thermal stabilizers have an ability to replace or displace active, labile substituent groups, such as tertiary and allylic chlorine atoms.

In our compositions we used Octyl Tin Mercaptide (OTM) as a thermal stabilizer. It is particularly effective in both initial colour and long term heat stability in most types of PVC resins used in this application. The properties of OTM are given in the Table 3.4.

Molecular formula: C₂₂H₄₄O₄S₂Sn

Table 3.4 Specifications of OTM *

Property	Typical value
Physical Appearance	clear, yellowish liquid
Element sulphur	8.80-9.50%
Refractive index at 25 ⁰ C	1.4995 - 1.5050
Element tin	14.0- 15.4 %
Density at 25 ⁰ C	1.080 - 1.100 g/ml
Viscosity (m Pas/25 ⁰ C)	0.055-0.065

* Shital Grade No. 65

3.1.4 UV Stabilisers: The UV absorbers dissipate the absorbed light energy from UV rays as heat by reversible intramolecular proton transfer. Bisphenol - A was used as in the present study. Bisphenol A is an organic compound with the chemical formula (CH₃)₂C(C₆H₄OH)₂ belonging to the group of diphenyl methane derivatives. It is a

colourless solid that is soluble in organic solvents, but poorly soluble in water. Bisphenol A has a vapour pressure of 5×10^{-6} Pa.

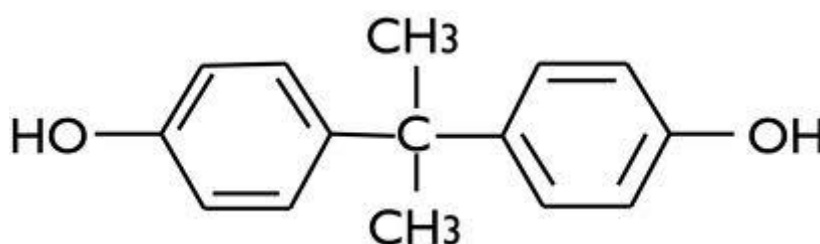
Molar mass: 228.29 g/mol

IUPAC ID: 4,4'-(propane-2,2-diyl)diphenol

Density: 1.20 g/cm³

Boiling point: 220°C.

Structural formula:



3.1.5 Antioxidants: Antioxidants are used to terminate the oxidation reactions taking place due to different weathering conditions and reduce the degradation of organic materials. IRGANOX 1010 from M/s Ciba Chemicals has been used in the present study. It is a sterically hindered phenolic antioxidant, non discoloring stabilizer for organic substrates such as plastics, synthetic fibers, elastomers. It protects these substrates against thermo-oxidative degradation. It has good compatibility, high resistance to extraction, low volatility, odourless and tasteless. The product can be used in combination with other additives such as co stabilizers, light stabilizers and other functional stabilizers.

Chemical Name: Pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)

Molecular formula: C₈H₇O₃

Structure of the chemical:

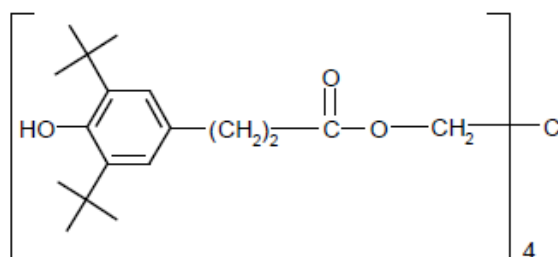


Table 3.5 Specifications of IRGANOX 1010*

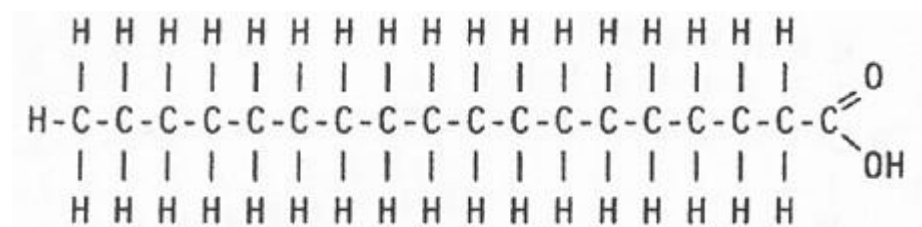
Property	Typical value
Molecular Weight	1178
Physical appearance	Free flowing powder
Specific Gravity at 20°C	1.15 g/cm ³
Flash Point	297°C
Bulk Density	630 g/l
Melting range	110-125°C

* Ciba Chemicals

3.1.6 Lubricants

Lubricants are needed to promote controlled release of PVC during processing from mill or calender rolls from the injection, compression or plastic molds and from the injection press and extruder screws and cylinders and also in forming dies.

In this study, Stearic acid and Butyl stearate were used as lubricants in PVC formulations. Stearic acid and Butyl stearate of M/s Loba Chemie Pvt. Ltd. and M/s ALA Chemicals Pvt. Ltd respectively were used and the product specifications are given in Table 3.6 and 3.7. Structural formula of Stearic acid and Butyl stearate are given below:

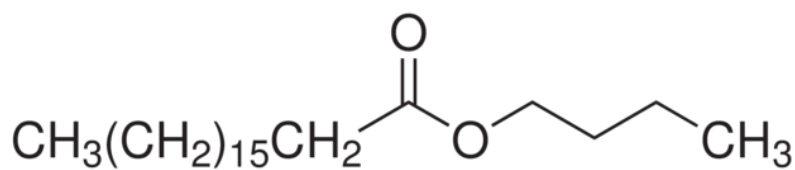


Stearic acid

Table 3.6 Specifications of Stearic acid*

S. No.	Property	Unit	Value
1.	Appearance and odour	--	White flakes
2.	Freezing point	°C	67
3.	Boiling point	°C	183

* Loba Chemie Pvt. Ltd.



Butyl stearate

Table 3.7 Specifications of Butyl Stearate*

S. No.	Property	Unit	Value
1	Appearance	---	White powder
2	Melting point	°C	179
3	Solubility in water	g/ml	Insoluble

* ALA Chemie Pvt. Ltd

3.1.7 Crosslinking Agents

The use of poly functional monomers as additives is shown to enhance significantly the chemical crosslinking of PVC films under certain radiation conditions. Trimethylolpropane Trimethacrylate (TMPTMA) of M/s Aldrich Chemicals as crosslinking agent in PVC formulations was used in the present study, whose product specifications are listed out in Table 3.8.

Molecular Formula of TMPTMA - $\text{C}_{18}\text{H}_{26}\text{O}_6$

Structural formula:

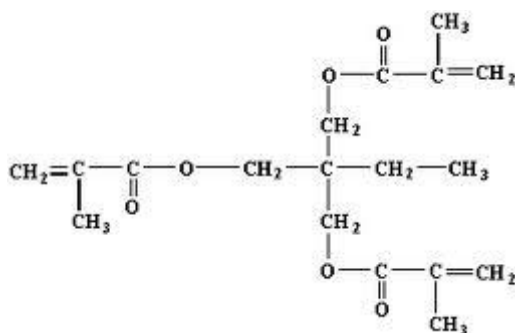


Table 3.8 Specifications of TMPTMA *

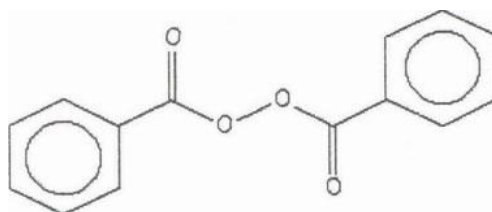
S.No	Property	Unit	Value
1	Appearance		colourless to light coloured
2	Physical form		clear liquid
3	Density at 25 °C	g/cm ³	1.06
4	Boiling point at 1.33 hPa	°C	155
5	Viscosity at 25°C	mPa·s	44
6	Flash point	°C	115
7	Index of refraction at 20 °C		1.47
8	Vapour pressure, 30°C	mbar	8
9	Surface tension	dynes/cm	33.6
10	Functionality	Theoretical	3

* Aldrich Chemicals

3.1.8 Benzoyl Peroxide

Peroxides are used for crosslinking of PVC. The peroxide crosslinking of PVC is expected to enhance penetration resistance and service temperature of PVC. Benzoyl peroxide is an organic compound in the peroxide family. It consists of two benzoyl groups bridged by a peroxide link. Its structural formula is $[C_6H_5C(O)]_2O_2$. It is one of the most important organic peroxides in terms of applications and the scale of its production.

Benzyl peroxide of M/s SD Fine Chemicals Ltd was used as a peroxide initiator in the present study. Structural formula of the chemical is



3.2 Preparation of plastisol: We had prepared PVC compositions by varying the concentration of DOP, and TMPTMA given in preceding sections. The required components of each batch are properly weighed and are mixed properly in a planetary mixer for about one hour. Planetary Mixer used for mixing is presented in the Figure 3.1. The speed of the mixer is kept at 600 RPM. Details of raw materials and their quantities are indicated in Table 3.9 and 3.10.



Figure 3.1 Planetary Mixer

The properly mixed plastisol solution is filtered to remove the undissolved components. Viscosity of the prepared plastisols is measured at different intervals using Brookfield Viscometer.

Table 3.9 Composition of PVC plastisol formulations without a cross linking agent

S. No	Ingredients	Batch 1(phr)	Batch 2 (phr)	Batch 3 (phr)
1	PVC	100	100	100
2	DOP	60	70	80
3	ESO	10	10	10
4	OTM	4	4	4
5	Al – 04	0.5	0.5	0.5
6	Bisphenol A	0.5	0.5	0.5
7	Stearic acid	0.5	0.5	0.5
8	IRGNOX-1010	0.5	0.5	0.5

phr – parts per hundred resin

Table 3.10 Composition of PVC plastisol formulations with a cross linking agent

S. No.	Ingredients	Batch 4 (phr)	Batch 5 (phr)	Batch 6 (phr)	Batch 7 (phr)
1	PVC	100	100	100	100
2	DOP	70	70	70	70
3	ESO	10	10	10	10
4	OTM	4	4	4	4
5	Al – 04	0.1	0.1	0.1	0.1
6	Bisphenol-A	0.5	0.5	0.5	0.5
7	Stearic acid	0.5	0.5	0.5	0.5
8	IRGNOX-1010	0.5	0.5	0.5	0.5
9	TMPTMA	1	3	5	10
10	Benzoyl Peroxide	0.2	0.2	0.2	0.2

3.2.1 Viscosity measurement

The Brookfield Dial Viscometer measures fluid viscosity at given shear rates. Viscosity is a measure of a fluid's resistance to flow. The diagram of the viscometer used in the present study is given in Figure 3.2. The Dial Viscometer rotates a sensing element

in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper spring. The degree to which the spring is wound, indicated by the red pointer, is proportional to the viscosity of the fluid. The Viscometer is able to measure over a number of ranges since, for a given spring deflection, the actual viscosity is proportional to the spindle speed and is related to the spindle's size and shape. For a material of given viscosity, the resistance will be greater as the spindle size and/or rotational speed increase. The minimum viscosity range is obtained by using the largest spindle at the highest speed; the maximum range by using the smallest spindle at the slowest speed.

All units of measurement are calculated in units of centipoise (cP) by using a look-up table known as "the Brookfield Factor Finder" to convert torque reading.



Figure 3.2 Brookfield Viscometer

Operation

The Brookfield Viscometer is powered by a precision synchronous motor. Exact speeds of rotation are assured as the motor will turn erratically and spasmodically if synchronization cannot be maintained. Speed changes are affected by a gear train having

either four or eight speeds. Maximum speed (RPM) is set at full clockwise rotation and minimum speed at full counter-clockwise rotation. Four speed Viscometers have a square speed control knob with one number shown on each of four faces. The instrument's rotational speed is indicated by the number facing up. Eight speed models have a square speed control knob with two numbers on each face; by moving the knob through two complete turns, speeds may be changed in sequence. To insure rotation at the indicated speed, it is important that the face of the knob upon which this speed is shown be closely parallel to the viscometer's dial.

The spindles are attached to the viscometer by screwing them to the lower shaft. The lower shaft should be held in one hand and lifted up. The spindle should be screwed to the left. The face of the spindle nut and the matching surface on the lower shaft should be smooth and clean to prevent eccentric rotation of the spindle. Spindles can be identified by the number on the side of the spindle nut.

All Brookfield Dial Reading Viscometers are provided with a clutch lever located at the back of the instrument. Depressing the lever raises the dial against the pointer and "holds" the instrument's reading. When the clutch is released the dial is lowered and the pointer will be freed. Any of the controls on the Viscometer - the motor switch, speed change knob, and clutch - may be operated independently of the other.

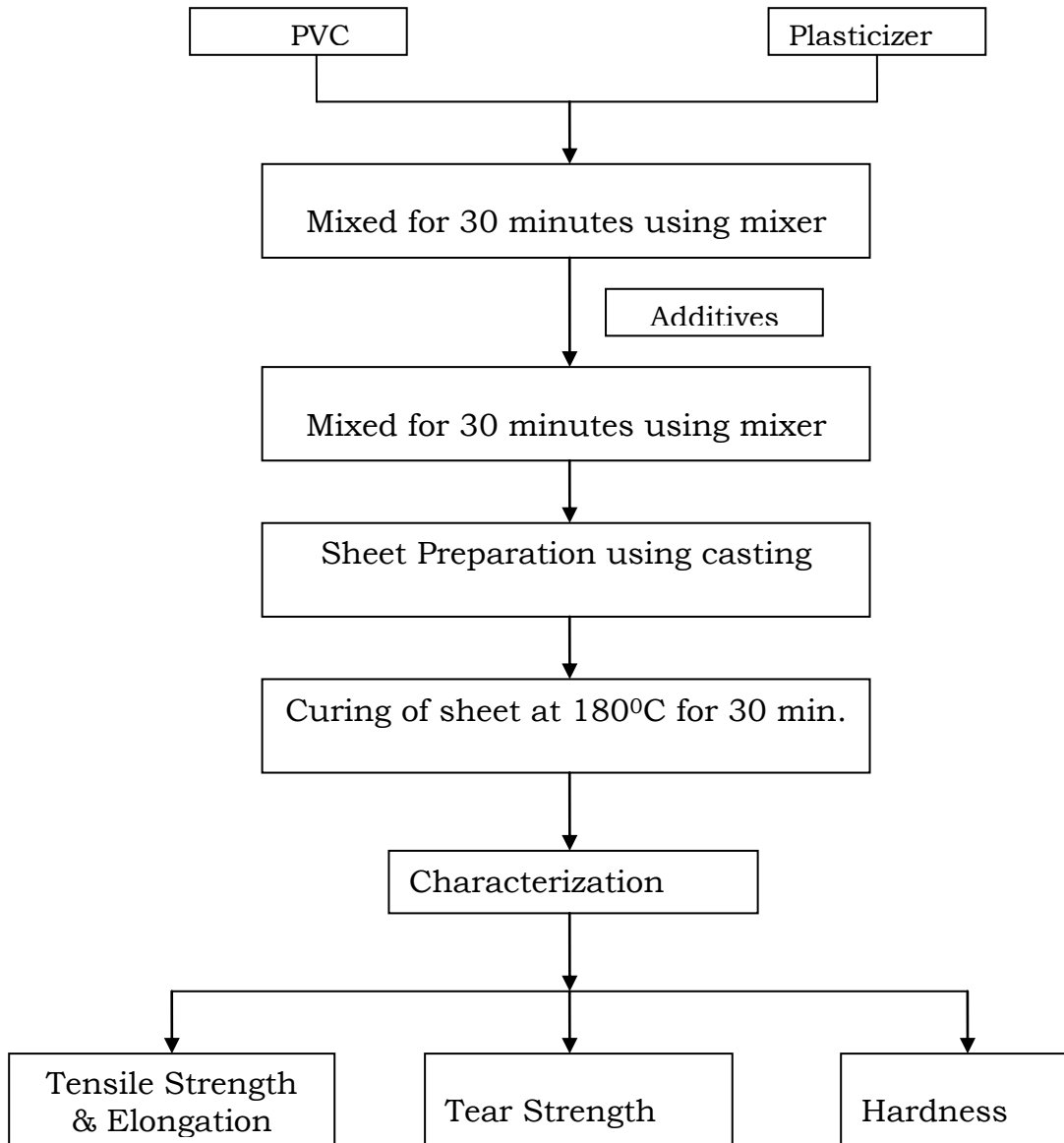
Conditioning: The prepared PVC Plastics are conditioned at temperatures of $23 \pm 2^{\circ}\text{C}$ for at least one hour before testing.

Procedure: PVC Plastics of each batch is taken in a 600 ml beaker and is analysed for the viscosity with the Brookfield Viscometer. The RPM of the Viscometer is set at 60 and spindle 4 was used for the measurement. This is repeated at time intervals of 1, 7, 14 and 21 days for each sample. The viscosity of the sample is given in the units of cP. Effect of viscosity with time was studied with this data.

3.2.2 Casting of PVC sheet

Thin sheets of size 20x20 cms are cast on a glass plate of thickness 2mm and are kept in an oven at 180 °C for 45 minutes to facilitate proper curing of the material. The prepared sheet of the each composition has been evaluated for the physico-mechanical properties to study the effect of gamma radiation on the developed compositions using a cobalt -60 gamma irradiator available at Shri Ram Institute for Industrial Research, Delhi. Effect of artificial weathering on developed formulations is studied from the artificial weathering chamber available at the institute.

Following is the flow diagram of the work plan.



3.3 Characterization of developed sheets

The various prepared formulations were characterized before and after radiation for various properties such as:

1. Tensile strength and elongation.
2. Hardness.
3. Tear strength.
4. Thermal stability.
5. UV Weatherability test.

6. Morphological study using SEM

3.3.1 Tensile strength and elongation % (ASTM D-638)

The tensile strength and elongation % of the different samples was determined as per ASTM D-638 using an INSTRON UNIVERSAL testing machine. 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 Test is the measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Testing machine is given in Figure 3.3.

The test samples were cut into the standard size according to specification. ASTM; D-638-80. At least five strips of size one inch width were cut from the sheet. Maximum load required to break these strips were noted and tensile strength was calculated using the following formula i.e.

$$\text{Tensile Strength} = \frac{\text{Max. load}}{\text{Area of the strip}}$$

Similarly, % elongation at break was determined using Instron machine.

Preparation of test specimen: Dumbbell shaped die was used for cutting the test specimens from the compression moulded PVC sheets. All surfaces of the specimen were free from visible flows and scratches.



Figure 3.3 Universal Testing Machine

Procedure

We had selected the load range such that specimen failure occurs within its upper two third. After measuring the cross-sectional area of the specimen at several points along its length, we adjusted the initial grip separation at least 50 mm for material having a total elongation at break of 100% or more and placed the test specimen between the grips of the testing machine. The grips were tightened evenly and firmly to the degree necessary to minimize slipping of test specimen during the test. The machine was started and readings of load versus extension were recorded apart from noting the load at breaking point of the test specimen. The tensile energy to break is the total energy absorbed per unit volume of the specimen up to the point of rupture. Dumbbell shaped specimens of PVC sheets before and after radiation are shown in Figure 3.4.



Figure 3.4 Dumbbell shaped specimens before and after radiation

Specifications used in the machine

Load range (N)	0-100
Extension range (mm)	0-1500
Speed (mm/min)	50
Sample length (mm)	25

Expression of Results

The tensile strength is given in MPa by the formula:

$$T.S = \text{Load/Thickness} \times \text{Width}$$

3.3.2 Hardness (ASTM 2240):

Shore hardness is a measure of the resistance of a material to the penetration of a needle under a defined spring force. It is determined as a number from 0 to 100 on the scales A or D. The higher the number, the higher the hardness. Thermoplastic elastomers are measured in Shore A and Shore D according to ASTM. For hard materials Shore-D is used, for soft/flexible material Shore-A is used. The hardness of different samples was determined using Shore-D hardness as per ASTM- 2240.

Conditioning: The specimens were conditioned at temperature at $23 \pm 2^{\circ}\text{C}$ before test.

Procedure: The specimen of 6 mm minimum thickness was taken. The surface of the specimen was made flat to have sufficient area to permit the pressure foot of contact. The specimen was placed on a hard horizontal surface and the Hardness Durometer was held in a vertical position with the point of indenter at least 12 mm from any edge of specimen, and the reading on dial was noted. The press on the specimen sample was applied without shock.

3.3.3 Tear Strength (ISD 624-91): This test method describes procedures for measuring the property of thermoplastics, called tear strength. It is the ratio of maximum force required to rupture the specimen and the thickness of the test piece.

Principle: The test consists of measuring the force required to completely rupture or tear the specified test piece. The tearing force is applied by tensile testing machine, until the test piece was completely ruptured. The maximum load is recorded.

Preparation of test specimen: Zig Zag shaped die is used for cutting the test specimens from the compression moulded PVC sheets. All surfaces of the specimen were free from visible flows and scratches.

Number of test specimens: At least five specimens were tested.

Procedure: The width and thickness of the specimen are measured at several points along its edge using Vernier Calipers. Minimum five measurements at different positions on the specimens are taken and the mean is taken. Then specimen is placed in the grips of the testing machine taking care that it does not slip. The axis of the specimen and the grip are aligned with an imaginary line that joins the points of attachment of the grips of the machine. A space of 0.25 inch is allowed between the ends of the gripping surface and the shoulders of the fillet. The test specimen is to be 4.5 inch apart from the grips, and is evenly firmed at a degree necessary to prevent slippage by the specimen. The speed of the machine is set at 50 mm/min and the machine is started. Maximum loads of the specimen are recorded for the test specimen when the strain reaches 0.02 and the elapsed time from the start of the test until this point is reached maximum load of the test specimen is recorded. Photographs of the zig-zag shaped specimens before and after radiation are shown in Figure 3.5.

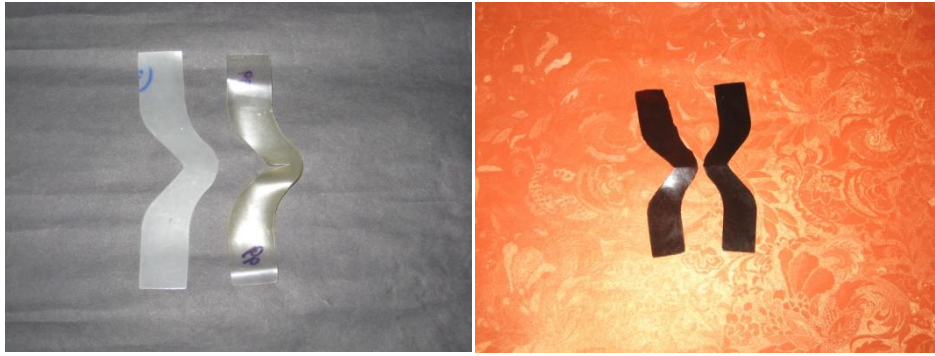


Figure 3.5 Specimens before and after radiation

Expression of results

The Tear Strength TS is given in kilo Newton per mm of thickness, by the formula:

$$TS = F/d$$

3.3.4 Thermal Stability (IS 5831)

The thermal stability is an accelerated method to determine the rate of degradation of the PVC compounds with time under the influence of temperature. Compounds with high thermal stability can withstand continuous processing temperatures. This test method is also known as Congo Red method.

Principle: Thermal stability is the time in minutes required for the degradation of the PVC compound at 200°C, after it was kept in the test apparatus. This is indicated by the red coloration on pH paper produced by the evolution of hydrochloric acid fumes.

Procedure: Each specimen was introduced into the test tube. The specimen should occupy the bottom of the test tube and project not more than 30 mm above the bottom. A strip of dry universal indicating paper was inserted into the open end of the glass tube so that the strip protruded about 5 mm out of the tube. The glass tube was then placed into the heating apparatus for a depth of 60 mm, which had already attained the test temperature specified. Then the time taken was measured for the universal indicating paper to change colour from a pH value of 5 to a pH value of 3.

Expression of results

If the time taken by the specimen is T_1 and final time is T_2 , thermal stability.

$$T = T_2 - T_1 \text{ in minutes.}$$

3.3.5 UV Weatherability test (ASTM G154)

Weathering is the adverse response of a material or product for climate often causing unwanted and premature product failure. The three main factors of weathering are solar radiation, temperature and water. UV radiation emanating from solar radiation causes considerable damage to the materials.

The weathering behavior of a plastic is one of the most important limiting factors in assessing and selecting a plastic for outdoor applications. The selection of a material by simple mechanical properties may well be sufficient in many cases but this is ineffective if the material loses strength or discolors in service.

Testing for weathering

Testing for weathering is a complex process but one essential thing is that the testing must be carried out on the same plastic (compounded and processed) as is intended for the application. Testing using a pure plastic resin will give unrealistic results because the reactive products created during compounding and processing will not be present. Pure laboratory testing involves using environmental chambers and artificial light sources such as Xenotest and QUV apparatus to approximately replicate outdoor conditions but with a greatly reduced test time under very controlled conditions. Laboratory testing can quickly assess the relative stability of plastics but has the major disadvantage that the quicker the test the lower the correlation to real behavior in the field.

Each test method has advantages and disadvantages in terms of control and time taken and it is common for a combination of tests to be carried out to determine the real response to actual field conditions.

Procedure: In the laboratory the PVC sheet specimens were exposed to the UV rays in equipment at the Rubber & Plastics laboratory at the Shriram Institute of Industrial research. The lamps used were UVA-340 with wavelength of 315-400 nm. Cycles of 20 hours UV at $75 \pm 3^{\circ}\text{C}$ followed by 4 hours condensation at $50 \pm 3^{\circ}\text{C}$ were used according the ASTM G154 and GM11. The artificial UV chamber used in the study is given in Figure 3.6. The UV ray curing was carried out for 100 hours which is equivalent for 30 days of natural weathering.



Figure 3.6 UV Weather Resistance Test Chamber

Three specimens of dumb bell and zig zag shaped samples from each batch are taken and marked by a suitable indelible marking on areas not used for testing. The marked specimens are then attached on to the specimen holders in the equipment in such a manner that the specimens are not subjected to any applied stress. To assure uniform exposure conditions, all the spaces are filled properly using blank panels of corrosion resistant material. The test conditions are selected under programmed throughout the test

period without any change. The specimens are periodically repositioned during the exposure period to ensure that each receives an equal amount of UV exposure. Continuous water circulation is maintained in the chamber to ensure non increase of temperature in the chamber. After the exposure period of 100 hours in the UV chamber, mechanical properties of exposed samples are tested according to the ASTM standards.

3.4 Scanning Electron Microscopy

SEM analysis of PVC sheets were carried out using a HITACHI (S-3700N) scanning electron microscope. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signal at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data is collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20x to approximately 30,000x, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semiquantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD)

Principle

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted

backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples. Secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

Instrumentation

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements
- Power Supply
- Vacuum System
- Cooling system
- Vibration-free floor
- Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates. Schematic diagram of the working of a scanning electron microscope is shown in Figure 3.7.

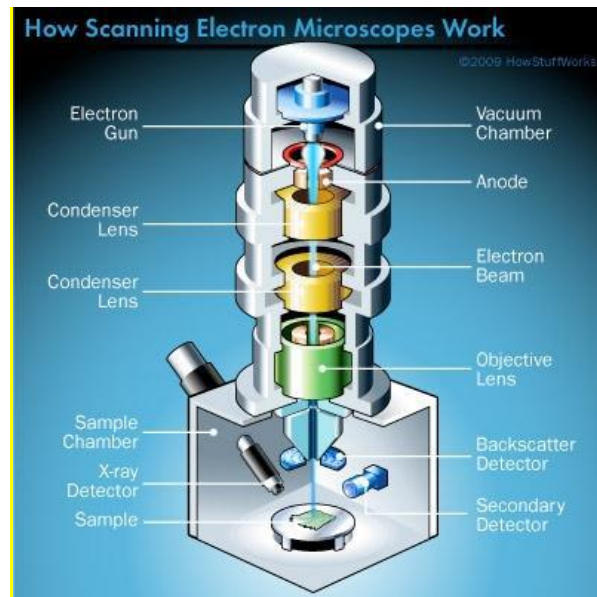


Figure 3.7 Schematic diagram of the working of a scanning electron microscope

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, we have discussed the effect of viscosity with time to study the stability of PVC plastisol before casting, the results of various properties obtained by evaluating the PVC compositions prepared by varying the concentration of plasticiser and crosslinking agent. In this chapter, we have also summarised the results obtained by evaluating the properties of PVC composition after exposure to gamma radiation and artificial weathering. Samples were exposed to gamma radiation with an intensity ranging from 25 to 100 Mrad.

4.1 Effect on Viscosity: Viscosity of PVC plastisol samples at various time intervals of 1, 7, 14 and 21 days are measured. Plastisol samples were prepared with varying DOP concentrations, with varying concentration of TMPTMA for the purpose of measuring viscosity. Viscosity levels measured at different intervals are presented in Table 4.1 apart from depicting the same in graphical form in Figure 4.1. Perusal of the results obtained, shows that the viscosity increases with increase in time and higher the plasticiser/resin ratio, the lower is the rate of viscosity fall. As a general rule, the viscosity of a PVC paste resin increases as standing but tends towards limiting value after long periods at ambient temperatures.

Table 4.1 Variation in viscosity with time and different compositions of PVC plastisols

Composition	Viscosity in centiPoise			
	1 day	7 days	14 days	21 days
60 phr DOP	2260	2378	2379	2523
70 phr DOP	1613	1986	2020	2160
80 phr DOP	1167	1173	1286	1320
1 phr TMPTMA	1069	1110	1130	1364
3 phr TMPTMA	990	1028	1090	1200
5 phr TMPTMA	1023	1047	1060	1180
10 phr TMPTMA	1065	1093	1040	1160

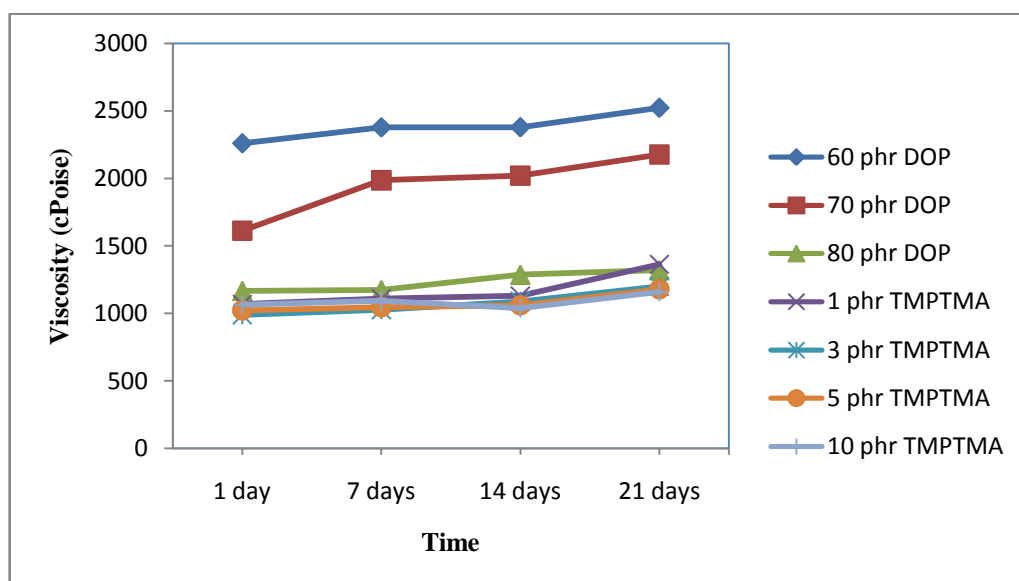


Figure 4.1 Variation in viscosity with time and different compositions of PVC plastisols

4.2 Effect of DOP concentration on PVC composition: To study the effect of DOP concentration on PVC, we had developed different PVC compositions by varying the concentration of DOP from 60 - 80 phr and studied its physico-mechanical properties.

4.2.1 Effect on tensile strength: The effect of plasticiser on tensile strength of the PVC compositions were studied by varying the concentrations of DOP from 60 to 80 per hundred of resin (phr) and the results obtained are presented in Table 4.2 and graphically in Figure 4.2. It has been observed from the graph that with increase in plasticiser concentration, the tensile strength of PVC composition decreases. This decrease in the tensile strength of the PVC compositions might be due to the incorporation of DOP into

the polymer and weakens the polymer-polymer interactions (Vanderwall's forces) which was explained in the mechanism of plasticisation.^[9] The DOP molecules act as shields to reduce polymer-polymer interactive forces and prevent the formation of a rigid network. This lowers the PVC glass transition temperature (Tg) and allows the polymer chains to move rapidly resulting in increased flexibility, softness and elongation.

Table 4.2 Variation in tensile strength (MPa) with change in DOP concentration

S. No	DOP concentration (phr)	Tensile Strength (MPa)
1	60	11.84
2	70	10.65
3	80	9.34

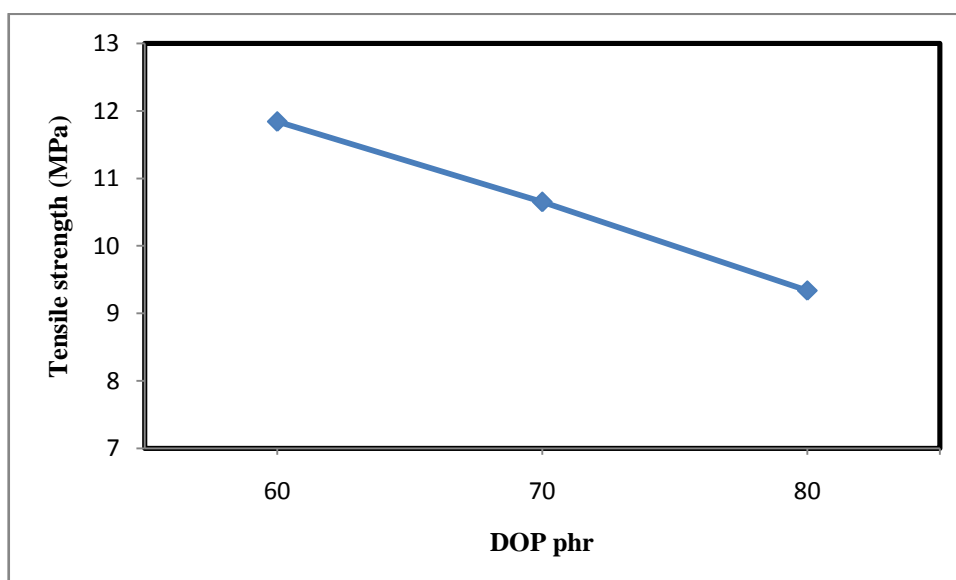


Figure 4.2 Variation in tensile strength (MPa) with change in DOP concentration

4.2.2 Effect on Elongation: The effect of plasticiser on elongation of the PVC compositions were studied by varying the concentrations of DOP from 60 to 80 per hundred (phr) of resin and the results are presented in both tabular as well as graphical form in Table 4.3 and Figure 4.3. The results reveals that with the increasing the concentration of the DOP, elongation at break of the PVC compositions increases. As tensile strength decreases elongation increases.

Table 4.3 Variation in elongation at break (%) with change in DOP concentration

S. No	DOP concentration (phr)	Elongation at break (%)
1	60	478.4
2	70	535
3	80	627.2

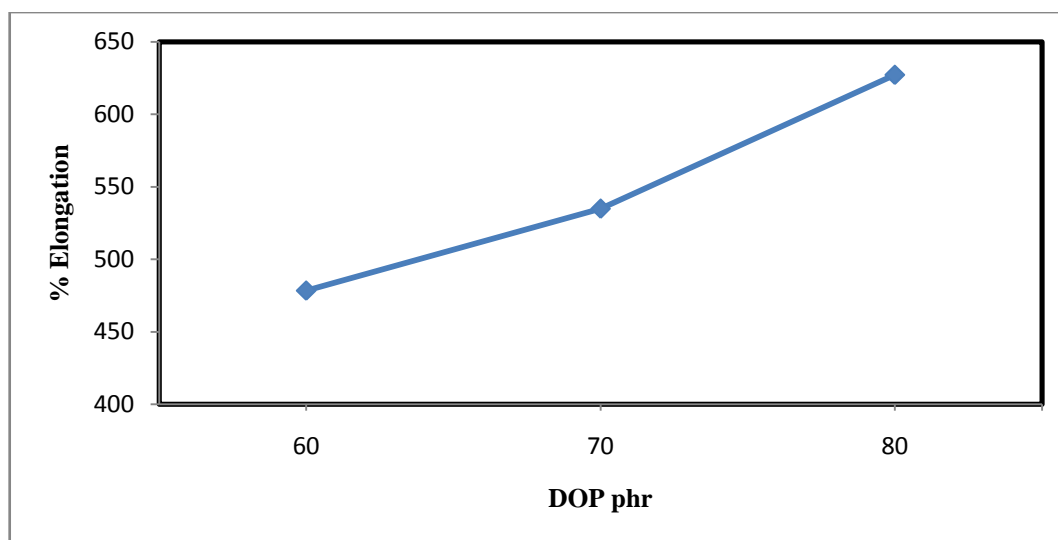


Figure 4.3 Variation in elongation at break (%) with change in DOP concentration

4.2.3 Effect on Tear Strength: The effect of plasticiser on tear strength of the PVC compositions were studied by varying the concentrations of DOP in 60, 70 and 80 parts per hundred of resin. Results obtained are presented in Table 4.4. The variation in tear strength with variation in DOP quantity is also presented in a graphical form in Figure 4.4. Results obtained shows that with the increase in the concentration of the DOP tear strength of the PVC compositions decreases. This decrease may be due to the interaction of plasticizer with the polymer which enhances the force required to rupture the polymer molecular chain.

Table 4.4 Variation in tear strength (N/mm) with change in DOP concentration

S. No	DOP concentration (phr)	Tear strength (N/mm)
1	60	34.07
2	70	29.45
3	80	22.65

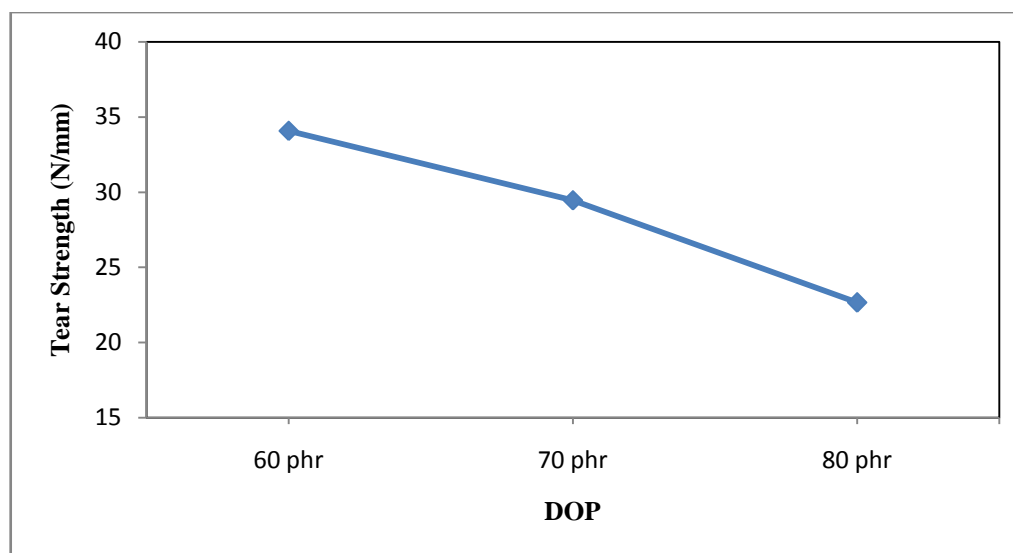


Figure 4.4 Variation in tear strength (N/mm) with change in DOP concentration in phr

4.2.4 Effect on Hardness: The effect of plasticiser on hardness of the PVC compositions were studied by varying the concentrations of DOP from 60 to 80 per hundred (phr) of resin. Results obtained are presented in Table 4.5. The variation in hardness with variation in DOP quantity is also presented in a graphical form in Figure 4.5. Results shown in the graph establishes that with the increasing concentration of the DOP, hardness of the PVC plastisols decreases. This decrease in the hardness of the PVC compositions might be due to the incorporation of DOP results in the expansion of the molecular chain and at the time of putting the load on the surface it provides more space for the movement of the polymer chain.

Table 4.5 Variation in Hardness with change in DOP concentration

S. No	DOP (phr)	Hardness
1	60	74
2	70	72
3	80	70

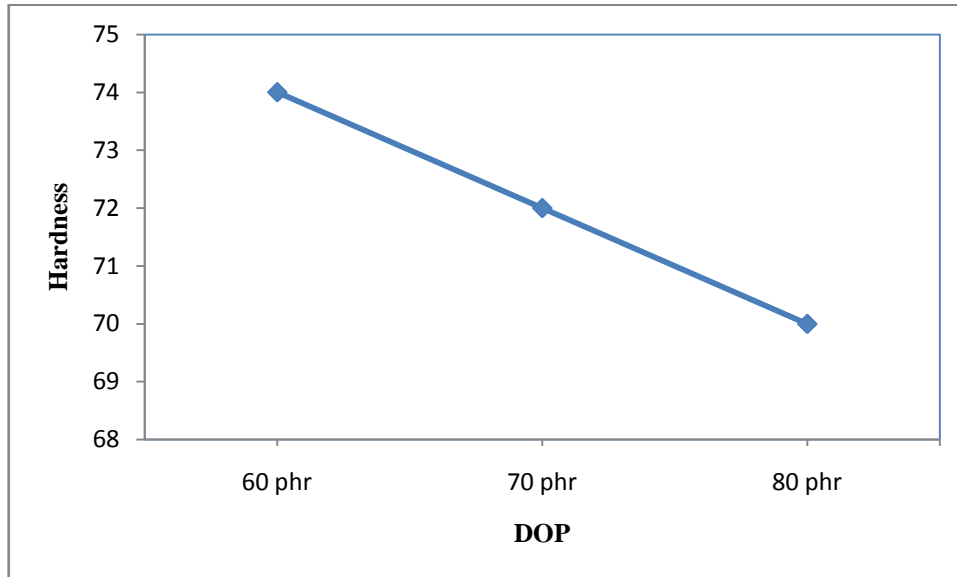


Figure 4.5 Variation in Hardness with change in DOP concentration

4.3 Effect of Gamma Radiation

The effect of gamma radiation on the PVC compositions prepared by varying the concentration of DOP were studied by evaluating the mechanical properties of the compositions after exposure at 25, 50, 75 and 100 Mrad. Results obtained for tensile strength, elongation at break, hardness and tear strength are shown in forthcoming subsections.

4.3.1 Effect on Tensile strength: The above cited specimens were also subjected to gamma radiation doses ranging from 25 to 100 Mrad. The results obtained are presented in the Table 4.6 and the same is represented in graphical form in Figure 4.6. Close look at the results obtained from the experimentation it is established that the tensile strength initially increases on increase in gamma radiation dose and decreases later on further increase. The increase in the tensile strength may be attributed to the fact that on radiation

there is an initial crosslinking, but at higher doses chain scissioning starts which results in degradation of the polymer. The percentage increase in tensile strength is 4%, 13% and 10% at 60, 70 and 80 phr respectively at 25 Mrad dosage of gamma radiation.

Table 4.6 Variation in tensile strength (MPa) with variation in DOP concentration and Gamma Radiation

DOP	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
60 phr	11.835	12.33	13.4	9.52	7.7
70 phr	10.645	12.086	13.01	9.1	7.85
80 phr	9.34	10.27	12.3	6.81	5.8

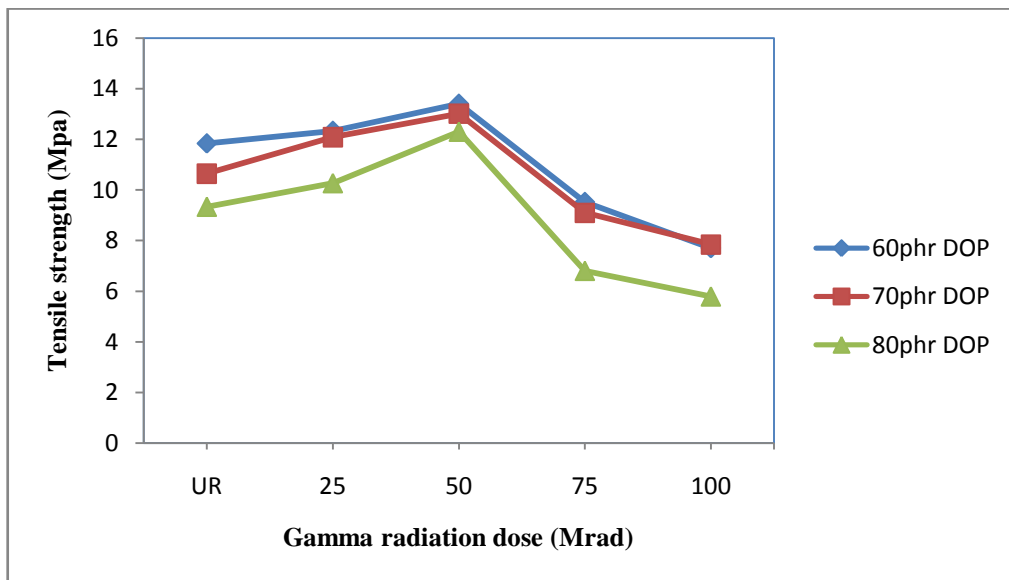


Figure 4.6 Variation in tensile strength (MPa) with variation in DOP concentration and Gamma Radiation

4.3.2 Effect on elongation

The results of % elongation obtained are depicted in the Table 4.7 as well as in Figure 4.7. Close look at the results obtained from the experimentation, it can be stated that the elongation at break decreases with increase in radiation. The percentage decrease in % elongation is observed to be 27, 30 and 37 at 60, 70 and 80 phr respectively when the specimens are irradiated to 25 Mrad. This can be clearly explained as the tensile strength increases; the effect on elongation is vice versa.

Table 4.7 Variation in elongation at break (%) with variation in DOP concentration and Gamma Radiation

DOP	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
60 phr	478.4	348.04	296.7	214.5	166.5
70 phr	535	373.44	258.2	195.7	146
80 phr	627.2	395.9	214.3	159	150.8

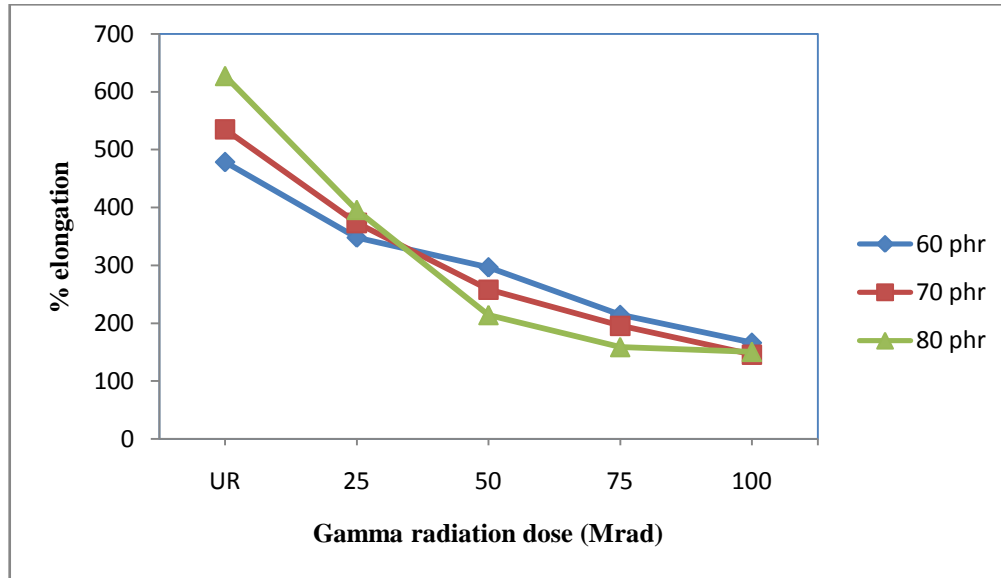


Figure 4.7 Variation in elongation at break (%) with variation in DOP concentration and Gamma Radiation

4.3.3 Effect on Tear Strength:

The tear strength results obtained are presented in the Table 4.8 apart from presenting the same in graphical form in Figure 4.8. Close look at the results obtained from the experimentation, it is observed that the tear strength increased at 25 Mrad dosages. However the same has come down with increase in dosage of gamma radiation of 25 to 100 Mrad. At 25 Mrad of gamma radiation, the tear strength of 70 phr plastisol was observed as 31.75 N/mm.

Table 4.8 Variation in tear strength (N/mm) with variation in DOP concentration and Gamma Radiation

DOP	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
60 phr	34.07	36.2	22.47	16.2	11.54
70 phr	29.45	31.75	22.2	11.02	8.63
80 phr	22.65	24.35	11.37	7.06	5.43

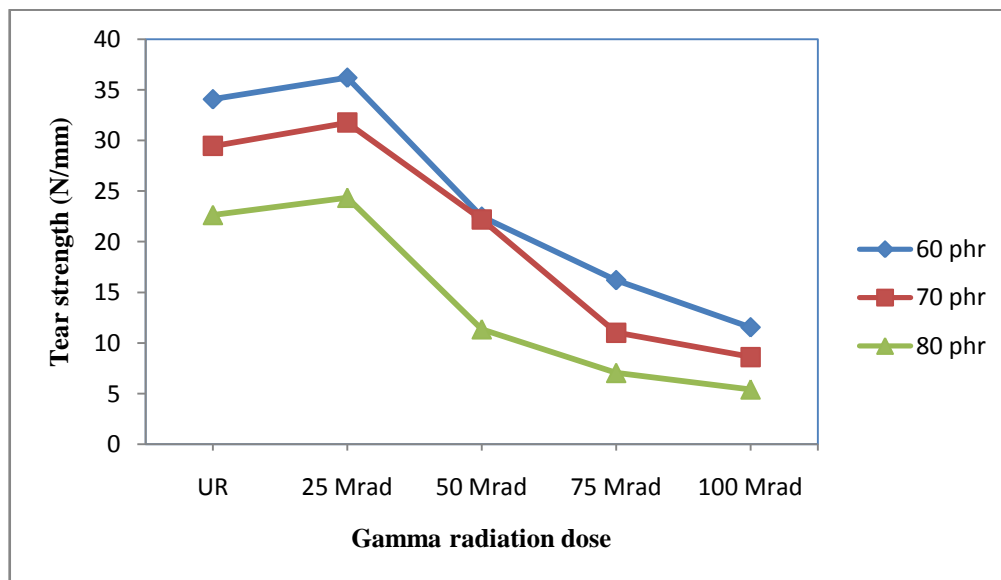


Figure 4.8 Variation in tear strength (N/mm) with variation in DOP concentration and Gamma Radiation

4.3.4 Effect on Hardness: The effect on hardness of the PVC compositions was studied by varying the concentrations of DOP from 60 to 80 per hundred (phr) of resin and are gamma irradiated. Results obtained are presented in Table 4.9 and Figure 4.9. Results show that with the increase in the dosage of the gamma radiation, hardness of the PVC compositions increased. This change in the hardness of the PVC compositions might be due to the leaching out of the DOP, making it rigid.

Table 4.9 Variation in Hardness with DOP concentration in phr and Gamma Radiation

DOP	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
60 phr	74	75	76	76	77
70 phr	72	73	74	75	75
80 phr	70	71	72	72	73

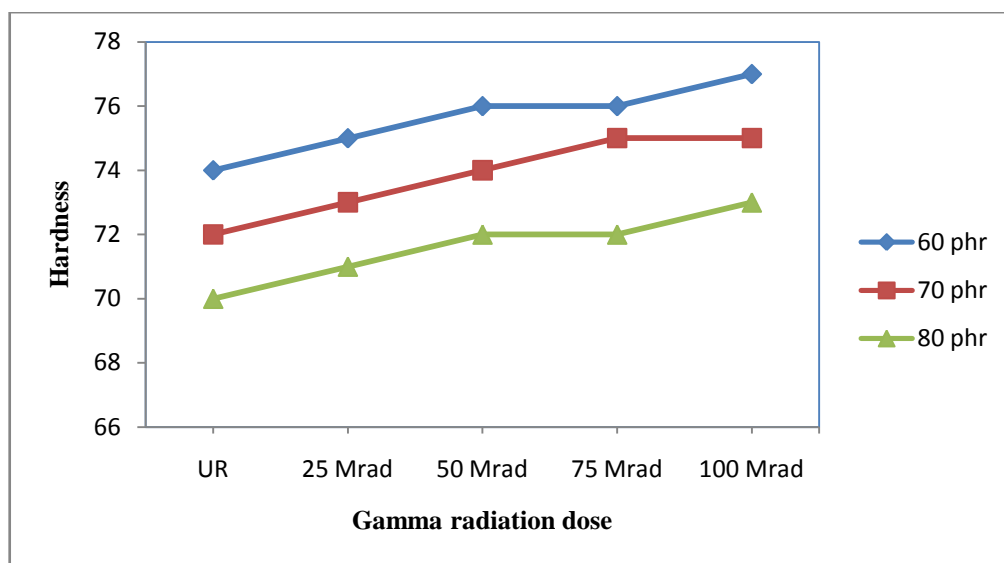


Figure 4.9 Variation in Hardness with DOP concentration and Gamma Radiation

4.4 Effect of crosslinking agent on PVC compositions

To study the effect of crosslinking agent in PVC plastisol compositions the DOP concentration was taken as 70 phr. This concentration was considered for the present experimentation/study as our viscosity at this concentration was 1613 cP. Charles E. Wilkes et al (2005) had also stated that DOP is recognised as the benchmark plasticiser for PVC. They had classified that a DOP of 25 phr is semi rigid PVC, between 35 and 85 phr DOP, PVC is considered as flexible and above 85 phr it is called highly flexible. Apart from this, at 70 phr the formulations which have been developed, in the present study, have retained optimum physico-mechanical properties before and after radiation. As we increased the concentration of the plasticizer we observed a sharp decrease in physico-mechanical properties. Keeping DOP at 70 phr, the cross linking agent was

changed in concentration to have first hand information on variation in properties. The quantity of TMPTMA was varied as 1, 3, 5 and 10 parts per hundred resin (phr) and various mechanical properties were evaluated and discussed below. These samples are subjected to gamma radiation with doses ranging from 25 to 100 Mrad.

4.4.1 Effect on Tensile strength: Results of tensile strength obtained are presented in Table 4.10 and Figure 4.10. It can be inferred from the table that with increase in cross linking agent concentration before radiation, the tensile strength has increased significantly, but at higher phr of crosslinking agent it has shown a reduced tensile strength. When the specimens are subjected to irradiation, there is a considerable increase in their tensile strength which can be attributed to the fact that many active sites are formed on PVC backbones and monomers produce high yields of radicals, giving good crosslinking with PVC chains and create three dimensional networks. However at high dosage, degradation starts resulting in the decrease of their tensile strength.

Table 4.10 Variation in Tensile strength (MPa) with variation in TMPTMA concentration and Gamma Radiation

TMPTMA	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
0 phr	10.645	12.086	13.01	9.1	7.85
1 phr	12.068	14.62	12.75	8.23	7.86
3 phr	12.208	14.85	13.9	7.56	4.25
5 phr	11.927	13.6	13.422	7.31	6.9
10 phr	11.342	12.61	12.35	7.21	4.7

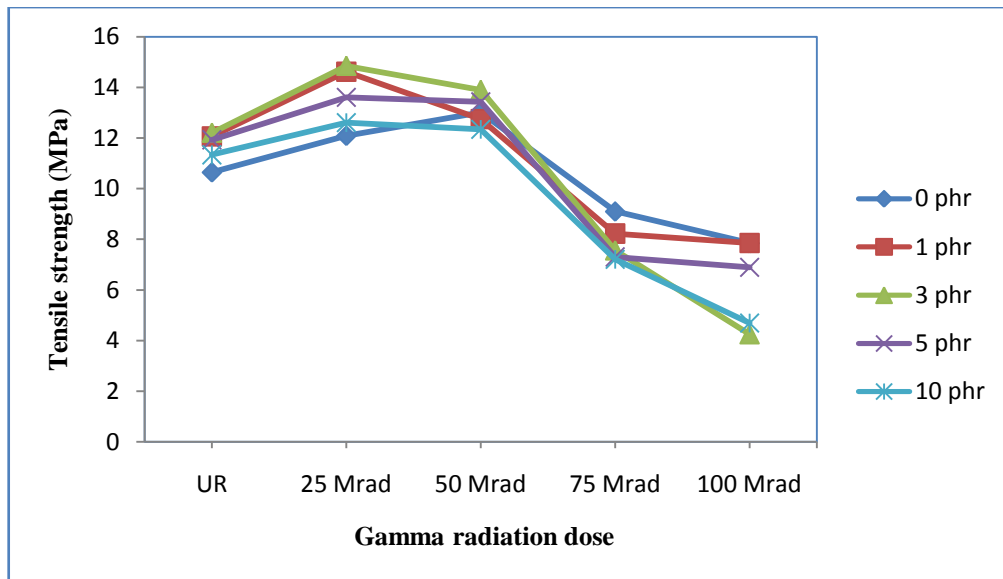


Figure 4.10 Variation in Tensile strength (MPa) with variation in concentration and Gamma Radiation

4.4.2 Effect on Elongation at break

The effect on elongation at break of plasticiser with variation in concentrations of TMPTMA was studied. Results obtained are presented in Table 4.11 and Figure 4.11. It can be seen from the graph that, with increase in cross linking agent concentration before radiation, the elongation at break has increased significantly, but at higher phr it has shown a reduced elongation at break, which imparts brittleness to the PVC sheet due to excessive crosslinking. On irradiation, the elongation decreases due to crosslinking. This can be attributed to the fact that formulations containing no functional monomers exhibit poorer physical properties and less integrity than those which contain these monomers. The cross linked network provides added strength which allows the polymer to extend further before it fails.

Table 4.11 Variation in Elongation at break (%) with variation in TMPTMA concentration and Gamma Radiation

TMPTMA	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
0 phr	535	373.44	258.2	195.7	146
1 phr	618.4	387.44	201.7	181.1	169.44
3 phr	653.6	342.16	193.6	175.74	132.42
5 phr	665.6	271.46	196.44	167.44	119.88
10 phr	650.4	143.78	181.9	138.3	105.9

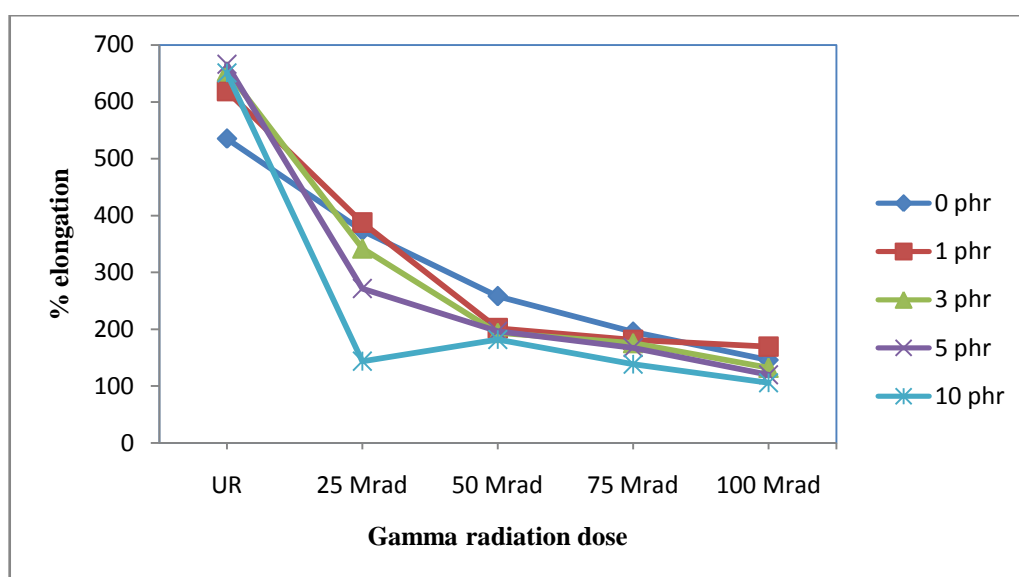


Figure 4.11 Variation in Elongation at break (%) with variation in TMPTMA concentration and Gamma Radiation

4.4.3 Effect on Tear strength: The variation in tear strength with variation in TMPTMA concentration and gamma radiation are presented in Table 4.12 as well as Figure 4.12. It can be seen from the results obtained that with increase in cross linking agent concentration before radiation, the tear strength has increased. This may be due to the fact that the monomers are just filling the amorphous regions of the polymer before radiation. Once they are irradiated there is an increase in tear strength which shows they are chemically crosslinked with the polymer, hence it hinders the motion of polymeric chain

axially. However, at very high doses they degrade and hence the decrease in tear strength.

This can be seen in the SEM image depicted in subsequent section.

Table 4.12 Variation in Tear strength (N/mm) with variation in TMPTMA concentration and Gamma Radiation

TMPTMA	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
0 phr	29.45	31.75	22.2	11.02	8.63
1 phr	23.71	32.62	13.86	6.62	12.4
3 phr	25.64	33.64	15.12	6.35	7.08
5 phr	30.86	32.35	16.8	7.04	6.84
10 phr	27.43	28.81	19.8	8.99	8.5

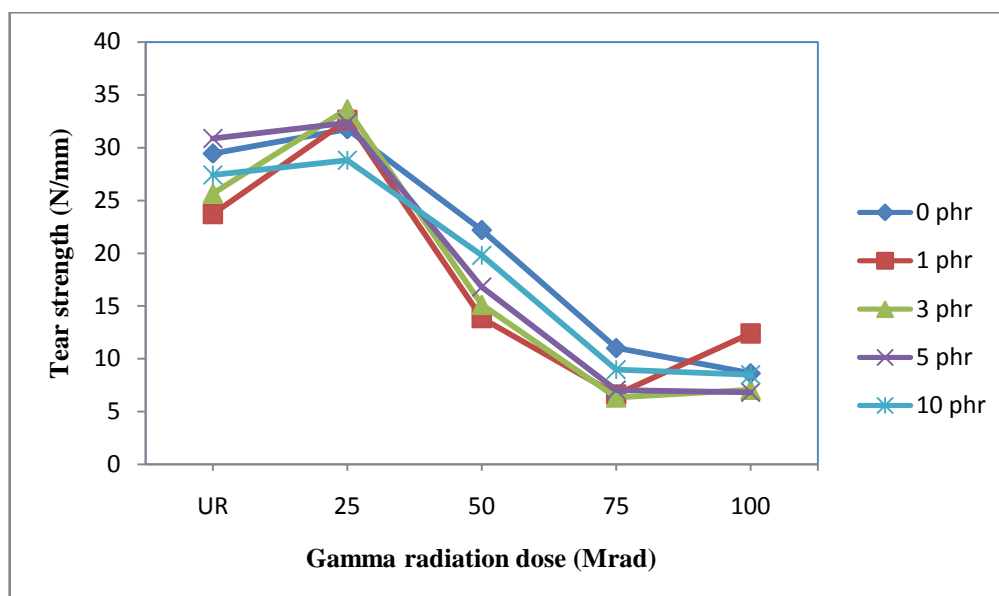


Figure 4.12 Variation in Tear strength (N/mm) with variation in TMPTMA concentration and Gamma Radiation

4.4.4 Effect on Hardness: The effect of crosslinking agent on hardness of the PVC compositions were studied by varying the concentrations of TMPTMA from 1 to 10 per hundred (phr) of 70 phr PVC plastisol and are gamma irradiated. Results obtained are presented in Table 4.13 and Figure 4.13. Higher functionality monomers like TMPTMA have the highest crosslink density, and hence there is an increase in hardness. When they

are irradiated, the hardness tends to increase due to increase in crosslinking. On higher doses, the hardness decreases due to degradation.

Table 4.13 Variation in Hardness with variation in TMPTMA concentration and Gamma Radiation

TMPTMA	UR	25 Mrad	50 Mrad	75 Mrad	100 Mrad
0 phr	72	73	74	75	75
1 phr	73	74	73	72	72
3 phr	74	74	72	71	71
5 phr	75	76	75	74	73
10 phr	76	76	74	73	72

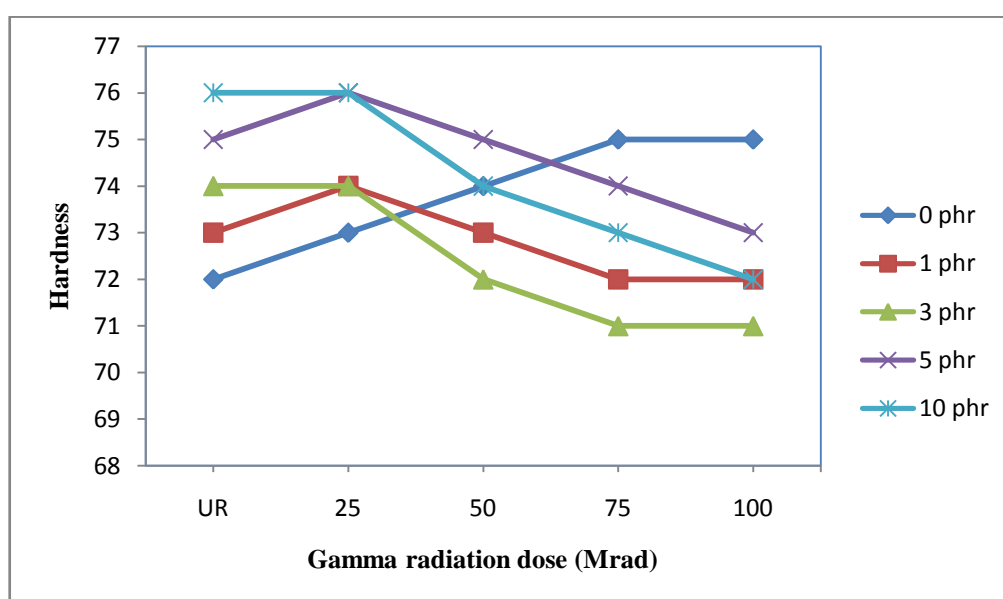


Figure 4.13 Variation in Hardness with variation in TMPTMA concentration and Gamma Radiation

4.5 Effect of UV radiation: The samples were exposed to artificial weathering by exposing them to a xenon lamp of power 0.55 watts/m^2 at 340 nm for 100 hours and were evaluated for different physico mechanical properties. The results of these specimens and percentage of variation are depicted in the Table 4.14 and Table 4.15. From the results, it can be stated that the tensile strength and tear strength have shown an increasing trend whereas elongation has decreased for all the samples. From this it can be inferred that the

specimens are UV cured which initiates crosslinking during the early hours of UV irradiation in the presence of UV stabiliser.

Table 4.14 Variation in mechanical properties by varying DOP concentration with UV radiation

		Tensile Strength (MPa)	% elongation	Tear Strength (N/mm)
60 phr DOP	UR	11.835	478.4	34.07
	UV	13	370	44.7
	% Change	9.8%	-22.6%	31.2%
70 phr DOP	UR	10.645	535	29.45
	UV	13.4	440.2	37
	% Change	25.8%	-17.8%	25.6%
80 phr DOP	UR	9.34	627.2	22.65
	UV	15.2	538.7	33
	% Change	62.7%	-14.1%	45.7%

Table 4.15 Variation in mechanical properties by varying TMPTMA concentration in 70 phr DOP with UV radiation

		Tensile Strength (MPa)	% elongation	Tear Strength (N/mm)
1 phr TMPTMA	UR	12.068	618.4	23.71
	UV	13.86	388.5	36.86
	% Change	14.8%	-37.4%	13.15%
3 phr TMPTMA	UR	12.202	653.6	25.64
	UV	14.3	527	31.85
	% Change	17.1%	-19.4%	24.2%
5 phr TMPTMA	UR	11.927	665.6	30.06
	UV	13.16	600	38.91
	% Change	10.33%	-9.8%	29.4%
10 phr TMPTMA	UR	11.342	650.4	27.43
	UV	12.74	421.7	34.25
	% Change	17.4%	-35.2%	24.8%

4.6 Effect on thermal stability: Thermal stability test is used to study the effect of heat on the polymer samples at 200°C and is measured by change in colour of pH paper with time. The time taken by the various samples to change the colour of pH paper is shown in the Table 4.16. The results show that most of the unirradiated samples are stable upto a time period of 90 minutes. The radiated samples have changed the colour in 1-3 minutes which shows they are degraded after irradiation.

Table 4.16 Time taken for change of colour

S. No	Sample	Time taken (mins)
1	1 phr TMPTMA	96
2	3 phr TMPTMA	94
3	5 phr TMPTMA	91
4	3 phr TMPTMA radiated (25 Mrad)	03
5	3 phr TMPTMA radiated (50 Mrad)	01
6	3 phr TMPTMA radiated (UV)	18

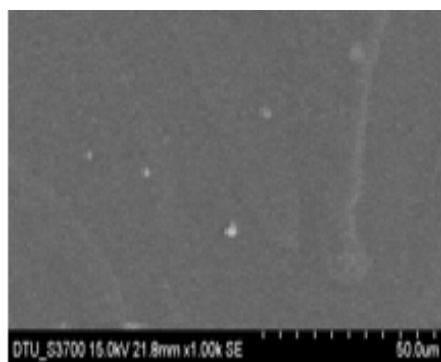
4.7 Study of morphology using Scanning Electron Microscopy (SEM)

Images were also taken using Scanning Electron Microscope (SEM) for various samples. Figure 4.14 depicts SEM images for the samples containing 70 phr of DOP and with varying concentrations of TMPTMA from 0 to 10 phr. By analysing the images, the following is deduced

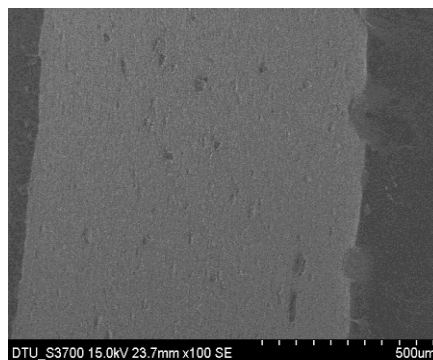
- Image a: It is observed that the plasticiser is dispersed uniformly in the plastisol as no spot is seen.
- Image b: Crosslinking has started.
- Image c: There is no phase separation due to uniform crosslinking.
- Image d: Due to excessive crosslinking, phase separation can slightly be seen.
- Image e: Phase separation is very significant and surface cracks can be visualised.

Figure 4.15 depicts SEM images for the samples containing 70 phr of DOP and 3 phr TMPTMA subjected to gamma radiation. By analysing the images, the following is deduced

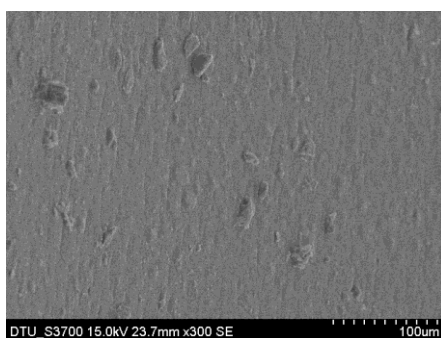
- Image a: There is no phase separation due to uniform crosslinking.
- Image b: Crosslinking is significant as compared to image a.
- Image c: Due to degradation of polymer, surface cracks are insignificant.
- Image d & e: Surface cracks are seen significantly.



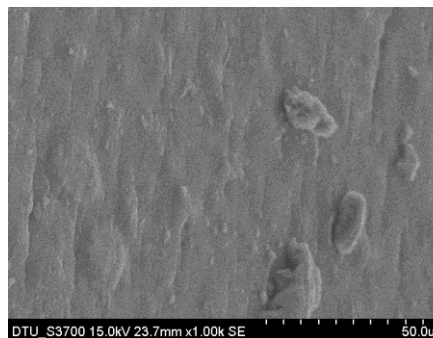
a



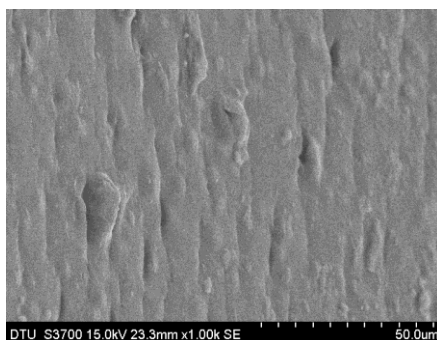
b



c

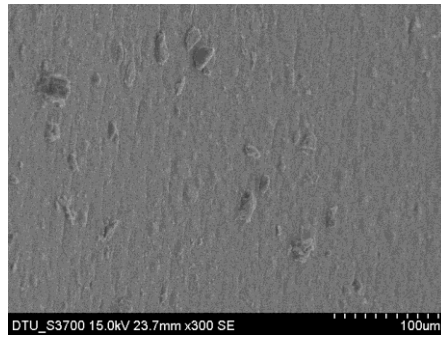


d

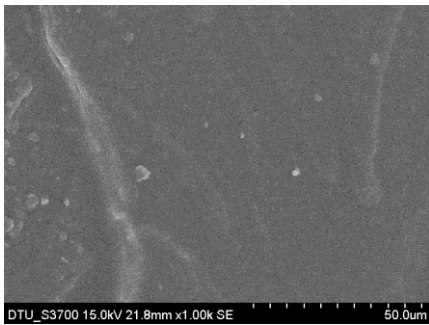


e

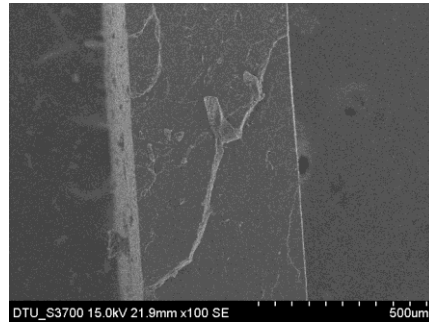
Figure 4.14 SEM image of compositions having various TMPTMA concentration (a) 0 phr (b) 1 phr, (c) 3 phr (d) 5 phr (e) 10 phr



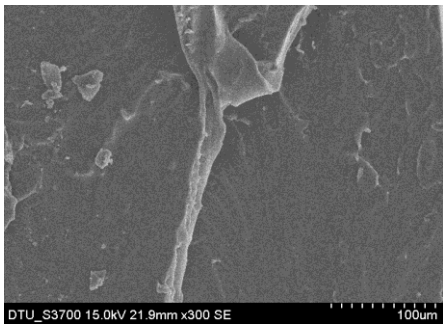
a



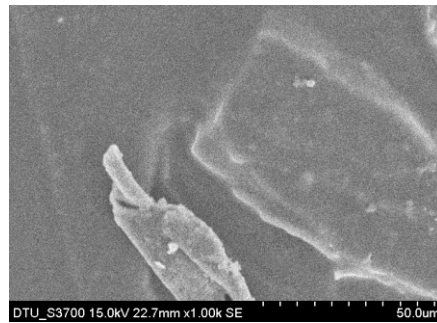
b



c



d



e

Figure 4.15 SEM image of PVC compositions after exposure of gamma radiation (a) 0 Mrad (b) 25 Mrad (c) 50 Mrad (d) 75 Mrad (e) 100 Mrad

CHAPTER-5

CONCLUSIONS AND SCOPE FOR FURTHER STUDIES

5.1 Conclusions

Based on the results obtained in the present investigation the following conclusions can be drawn.

- Mechanical properties of PVC formulations were enhanced with the addition of a crosslinking agent. Though they got degraded at 50 Mrad only, but at low doses of up to 25 Mrad the percentage increase in their mechanical properties is higher than the unirradiated ones.
- Maximum percentage increase in Tensile and Tear strength is achieved at 3 phr of TMPTMA. Hence, 3 phr of TMPTMA is the optimum concentration to get good results.
- Thermal stability of all developed compositions is good, which got reduced abruptly on irradiation.
- On artificial weathering, the physico mechanical properties of the developed compositions improved.
- Developed formulations can be used as radiation resistant material in medical facilities as the operated doses in the hospitals are very less ranging from 0.5 to 2.5 Mrad.

5.2 Scope for further study

The following aspects can be taken up for further investigation:

- Study of gel content of irradiated compositions of PVC.

- Study can be carried out to evaluate the leachability of DOP plasticiser after radiation.
- Advanced X-ray Diffraction studies and SEM analysis can be taken up for quantitative analysis and more accurate study of the formation of different critical compounds that affect the properties of PVC compositions.
- Chemical resistance tests on the developed PVC compositions can be carried out.

CHAPTER- 6

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