DEVELOPMENT OF A METHOD TO PREDICT THE PLASTICIZER EVAPORATION OF PVC INSULATED ELECTRICAL CABLES

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Degree of Master of Science

Department of Materials Science & Engineering

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Thesis submitted in partial fulfillment of the requirements for the degree

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DECLARATION

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ABSTRACT

Though insulation is critical to the performance of an electrical cable the assessment of the status of an insulation is still a major challenge. Since the root cause of most electrical cable failures is due to insulation deterioration, if the rate of aging can be predicted, properly scheduled, appropriate maintenance programs can nearly eliminate cable failures.

The kinetics of plasticizer evaporation of polyvinyl chloride based locally manufactured electrical cable insulations were investigated. Plasticizer evaporation is a slow process under low temperatures and would take years to study under such conditions. Therefore, accelerated conditions were used to get readings within the limited timeframe. Nevertheless, data obtained under accelerated conditions was mapped to normal conditions through Arrhenius approach.

Deconvoluted derivative thermograms were used to identify the initial plasticizer percentages and Arrhenius approach was used to map accelerated condition measurements to ambient temperature evaporation rates.

As cables are subjected to time varying temperature profiles a method for finding the equivalent temperature could be developed using kinetics of plasticizer evaporation whereby the operating life of the cable can be determined. The developed method could be applied for an electrical cable under a roof which is subjected to fluctuating thermal stress throughout the day and required time to evaporate critical level of plasticizer was determined.

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LIST OF ABBREVIATIONS

PVC	Poly(vinyl chloride)
PPVC	Plasticized poly(vinyl chloride)
PB	Partial Discharge
UV	Ultra Violet
T_g	Glass Transition Temperature
EVA	Ethylene Vinyl Alcohol
GI	Galvanized Iron
PE	Polyethylene
PP	Polypropylene
CPE	Chlorinated polyethylene
PU	polyurethane
TPR	Thermoplastic Rubber
SBR	Styrene Butadiene Rubber
EPR	Ethylene Propylene Rubber
CSPE	Chlorosulfonated polyethylene
EPDM	Ethylene Propylene Diene Monomer
FEP	Fluorinated Ethylene Propylene
ETFE	Ethylene Tetrafluoro Ethylene
PVDF	Polyvinylidene Fluoride
TPE	Thermoplastic Elastomer
DEHP	Di-2-ethylhexyl Phthalate
DOP	Dioctyl Phthalate
LOI	Oxygen Index
TGA	Thermogravimetric Analysis
DTG	Differential Thermogravimetry

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D.P. Egodage

CHAPTER 01

1. INTRODUCTION

1.1 Background to the study

Electrical cables are the medium of transmission and distribution electrical energy to electrical devices. The overall performance of all electrical devices is dependent on the performance of the power cables. The ever increasing energy demands of a dynamic civilization ensures that the amount and density of cable usage will continuously increase for the foreseeable future.

Power cables are classified into four classes depending on their operating voltage; low, medium, high and extra high voltage power cables [1]. Cables are subject to a range of stresses during operation with thermal, electrical, mechanical, chemical being the main stresses. Over time, polymeric insulations of cables degrade due to these external stresses [2][3]. The severity of the external stress on the endurance of the cable can be ranked as follows [4].

1. No stress (0)
2. Electrical stress (1)
3. Thermal stress (2)
4. Electro thermal/ service stress (3)

Although, numerous studies investigating the influence of electric fields on the degradation of cable insulations have been conducted [5][6] the above ranking shows that electrical stress alone would not have significant impact on the endurance of an electrical cable [4].

The performance of electrical cables rather depends on their insulation system. The insulation separates the current carrying conductor from other conductive materials and also protects it from environmental effects that would lower the conductor’s performance if exposed to them. It protects the enclosed conductors from temperature extremes, abrasion, current/signal loss and moisture [7]. While ensuring the extended and problem-free life of cables it is always beneficial to reduce the volume of electrical insulation [8].

The loss of insulation properties of a dielectric material is termed as “dielectric breakdown”. The electrical breakdown of dielectric materials can be divided into two categories.

1) Global breakdowns
2) Local breakdowns.

The complete failure of the electrical insulation is reported as global breakdown [9]. Formation of permanent conducting channels within solid insulation materials makes it unusable. The deterioration of insulating properties of a small region of the insulation material is known as partial breakdown (PB) or local breakdown. The remaining insulation material continues to perform as a dielectric providing electrical insulation after a partial breakdown. Under extreme conditions, dielectric properties of the remaining insulation material also eventually degrade due to Partial Breakdown. Catastrophic failures of electrical machines and systems are generally initiated by occurrence of unpredicted partial breakdowns in the insulation material. Therefore, partial breakdowns must be eliminated as far as possible.

Despite the importance of insulation material to the final performance of the cable, the evaluation of insulation quality is still a great challenge [10]. As the majority of cable breakdown originates from insulation degradation, correct forecasting of the rate of degradation will enable appropriately scheduled proper maintenance programs that will minimize catastrophic cable failures.

Thermal stress is the major cause of insulation degradation. But the degradation of the insulation materials takes time, hence, accelerated conditions are needed to study insulation degradation kinetics [11]. A powerful method for predicting the degradation kinetics at low temperatures is the Arrhenius approach. High temperature (accelerated) degradation kinetics can be mapped to ambient temperature degradation rates using the Arrhenius approach [12].

Even though extensive research attempts are carried out to study degradation of cable insulation materials, proper nature of these materials' degradation have not completely relieved so far [13]. Accordingly, development of an empirical mathematical model is very important to estimation of the degree of degradation of electrical cable insulation [14].

The repairing and reinstallation of cables is expensive, proper identification of the degree of degradation is needed to estimate the remaining lifetime of the cable. Hence, reliable and trustworthy methods must be found to test the cable's usability and fitness to the system. The last few decades have seen an intensification of efforts to study the degradation behaviour of cable to estimate the life time and insulator quality.

The correct operation of electrical devices and systems, from the tiny capacitor to giant generators requires engineers to design proper insulation. Thus, engineers need to evaluate the performance of insulation materials under various stress conditions. However, very few Sri Lankan cables manufacturers specify the expected life time of cables they produce. Even amongst these few exceptions, life expectancy has been determined only for idealized steady operating conditions. In practice such conditions are rarely experienced. Cables usually move via heat sources and move across regions that obstruct heat dissipation like ceilings and walls. Under such scenarios, excessive heat cannot be avoided.

Blanket substitution of already installed cables is an exorbitant and a time-wasting exercise. But, the reliable evaluation of the present status of the cable insulation will permit selective substitution, a prudent and economical step that will minimize chances of catastrophic failures.

Poly(vinyl chloride) (PVC) with its excellent electrical, chemical and mechanical properties nominate it as a widespread insulation material [8] for a variety of operating conditions and applications.

Generally, PVC is a rigid and brittle material. To use them in cable application they must be flexible. PVC can be converted to a flexible material using plasticizers allowing it to be used for sheath and insulation of the electrical cables [9]. PVC which is subjected to plasticization are usually termed as plasticized polyvinyl chloride (PPVC).

Plasticizers are incorporated to PVC to impart flexibility, durability, to increase the workability when processing and to lower down the glass transition temperature of the material. They are organic compounds with low volatility [9], [10]. Pristine PVC has a glass transition temperature close to 90 ^{0}C [9]. Plasticizers can bring down the glass transition temperature of the PVC, usually below 80^0C [9]. Deficiency of plasticizer of the cable sheath and insulation makes the cable material brittle and introduces micro voids in the insulation material. During storage, manufacturing and in use polymer materials are subjected to mechanical forces and environment changes [15]. Extrusion faults can be occurred due to incorrect operating temperatures. The range of temperatures which PVC materials can befoamed are usually narrow, there can be a non-homogeneity in the mixture if temperatures are too low and too high a temperature will cause to formation of microporous [16]. As a result of this, microcracks may be generated naturally in the polymer. These present cracks within the material can be act as paths for moisture penetration into micro voids which ultimately lead to short circuiting or dielectric breakdown producing a large damage to the functionality of the insulation [17].

Plasticizers gradually evaporate from the insulation deteriorating its performance. Previous research into PVC cable insulations under non-identical ambient conditions have found that plasticizers evaporate dissimilarly in different areas of the material. The effect of plasticizer loss is significantly higher for jacketing insulations compared to core insulations as they subjected to higher temperatures than insulations.

The intension of this research is to comprehend the initiation and propagation of the thermal degradation behavior of plasticized PVC and its correlation to life expectancy of electrical cables. Nevertheless, the process of thermal degradation is a moderate speed process requiring years to estimate life time under ordinary ambient conditions. Consequently, accelerated ambient conditions will be applied to estimate lifetime in a short timeframe. However, collected data under accelerated ambient conditions can be mathematically mapped to the ordinary ambient conditions.

1.2 Objectives of the study

1) To model the evaporation kinetics of the plasticizer from the polymer surface into the surroundings.

   As plasticizer evaporation is a slow process it is difficult to investigate plasticizer evaporation kinetics at low temperatures as it takes time. So, investigation will be done under accelerated conditions and will be mapped to ambient conditions in order to determine the evaporation kinetics.

2) Development of a rating index depending on the time varying temperature variations is another objective of this study.
   In practice, cables are subjected to time varying heating profiles. However, cable ratings are based on fixed temperature performance. If these time varying heating profiles are known depending on the temperature function which cables were subjected an equivalent temperature can be found. So, it will represent loss of plasticizers during the time varying temperature profile.

1.3 Organization of the thesis

This thesis contains five chapters. Chapter 1 is a brief introduction to the study that includes the cable structure, materials and additives used. In addition, stresses acting upon cables and their effects are briefly discussed. In chapter 2, an extended literature survey is presented. Cable terminology and the structure of insulation materials are discussed and the central topic of PVC insulation degradation and plasticizer evaporation due to thermal stresses are discussed. Chapter 3 contains details about the materials and methodology used for the study. In chapter 4, the results obtained, and their analysis are presented. Plasticizer evaporation kinetics at high temperature and its mapping for lower temperatures is demonstrated. Moreover, a rating index for a cable dependent on the temperature profile will be introduced. Chapter 5 provides a summary of the findings from this study.

CHAPTER 02

2. LITERATURE REVIEW

The principle function of electrical cables is electric power transmission and distribution. They are collections of one or more electrical conductors which are insulated separately, generally covered altogether with a sheathing material [14]. These electrical cables may be permanently located within buildings as wiring or placed underground or laid overhead or bare to ambient conditions. For portable electrical machineries, flexible electric cables are used. The design considerations for the electric cables are mainly are voltage, current, maximum operating temperature and end user requirements according to the application [1],[14],[18],[19],.

Depending on the configuration, size and the performance there are a variety of electrical cables [20]. Some of them are,

- High voltage primary distribution cables
- Secondary distribution cables (underground and overhead lines)
- Commercial and industrial low and medium voltage power cables
- Control cables

Electrical cables are usually constructed with a metallic conductor enclosed by several insulation coatings. As air is not a very good insulation material, insulation material is introduced to resist electric currents in the radial direction, to prevent electrical leakage and to protect the conductor integrity by concealing it from environmental attacks such as humidity and heat. The protection and effectiveness of the metallic conductors is largely based on its insulation [18],[19].

Jacketing materials safeguard the insulated cables from external effects such as mechanical abrasion and UV radiation. Some cable types such like medium and higher voltage electric cables have extra layers in addition to insulation and jacketing. They are semi-conducting layers placed between current carrying wire and insulation and between layers of the insulation and jacketing [18],[19].

2.1 Cable Terminology

2.1.1 Conductor

The material used for wire or the conductor can be aluminum or copper. Due to higher conductivity, copper conductors are preferable either as single or multiple stranded to achieve the desired cross section. Higher conductivity reduces power loss from resistance. Multiple stranded conductors improve the flexibility of the cable and moreover they are compressible and can be compacted or fragmented to achieve the required flexibility size and the density of the current [1],[18]–[22].

2.1.2 Electrical Insulation or Dielectric

As the conductor in cables are energized in use, cable insulation must have sufficient physical and electrical properties to halt breakdown. Depending on the applied high or low voltage stresses, insulation can be designed to meet the electrical requirements of the cable. To provide adequate physical protection from mechanical action, insulation thickness should be correctly designed for low-voltage cables rated 600 volts and below, the dielectric strength, conductivity, power factor and shielding/non shielding are also other important design considerations [1],[18]–[22].

2.1.3Jacket

The jacket is also named as outer sheath. Jacketing material imparts safety against mechanical, thermal and chemical actions applied and acts as a direct encapsulation to the insulation and wire. Installation and environmental requirements will be more predominant than electrical requirements when designing the jacketing for the cable. PVC and nylon are the most widely used jacketing materials to impart required chemical, physical or thermal protection [19]–[22].

2.1.4 Conductor Shield or Screen

The conductor shield is typically a semi-conductive material. It is used to shield out the conductor contours and applied over the conductor circumference by extruding. It provides a smooth and compatible surface for the application of insulation [1], [19], [20]. This extruded conductor shield is typically a compatible material that attaches itself to the insulation or otherwise a peel-able material such as ethylene vinyl acetate (EVA). Due to the presence of this shield, the shape of the outer conductor contours will not distort the resulting dielectric field lines.

2.1.5 Beading (Inner Sheath)

The inner sheath is can be seen in multi core cables. It acts as a binding material for insulation in multi-core power cables and supplies bedding to the armour/braid, it also provides earths the cable. This layer is usually constructed of PVC or rubber, apart from which copper wires which are annealed and tinned, nylon braid, cotton braid is also utilized. Braiding imparts high mechanical protection and flexibility [1].

2.1.6 Armouring

There are two primary types of amouring; G.I. wire and G.I. steel strip. The armouring is constructed by positioning G.I. wires or strips singly on beading. Its main purpose is to provide a sufficient path to earth the current if there is any insulation failure in the cable. It also provides additional shielding from mechanical actions and strengthens the cable [1].

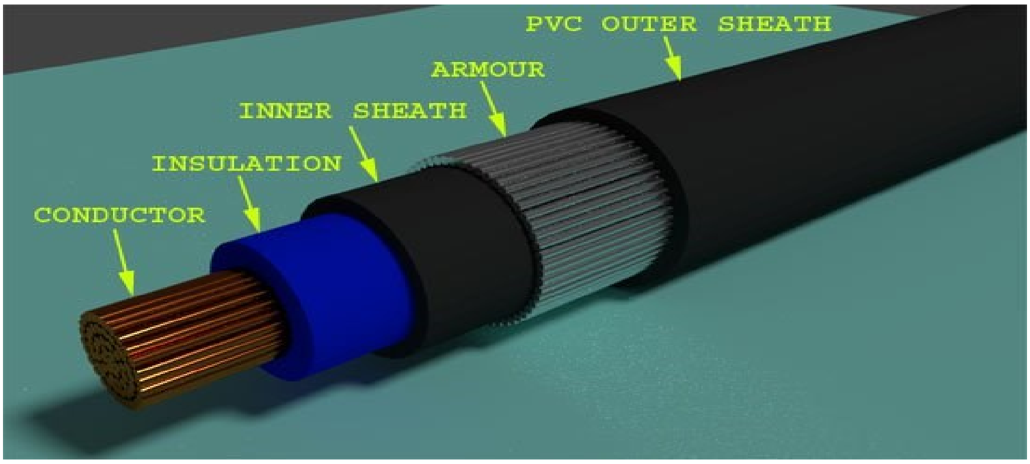

Figure 2.1: Construction of a Cable

2.2 Construction of a low voltage cables

2.2.1 Construction of a Non-shielded cable

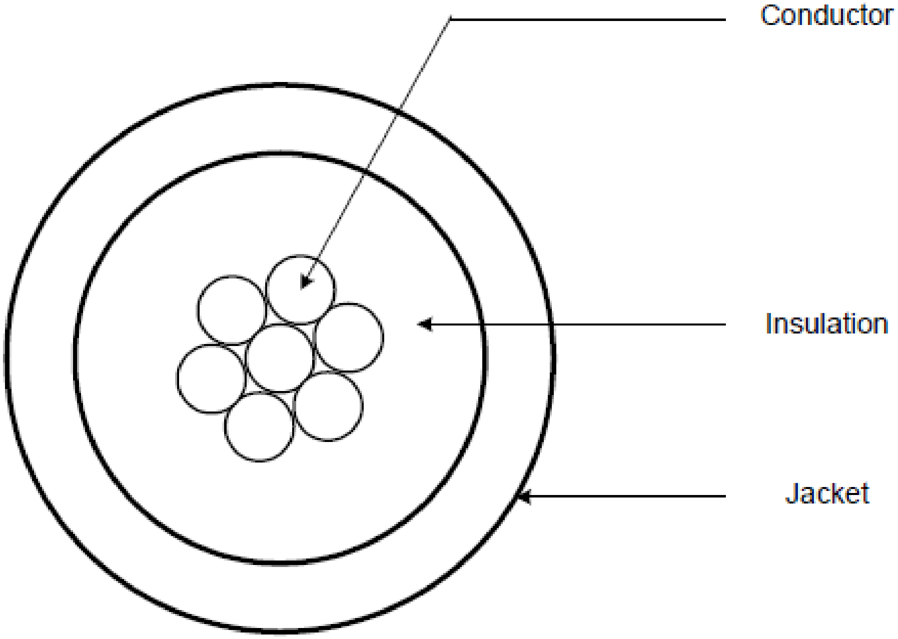

Figure 2.2: Construction of a non-shielded cable

There are main two primary components in a non-shielded cable are the conductor and the layer of insulation or dielectric. In addition, some cables have a jacket or outer sheath.

2.2.2 Shielded Cables

The basic difference from non-shielded cable is the addition of conducting layers to the cable structure. The essential structure of a shielded cable is shown in Figure 2.3.

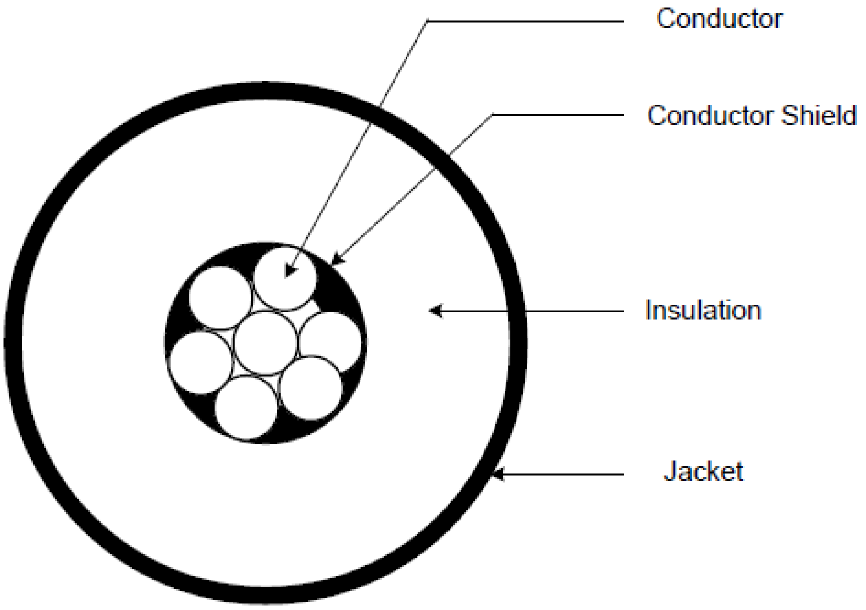

Figure 2.3: Construction of a shielded cable

2.3 Insulation and Jacketing Materials used in Cable Industry

Insulation is placed immediately adjacent to the current carrying conducting wire as a dielectric layer. Dependent upon the application specifications there are a number of considerations when selecting a dielectric material for insulation; stability and durability, insulation ability or dielectric strength, ability to withstanding high temperature, moisture barrier properties, acceptable mechanical strength and flexibility [20].

Polymers are the contemporary insulation material of choice owing to their excellent dielectric behavior [19]. Historically, inorganic materials such as paper and ceramics had been used for insulating [1]. Polymeric insulation can be categorized as plastics, rubbers and fluoropolymers [20].

2.3.1 Plastics

Polyvinyl Chloride (PVC)

PVC insulation is a comparably low cost and user-friendly material with wide applicability. The operating temperature range for PVC is -55°C to 125°C [23]. It has excellent flame, ozone, acid and moisture resistance [24]. Its odorless, tasteless and non-toxic nature enables it to be used in medical and food industries [25]. For both heavy duty and simple applications, PVC can be used for insulation and jacketing. High flex life is needed for cable materials and is not used at lower temperatures due to embrittlement [26]. One disadvantage of PVC is its high attenuation and loss of capacitance leading to power dissipation in electrical configurations [18].

Semi-Rigid PVC (SR-PVC)

This is a widely used insulation material having good abrasion resistance. It also has good heat, moisture, flame and alkali resistance [27].

Plenum Polyvinyl Chloride (Plenum PVC)

PVC burns emitting toxic gases. Plenum PVC has a special flame retardant coating hence it is usually used indoor. Insulation must satisfy more extreme fire safety required to rate as Plenum rated [18].

Polyethylene (PE)

This material is widely utilized for low capacitance applications and in high speed transmission due to its excellent electrical properties. It is low cost and its dielectric constant is easily modified by additives.

Polyethylene can be crosslinked to reduce cracking of the material and for solder and solvent resistance. The operating temperature range for this material is between -65°C to 80°C. Polyethylenes are usually rigid, hard and inflexible yet flammable. Flame resistant can be imparted by addition of flame retardants. However, this will reduce the dielectric constant and power losses will be increased [4],[10],[18],[28],[29].

Chlorinated Polyethylene (CPE)

Chlorinated Polyethylene shows excellent heat, oil and weather resistance. It is a more environmentally friendly and low-cost material. It has good flame resistance and maintains performance when exposed to fire allowing it to be used as an alternative to PVC. CPE is majorly used in power transmission, in control cables in power plants and in manufacturing industries [18],[30].

Polypropylene (PP)

Polypropylene has similar behavior as the Polyethylene, but temperature range it can be used is wider than PE. Usually it is between -30°C to 180°C. It is used basically for thin wall main insulations. It has flexibility to foam to improve the electrical properties [12], [18], [31].

Polyurethane (PU)

Polyurethane has very high toughness, good flexibility, even at low temperatures. It also has very good ratings for chemical, water and abrasion resistance. PU is a flammable material. Flame-resistance can be imparted into the material, but strength and the surface finish material will be lower. The major weakness is its poor electrical properties hence it is mainly used as jacketing material [18], [32].

Nylon

Nylon is typically coated over softer insulation materials imparting toughness, abrasion and chemical resistance. It has good flexibility. But moisture absorption is one major weakness of this material that degrades its electrical properties [18].

2.3.2 Rubbers

Thermoplastic Rubber (TPR)

Thermoplastic rubbers are used in many applications. It can use as an alternative to thermoset rubbers. Better colorability, enhanced processing speeds and heat resistance in a broad usable temperature range are some advantages of this material. Even without crosslinking it shows good heat and weather resistance [18].

Neoprene (Polychloroprene)

Neoprene is a synthetic rubbery material, it is cross-linked to obtain required properties and is a thermoset. It has excellent abrasion, flame resistance, oil and solvent resistance, long service life, heat resistance in a wide temperature. It is widely used in military applications and is the preferred material in hand-held cord sets [18].

Styrene Butadiene Rubber (SBR)

Styrene Butadiene Rubber is a thermoset material with properties alike to Neoprene. Usable temperature span of this material is -55°C to 90°C [18].

Silicone

Silicone has very high heat and flame resistance allowing it to be utilized in temperatures up to 180°C. It also has moderate abrasion resistance, very high flexibility, long life in storage and high bonding properties which are useful in numerous electrical applications [18], [33].

Fiberglass

Fiberglass is the commonly used glass insulation. The usable temperature range of this material is very high. Fiber glass can be used temperature as high as 482°C without interruption and therefore used in very high temperature applications like glass and ceramics kilns and foundries. Although having low abrasion resistance [18] it has good moisture and chemical resistance.

Ethylene Propylene Rubber (EPR)

Ethylene Propylene Rubber has outstanding thermal and electrical properties allowing cables to be designed with low insulation cross sections. This material has good heat, oxidation, weathering, moisture, acid, alkali resistance and very good flexibility. It is heavily used in the mining industry. The usable temperature range for this material is -50°C to 160°C. But EPR is relatively soft and has low tear resistance compared to other insulation materials, hence, particular attention should be paid to avoid damages during installation [10], [14], [18], [28], [34].

2.3.3 Rubber

A variety of both natural and styrene butadiene rubber compounding formulas can be used to make cable insulation for a range of applications. Depending on the formula, the usable temperature range and other electrical and physical properties can be changed. It has excellent flexibility at low-temperature, moisture and solvent resistance, high electrical properties and very good abrasion resistance [18] however they have poor oil and ozone resistance.

Chlorosulfonated Polyethylene (CSPE)

Chlorosulfonated Polyethylene, marketed as Hypalon by Dupont [16], has a wide usable temperature range and is more suited for low-voltage applications. It has good resistance to chemicals and UV rays. It is used in instrument and lead wire, coil and transformer lead.

Ethylene Propylene Diene Monomer (EPDM)

This rubber insulation type has very high temperature, ozone, weather, and abrasion resistance and very good dielectric strength. It has excellent flexibility at wide temperature range allowing it to be used between -55°C to 150°C. Silicon rubber can be replaced by EPDM in certain applications [14], [18], [35].

2.3.4 Fluoropolymers

Perfluoroalkoxy alkane (PFA)

Perfluoroalkoxy alkane can be used in the temperature range from 65°C to 250°C. The dissipation factor the material is low. This makes it an efficient insulator. Its low thermosetting susceptibility post processing makes it usable for a wide range of applications and it can be processed into long cables [16]. However, its high price limits its usage.

Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene is a thermoplastic material with moisture, oil chemical and heat resistance and exceptional flexibility. It can be utilized in a broad range of temperature from -73°C to 204°C. However, its mechanical properties are somewhat lower than that of other materials [18].

Fluorinated Ethylene Propylene (FEP)

Fluorinated Ethylene Propylene has a broad range of applications due to ease of processing. Its outstanding property is its high flame resistance. This material is widely utilized in plenum cable and military applications [18] due to improved data transmission quality when foamed.

Ethylene tetrafluoroethylene (ETFE) &
Ethylene chlorotrifluoroethylene (ECTFE)

These two polymers have higher strength and flexibility compared to FEP. They can be converted into thermosets by irradiation. Improvement in data transmission and weight reduction can be achieved by foaming, although it has lesser electrical advantages than FEP [18].

Polyvinylidene Fluoride (PVDF)

Polyvinylidene Fluoride has several important insulation properties; flexibility, lightweight, thermal stability, chemical, heat, fire, abrasion and weather resistance. Its excellent properties and inexpensiveness allows it to be used in a broad range of industries and applications. Its flame resistance makes it fit for use in areas exposed to air circulation in the building [18].

Thermoplastic Elastomers (TPE)

Thermoplastic elastomers are composed of a mixture of plastic and rubber. It can be formed by molding, extrusion, and reusable as a plastic while keeping the flexibility of the rubber and is used where elastomers are unsatisfied to deliver the required span of physical properties. However, low chemical, heat resistance, poor thermal stability and high cost are major disadvantages of this material [16]. It is largely used in automobile and domestic applications

2.4 Characteristics of Poly (vinyl chloride) (PVC) Insulation

Poly (vinyl chloride) is a synthetic thermoplastic material synthesized from the polymerization of vinyl chloride. This material becomes a formable homogenized liquid when heated above melting point and solidifies upon cooling, therefore it is recyclable [24], [25], [36]. It is one of the most widely used plastics due to its low cost.

Pristine PVC is an odorless, white, stiff and brittle solid which reduces its applicability. The discovery of plasticizers and heat-stabilizing additives have enabled the development of flexible and heat resistant PVC compounds. This lead to the commercialization of PVC compounds [37]–[39].

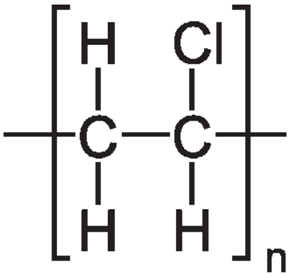

Figure 2.4: Repeat unit of PVC

PVC is used in a wide array of consumer products depending on its flexibility.

Properties such as durability, toughness, oil and chemical resistant, chemical stability, mechanical stability, high transparency, fire retarding properties and processability and mouldability make PVC common in the construction industry. It is used to make pipes, pipe accessories, vinyl flooring, packaging materials, furniture, textile finishes, roof membranes, automotive parts and toys.

The inherent fire retardation property, excellent electrical insulation and ease of processing makes PVC suitable for wire and cable applications in electrical insulation [25], [36], [40], [41]. However, its high dielectric constant and dissipation factor is major drawback. Though the moderate thermal stability of PVC has been field of concentrated research, the relationship between microstructure and degradation mechanism of PVC is still not fully understand [24], [39].

2.4.1 Glass Transition Temperature of PVC (T_g)

The melting point of a perfectly syndiotactic PVC is considered as 400°C. However, it is hard to produce perfectly syndiotactic polyvinyl chloride and the actual product has a mixture of stereoisomers. Thus, commercial PVC has a melting point within the range of 102°C to 120°C [26], [37], [42].

Industrially used PVC is characterized by its second order transition or the glass transition temperature (T_g) due to amorphous nature of the material. Glass transition temperature is the temperature at which the polymer converts from a rigid glassy to a flexible and viscous rubbery state. Below this temperature, the amorphous regions of the polymer are in a glassy state and is hard, stiff and brittle. Above this temperature, state segmental motion of the polymer chains commence and it shows rubbery behavior becoming soft and flexible [26], [37], [40], [42].

The glass transition temperature of PVC compound changes with the molecular structure of the polymer and is generally in the range of 70-90 °C [26], [37], [42].

2.4.2 Additives used for PVC

Various additives are blended with PVC during compounding to improve the properties. Common additives are plasticizers, fillers, antioxidants, lubricants and pigments.

Plasticizers

A variety of plasticizers are utilized in PVC. Commonly used plasticizer groups are phosphates, abietates, adipates, azelates, benzoates, chlorinated paraffins, citrates, glycol ethers and their esters, pentaerythritol derivatives, phthalates, polymeric, sebacates, trimellitates, pyromellitates and many application-based plasticizers [17], [42]–[45].

Plasticizer must be properly incorporated within the PVC matrix to be productive. Plasticization is usually done by heating and blending till either the matrix PVC goes into the plasticizer or the plasticizer goes into the matrix PVC. The plasticized polymer is later extruded around the wire of the cable or shaped into a desired shape in other application. Depending on the plasticizers, mechanical and physical properties of the polymer will change. The main property change is the flexibility [41], [44], [46], [47].

Phthalates used in insulations

Phthalates are the most widely used plasticizer in cables. Phthalate are esters of phthalic acid. Common structure of the phthalate plasticizer is shown on the figure. Following list shows the common phthalate types according to the usage. The most commonly used phthalate is Dioctyl phthalate.

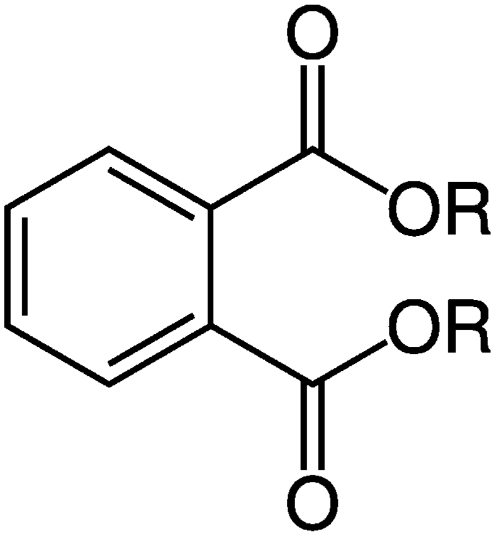

Figure 2.5: Structure of phthalate plasticizer

Table 2.1: List of plasticizers

Plasticizer	Molecular Weight (g/mol)
DMP (Dimethyl phthalate)	194.18
DEP (Diethyl phthalate)	222.24
DAP (Diallyl phthalate)	246.26
DPP (Di-n-propyl phthalate)	250.29
DBP (Di-n-butyl phthalate)	278.34
DIBP (Diisobutyl phthalate)	278.34
BCP (Butyl cyclohexyl phthalate)	304.38
DNPP (Di-n-pentyl phthalate)	306.40
BBP (Buthyl-benzyl-phthalate)	312.36
DCP (Dicyclohexyl-phthalate)	330.42
DNHP (Di-n-hexyl-phthalate)	334.45
BDP (Butyl-decyl-phthalate)	362,50
DEHP or DOP (Di 2-ethylhexyl phthalate)	390.56
DNOP (Di(n-octyl) phthalate)	390.56
DIOP (Diisooctyl phthalate)	390.56
ODP (n-Octyl n-decyl phthalate)	418.61
DINP (Diisononyl phthalate)	418.61
DPHP (Di(2-propylheptyl) phthalate)	446.66
DIDP (Diisodecyl phthalate)	446.66
DUP (Diundecyl phthalate)	474.72
DIUP (Diisoundecyl phthalate)	474.72
DTDP (Ditridecyl phthalate)	530.82
DIUP (Diisoundecyl phthalate)	530.82

Source: [15]

Most commonly used plasticizer type is Bis(2-ethylhexyl) phthalate (DEHP). This is also called DOP. Globally, phthalates dominate more than 50% of the plasticizers market. This is due to its good plasticizing ability and affordability [40], [42], [48], [49].

Phthalates act as both a lubricant and solvent. However, it is not covalently bonded to the PVC polymer (Figure 2.6). They are only bound physically to the polymer during the heating process though weak O—H electrostatic interactions [50], [51].

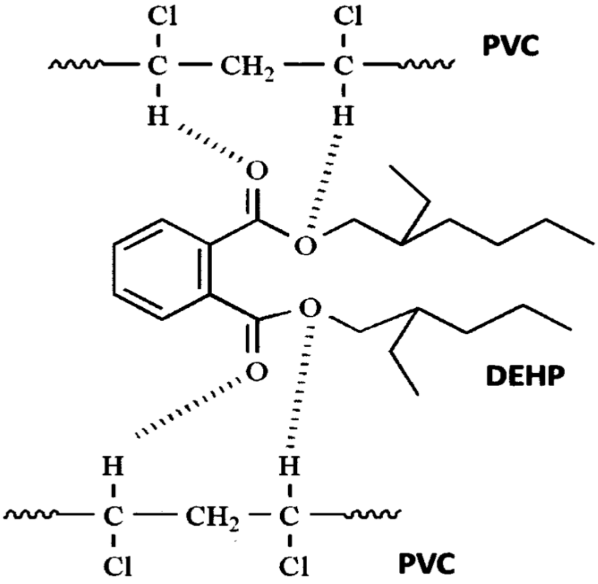

Figure 2.6: Bond between plasticizer and PVC

Phthalate bound particles can be diffuse through air over long distances, however, they do not last in the external environment due to degradation. Biodegradation, photo-degradation, and anaerobic degradation are the common degradation mechanisms. Long term exposure to elevated doses of phthalates have adverse medical consequences and phthalate concentrations within urban buildings are higher than in rural areas [51].

DEHP

Di-2-ethylhexyl phthalate (Figure 2.7), also called dioctyl phthalate (DOP) is the most commonly plasticizer for PVC globally [25], [52].

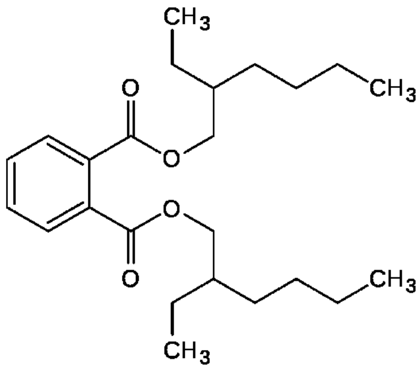

Figure 2.7: Structure of the Repeat Unit of DOP

Fillers

Fillers are incorporated into insulation and jacketing material formulas to reduce cost and improve electrical, mechanical and physical properties. Higher filler content is used for jacketing materials than for insulation. Fillers have the added advantage of increasing the thermal conductivity of the polymer [52], [53].

Calcium carbonate is the most commonly used filler for PVC. It can improve flow properties and processing of the PVC. Limited forms of calcium carbonate are used; chalk, limestone and marble of various fineness. The surface of the calcium carbonate filler can be surface treated to reduce the absorption of plasticizer. This filler must not be used for cables exposed to acidic environments as calcium carbonate reacts chemically with acids. Calcium carbonates increase the oxygen index of the polymer (higher oxygen concentrations of support combustion of the polymer), however in a fire, PVC releases hydrochloric acid reducing fire damages [41].

Hydrated Aluminum silicate is utilized generally in high temperature resistant cable applications to enhance the electrical properties. Noncalcified types of aluminum silicate filler is not suitable, as they usually include Sulphur compounds. Sulfide discoloration can be caused if lead compounds are present. The use of calcified hydrated Aluminum silicates also has a harmful effect as they increase the abrasion of machine parts [41].

Pigments

Pigments are used for coloration of insulation and jacketing compounds. Titanium dioxide is utilized as a color carrier if not the compounds are black. But Titanium dioxide affect to the dielectric constant (Єr). And also, attention must be paid when following the current tendency of applying Ca/Zn alternative of Lead primary stabilizers, Ca/Zn stabilizers do not show any pigmenting effects. In some incidents when stabilizer has been changed, an adjustment of the pigment system is essential [54]–[56].

Special Additives

Lubricants

External lubricants are used when cables are manufactured by reducing sticking of melted PVC on hot metal surface of the processing equipment. Other benefits are increase of the production rate and the good quality of the extrudate surface [16], [19].

Internal lubricants are not essential typically. As plasticizers are used, they minimize the internal friction between the PVC polymer chains. Cable formulations carry neutral Lead stearate as a co-stabilizing lubricant also Calcium stearate which is more of an internal lubricant. Fatty alcohols, waxes, paraffin and low molecular weight polyethylene are additionally utilized for extra lubrication. It is not recommended to use fatty acids like stearic acid as they may react with the basic ingredient of the Lead compound and it will head to change of the rheological properties also the stability. Lubricants such as paraffin and PE waxes which are non-polar will impact the electrical properties in PVC insulation [1], [41].

To eliminate hygienic problems at work, Antimony trioxide is commonly utilized in granulated or pasted forms. Moreover, it can be provided in a previously processed stabilizer/lubricant package. Usually, the amount use is 3 -5 phr [54].

When toxicity is regarded, Aluminum hydrate (AKOH) provides a less risk option. The amount use is nevertheless greatly higher than Antimony trioxide and generally in the range of 20-30 phr [54].

Flame Retardant

Chlorinated paraffin and Phosphoric acid esters have good flame-retardant properties. Insulation materials are generally incorporated with the flame-retardant fillers. The Oxygen index (LOI) is a measure that is used to identify inflammability. This parameter indicates amount of Oxygen that must be existed in the surrounding atmosphere to burn the polymer. Usually the LOI is around 25 for plasticized PVC. Higher value of LOI can be achieved using especially designed flame-retardant compounds. Nevertheless, only the LOI is not enough to fully implicate the flammability of cables [57].

UV-Absorber

Carbon black is not only a filler it is also act as a protector against light. As all cables in outdoor applications are black light absorbers have been requested. In colored or transparent materials Benzotriazole, Benzophenone or Oxanilide UV-absorbers are used [39].

Stabilizers and co-stabilizers

Lead compounds

PVC insulation and jacketing materials are usually stabilized by with basic Lead compounds except few special applications [16].

2.5 Theories of Plasticization

Several theories have been developed for the plasticization process depending on the characteristics of the material. An important review of theoretical plasticization process is described by Sears and Darby [6]. Plasticization is explained by three main theories with some modifications.

2.5.1 Lubricating Theory

According to lubricating theory plasticizer in PVC performs as a molecular lubricant enabling the polymer chains to move liberally over one another once a force is applied to the plasticized polymer. This theory assumes that the polymer chains that are not plasticized do not move liberally due to surface irregularities. In this model, one fragment of the plasticizer is strongly attached to some parts of the polymer, while other fragment is not. The fragment attracted to polymer acts as a solvent for the polymer, while the other fragment acts as a lubricant [41].

To occur plasticization this theory suggested some important factors. They are,

1) Existence of groups that bear points of attraction in both polymer and plasticizer
2) To allow the attractive forces to function, location of these groups should be proper.
3) structure of the plasticizer molecule is important to offer required physical characteristics to obtain expected results.

2.5.2 Gel Theory

It supposed that polar groups in the plasticizer and the polymer molecules are loosely tied together at varying intervals so as to create dipoles which are solvating on the chain of the PVC. The non-polar tail portion of the plasticizer that are not compatible with PVC would be likely to form tiny clusters. It leaves a huge number of unshielded polar chain which to generate powerfull polymer-polymer interacts which compose a gel structure. This will generate a viscous flow. Added plasticizer increases the micro-Brownian motion [41].

2.5.2 Free Volume Theory

Free Volume is an indication of the internal space present within a polymer. By increasing free volume more space or free volume is produced for molecular or polymer chain mobility. When polymer is in the glassy state polymer chains are close-packed but there are imperfections. As free volume is minimum, the polymer chains cannot move easily. So, the polymer shows rigid and hard nature. If the polymer is heated to more than Tg, the thermal energy and vibrations of the polymer chains build extra free volume which permit the polymer chains to move quickly. So, this creates the polymer system more flexible and rubberier. To increase the free volume the polymer backbone can be modified. One example is addition of more side chains or end groups. If small molecules like plasticizers are incorporated, it will lower the glass transition temperature by destroying bond between the PVC chains and forming free volume to create the PVC soft and rubbery. Chains of PVC can then rapidly move past each other. If the plasticizer equally distributed into the PVC, it would show same as an uncured rubber with high amount of creep and high compression set [41], [58].

2.6 Degradation and failure of Cables

When power systems are functioning, they are subjected to different types of stresses. Electrical, thermal, mechanical and environmental stresses are the major stresses. These stresses and bad practices of installation and maintenance are made insulation degradation and also lead to cable breakdown [59], [60].

Failure of cables will not be cause as sudden failure is usually follow by a degradation stage which may occur in several years. The way to improved estimation of cable durability and life time should be done by identification and characterization of degradation mechanism and its rate of occurrence and forecasting of lifetime should be done.

Degradation or the aging phenomena in polymers is commenced and speed up by numerous factors like field of electricity, temperature feel to the cable, moisture content and UV-light. These factors can act as main reasons for cable aging, either alone or concurrently correspond to cable working conditions and surrounding. The reason to fail many are due to insulation degradation, if the rate of degradation can be forecasted, suitably scheduled, correct maintenance schedule can almost terminate cable failures [59].

Due to environment or surround conditions chemical or physical degradation mechanisms at the molecular level of the insulation can initiate. Usual visible changes in the properties of insulation can cause functional failure in the cable, include reduce of elongation at break, increase of hardness, raise the density of material, increase in dielectric loss, etc [56].

In most insulations, the properties change electrically are not massive. Reduction of cable functionality is normally governed by the mechanical property changes, splitting of the insulation lead to electrical failure. The electrical function loss happening prior to surface crack is usually found when design of the material is inappropriate. [13], [23], [59], [61].

The failure of insulations while in operation can generate sizable damage to an equipment and to the systems that they are connected. It has been identified that failures frequently may be associate to the development and severity of partial discharges within voids present in insulation. So, the partial discharge technique is an suitable technique to determine the status of the cables [62].

PVC is one of the most widely used polymers. Thus, its primary chemistry of degradation has been examined to some extent. The issue is that most examinations have been done only for pristine PVC, usually nearly to 50% of the weight may contain different additives. These additives are believed to have an effect on the PVC degradation.

Many studies have been focused on the migration of plasticizers from PVC to a liquid media, but rarely from PVC to a gas phase [49], [63]. Audouin et al. [64] have chosen the weight loss as an indicator to quantify the physical loss of the plasticizer. Gedde and coll. [65] have determined the changes (against time of exposure) in the concentration profile of di-(2- ethylhexyl) phthalate plasticizer (DEHP) in the thickness of an industrial PVC insulation in air between 80 and 155°C.

2.6.1 UV Degradation

There are two methods involved, which are slightly different mechanisms. They are photooxidation mechanism and mechanistic scheme [36].

Photooxidation mechanism

Initially hydrogen will be abstracted by the carbon chain. Then these radicals formed react with oxygen at molecular level to form a peroxyradical. Hydroperoxides are created and collected at usually small stationary amounts, after that O−O bondage is homolyzed by thermolytic or photolytic processes and there will be a creation of micro-radicals. Hydrogen abstraction from PVC backbone by the radical formed may lead to an alcohol or acid chloride. Carboxylic acid will be formed due to hydrolysis of acid [36].

Mechanistic Scheme

This scheme suppose that reactions of crosslinking may happen by rearrangement of radicals which contain oxygen or a polyenyl radical [36].

2.6.2 Mechanodegradation

Mechanochemical degradation happens during forming and utilization of PVC products. Most forming methods require high temperature which may lead to degradation of the material. So, it is very hard to separate both influences [36].

2.6.3 Thermal Degradation

When polymeric insulation, jacketing materials and organic and inorganic additives uncover to heat and they are subjected to degradation. Degradation create differences in the properties of materials physically with time the required properties of the material are lost. Due to this reason material is failed and unable to operate satisfactorily. Accordingly, thermal stress can create failure without harming the specimen [40], [42], [48], [66].

Life tests are usually performed to estimate durability of insulating materials. In these life tests specimens are exposed to constant stress until the failure. Failure time in operating conditions can be forecasted from statistically from life tests. The failure time is estimated in a shorter time period than the real lifetime under service conditions, the tests are needed to conduct in extreme conditions than the operating conditions. These tests are considered as accelerated life tests. Extrapolation to service conditions is needed to achieve the real lifetime [17],[24].

When processing the insulations, they are exposed to high temperatures this will lead to degradation of the material. The characteristics of the ultimate product based on the group of plastic, the additives utilized and the manufacturing temperature. Even though degradation difficult to be terminated completely, it must be minimized to ensure the quality of the ultimate product [17].

PVC is one of most vast commercially used polymers. So, it is important to study fundamental degradation reactions. Since most studies have been carried out only on pristine PVC it is important to study PVC blends used in cables as they utilized additives nearly 50% of weightage. Additives use, are specially stabilizers can be supposed to have an influence on the degradation [24].

Thermal degradation of PVC has three main stages. When the temperature of a polymer is increased than ambient temperature the plasticizers incorporate in PVC started to evaporate to surrounding and that would go to completion around the temperature 330^0C. The second mechanism is dehydrochlorination which is the process of HCl molecules are released to environment and after removal of HCl polyunsaturated material is remained. It is sometimes named as polyacetylene [40]. The HCl removal mechanism is shown in the figure below.

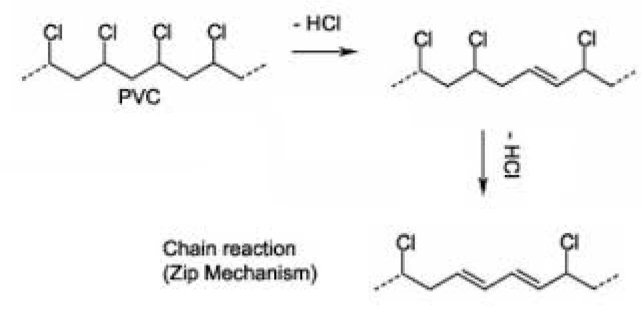

Figure 2.8: Formation of polyacetylene

The third mechanism is char formation due to breakdown of the carbon bonds [36].

Several studies carried out on PVC material have indicate that quantifiable concentration of HCl are evaporated when 100ºC is reached. Wolter et al. report that there is an induction period before these processes start at low temperature. That means that a significant time period spends to evaporate HCL when subjected to adequate high temperature. But some other researches have indicated that there's no for dehydrochlorination of PVC above 180ºC the induction period [63].

The significance is the performance of PVC cable insulation and jacketing differ from pristine PVC. Hirschler et al. examined plasticized PVC used for cable manufacturing in air medium and discovered predominantly no dehydrochlorination at 90ºC [67]. A countable emission of HCl arise at 105ºC. This is highly related to the temperature range discovered for pristine PVC. Some other studies that investigate same PVC cable materials indicated elevated degradation temperatures. This is may be due to experimental methods are not properly fit to lower temperature regions. Chandler et al. Discovered dehydrochlorination at temperature 260ºC and Armstrong et al. discovered it at temperature 240ºC for an already-aged cable [68].

For pristine PVC an investigation indicates that elimination of HCL was necessarily accomplished when temperature 250ºC was outreached. Some other investigation indicated a peak at 250 ºC and another two investigations indicated that a peak value near to 285ºC. So, the correct temperature span for dehydrochlorination is distinctly depends on the test conditions [40].

Nevertheless, for plasticized PVC cable formulations, dehydrochlorination is at elevated temperatures [35]. One investigation indicated the reaction is not accomplished fully until the temperature 360ºC is reached. At 350 – 500 ºC the second-stage of the pyrolysis occur. There will be few parallel reactions. Polyenyl macroradical creation, dehydrocyclization, aromatization, and chain scission are them. At the completion of the reactions charred will remain as crosslinked product [37], [69].

Even for pristine PVC recognition of its thermal degradation is difficult. Because initiation of HCl emission or the hydrochlorination is unpredictable for actual polymer as it is influenced by structural abnormalities. Process of dehydrochlorination is autocatalytic. The existence of HCl gas boots the reaction. Accordingly, to solve this problem in cable insulations use $CaCO_3$ is used to act as a scrubber [27],[16].

As thermal degradation for Pristine PVC start at lower temperature, forming cannot be done. Hence, in commercial PVC compounds, to gain thermal stabilization stabilizers are included. This will inactivate HCl that is going to formed and then minimize the process of autocatalytic of the process. Mizuno et al. Discovered that, in comparison to a compound of PVC that was unstabilized, a PVC compound stabilized by lead-based stabilizer ulter the degradation temperature by approximately 30ºC [70]. But Alvares et al. Discovered dehydrochlorination for pristine PVC in air is at 220ºC but for several PVC compounds that is used for actual electrical cords and cables exhibit very low temperature [40],[16].

The dehydrochlorination temperature in PVC from cables was same or lower to that pristine PVC. Plasticizers usually have a negative influence on PVC. In several studies are presented on the relation of temperature effect on mechanical properties of the PVC insulation material are available. According to studies countable degradation is noticeable when 120ºC is reached, but it is difficult to associate to ignition or breakdown in electrically [16].

In numerous incidents, emission of plasticizer is probable to happen at only low temperatures. Extreme elimination of plasticizer will produce embrittlement of the material and this can head to cracking, but no investigation can be found that have been carried out to study electrical failure under this incident [39].

One study indicated for PVC plasticized with DEHP which was exposed to 30h of thermal disclosure at 100ºC generate, a loss of 30% of the plasticizer Mann et.al conducted investigations on cable insulation and discovered that considerable concentrations of plasticizer were evaporated already at 85ºC. Depending on this result he finalized that there is a toxicity when the PVC insulated cable is in a surrounding where the products of degradation cannot be quickly evaporated. So, rapid burning can be expected [52].

Anandakumaran and Stonkus et al. investigated plasticizer elimination in PVC cables which are commercially available and discovered that about 25% was evaporated by subjected to heat at 120 ºC for 70 days and at 130 ºC for 24 days. In opposition a study on HV PVC cables used for 18 years display that these had sustained only around 2%

plasticizer loss. These cables were exposed to atmosphere without suffering considerable overheating or other type of stresses during their usage [71]. This investigation also discovered that the stabiliers of lead stearate/lead phthalate had been reacted with HCL only about 20%. Zaikov et al. showed that elimination of plasticizer originates generation of voids in the PVC matrix and these voids will lead to breakdown of the insulation [45].

But Stricker et al. point out that even though cable lifetime has not been determined, a life time of 20 to 50 years can be expected. The lifetime cables were tested by heating cables under elevated temperature conditions. Eight dissimilar types were examined. Some of them are without sheath and others with sheath of PVC or nylon. Considerable plasticizer elimination took place for all kinds at 71 – 77 ºC for roughly one month. Stricker et al. showed the plasticizer elimination as the termination of productive life span for the cables. So, there were no further electrical, or chemical was not carried out. His conclusion is that 90 or 105ºC rated cables should not be utilized above 71ºC [72].

The ignition temperature pristine PVC is very high however this is not applicable to cable compounds. Several authors reported the range of 263 – 454ºC for commercial PVC cables, this is a wide span and adequate information have not been published. So, depending on the PVC additives composition ignition temperature can be changed. Correspondingly, the trial ignition temperatures recorded the between 240 – 422ºC. The author has discovered in a late case in a PVC insulated extension cord ignition is at 250ºC. This reduced ignition temperature value was caused by the utilization of a secondary type of plasticizer in the polymer compound [16].

They are basic organic compounds (e.g. ordinary mineral oil, chlorinated paraffins, etc.). Addition of secondary plasticizers are done for cost-saving purposes as they have low cost than phthalates. Mitsuhashi et al. Indicated that ignition of cable insulation may take place from the metallic electrical conductor surface which is heated. Therefore, they carried out tests depending on this order and acquire a heated surface ignition temperature of 550ºC [16].

The other forms of degradation are due to different form of radiation like ϒ, argon plasma and corona discharge.

2.6.3 Thermal Stress of cable under a roof

Cable under a roof is subjected to fluctuating thermal stress throughout the day according to outside temperature. Depending on the roofing material magnitude of the thermal stress will be varied. Therefore, careful analysis should be carried out for cables under a roof.

2.6.4 Degradation by plasticizer loss

Plasticizer loss not a simple process, which incorporated with three simultaneous physical processes,

1) Volatilization process: interfacial mass transport between polymer and surrounding which is a solid-gas phase reaction
2) Process of transport of plasticizers through the interface
3) Diffusion process: transport through the polymer matrix up to the surface of the material [11]–[13].

PVC insulation materials generally lose their additives through volatilization and diffusion processes [31], [58], [73]. The study reported by Kovačić et. al and Calvert et. al, proposes that the additives in the surface of the polymer material volatilize into surrounding and lower down the concentration of plasticizer at the surface. This directs subsurface additives into the surface to compensate for the loss of plasticizer[11],[12].

2.6.5 Kinetics of Plasticizer evaporation

The removal of ingredients (plasticizers, stabilizers etc..) from polymers heads to deviate their desired Physico mechanical properties. The removal of substances which are comprising mainly monomers and their derivatives has a harmful result on humans and also cause to environmental pollution. The procedure of removal of ingredients continue with the transport of ingredients within the polymer to its interface and their elimination from the polymer interface by various mechanisms based on the nature of the surrounding medium [68].

Development of a model is important to forecast the removal kinetics of ingredients under operation conditions of polymer. Modelling of the removal kinetics of substances gives an approximation of the operation life span of the polymers.

Moreover, modelling of evaporation of kinetics make it possible to determine the rate of mobility of ingredients from the interface into the surrounding medium. A probable way to modelling the kinetics of evaporation of plasticizers compromise the introduction of an empirical model which satisfy the experimentally collected kinetic dependences of evaporation reactions. One benefit of this method is the significant amount of practical data gathered during the study of the evaporation kinetics of additives at various operation conditions and in accelerated conditions of [74] [75].

The rate of a solid-state reaction can be written as a function of conversion fraction.

$$\frac{d\alpha}{dt} = K(T)f(\alpha)$$

$$\alpha = \frac{m_0 - m}{m_0 - m_f}$$

Where,
f(α): The reaction model
α: Conversion fraction
K(T): Rate constant at temperature T
m_0: Initial Weight
m: Weight at time t
m_f: Final weight
Δm: Weight Loss
t: Time

For first order reactions $f(\alpha) = 1 - \alpha$

$$\left(\frac{-1}{m_0 - m_f}\right)\frac{dm}{dt} = K(T)(1 - \frac{m_0 - m}{m_0 - m_f})$$

$$\frac{dm}{dt} = -K(T)(m_0 - m_f)$$

The solution of this equation is $m = m_0 \exp(-Kt)$

Thus, $$\Delta m = m_0 - m_0 \exp(-Kt)$$

So, the rate of evaporation of additives can be presented as a function of remaining weight of the additive and its temperature. If the evaporation process is not rapid than the diffusion process, then the rate of loss of additives from the surface of the polymer, is a linear function of remaining concentration. Nevertheless, if the depletion of additives is dominated by diffusion process, then it shows a nonlinear behavior[13].

It is an ordinary accepted fact the rate of evaporation or the loss of low molecular weight additives are determined by first order kinetics. Simply evaporation of plasticizer is a first order kinetic process [15],[17] that based on weight and temperature.

In the range room temperature to 200 ^{0}C the main reason for degradation of cable insulation and jacket degradation are the removal of plasticizers[19]. The removal of plasticizers changes the glass transition temperature T_g to higher temperatures and converting insulation material to a brittle material. So, flexibility of the cable becomes low. These dry and inflexible cables introduce micro cracks. Moisture can be absorbed via these micro cracks in the insulation and it could heads to partial dielectric breakdowns of the cable [20]. Therefore, removal of plasticizer from the cable has a considerable effect on the cable lifetime.

The plasticizer removal at temperatures lower than ambient temperature is an intensively slow process. Therefore, it is not practicable to investigate this process using mass loss at isothermal conditions.

2.6.6 Arrhenius Behavior of Plasticizer Evaporation

Accelerated aging is one method to model the actual aging condition. Arrhenius equation is usually used as a physical model for predicting the lifespan using accelerated thermal aging. For accelerated aging heating has to be done and monitored. Recording of degradation at the actual environment can be to validate the model. It can be seen the rate of the thermal degradation reduces in an inverse way to the temperature from the Arrhenius equation [46], [47], [52], [78].

$$k(T) = Ze^{(-E_a/RT)}$$

Where, $k(T)$: Rate constant ($f(T, C_0)$)
E_a : Activation energy for the process (KJ/ mol)
R: Gas constant (J/molK)
T: Absolute temperature(K)
Z: Preexponential factor

The reaction rate on a log scale against 1/T should show a linear behavior if the evaporation process shows Arrhenius behavior. The slope of the graph gives the activation energy Ea. Activation energy determines the sensitivity of the rate of degradation. Carrying out an accelerated aging over a wide range of temperatures occasionally exhibit a ‘‘break point’’ in the plot which can be attribute to a conversion in the kinetic regime. The activation energy will not same over the entire temperature. In number of examples where difference in slope have been encountered exhibit lower activation energy at lower temperatures. In such scenario, an extrapolation depends on the data obtained at higher temperature would implies a considerable deviation of the degradation at lower temperatures [78].

Depend on the activation energy information about reaction mechanism can be obtained or in some occasion data can be extrapolated to different conditions. Extrapolation or interpolation to new temperature values can be done cleverly. If in sequence of basic reactions, there is reaction which is slower than others the activation energy is the average thermal energy required to initiate the rate determining step of the reaction.

However, the accuracy of mapping from the Arrhenius law should always be doubted. Several conditions should be satisfied it to be true. The reaction must occur constantly over the temperature range considered and considerable physical transitions (e.g. crystallization or glass transition) must not to be present within the considered temperature span. It can be used if both of conditions are satisfied only [12].

CHAPTER 03

3. EXPERIMENTAL

3.1 Materials

The selected cable material for study was a typical cable used for domestic electrical wiring and lightening purposes available in the Sri Lankan market. It is assumed that the samples have not been exposed to heat or adverse environments prior to the study. Brown colored single strand with 1mm thickness of plasticized PVC insulations and plasticized PVC jacket of the cable were studied.

3.2 Methodology

Thermogravimetric Measurements

The initial plasticizer content in the insulation was determined by thermo gravimetric analysis (TGA). The thermo gravimetric (TG) and deferential thermo gravimetric (DTG) thermograms of studied samples were recorded from 20^0C to 600^0C at a rate of 10 ^{0}C/min under air flow using SDTQ600 by TA instruments with temperature sensitivity 0.001 ^{0}C. Sample quantity was 25 mg and airflow rate set to 100 mL min^{-1}.

The evaporation of plasticizers from plasticized PVC insulation was analyzed by thermogravimetry in isothermal condition at 80 ^{0}C, 100 ^{0}C, 120 ^{0}C, 140 ^{0}C for 120 min under air flow.

Temperature Measurements of the Cable

Temperatures of the cable placed under a roof was measured in order to investigate equivalent temperature and time required to evaporate the plasticizers from cable. Temperatures were recorded using TMP36 Temperature sensor.

CHAPTER 04

4. RESULTS AND DISCUSSION

4.1 Initial Plasticizer Content in Insulation

The TGA curve of insulation material in the range 50–600°C when heated in air is presented in Figure 4.1. It can be used to characterize the multi-step thermal degradation of the insulation of PPVC.

1. The first step (up to 330°C) is evaporation of the plasticizers.
2. The second step (from 200°C to 340°C) is mainly related to the zip-elimination of HCl and the generation of a series of conjugated double bonds in chain of the polymer. The produced HCl is a highly corrosive gas and the highly reactive double bonds formed in the polymer chains absorbs light in the visible and UV region. This causes discoloration of the material converting yellow color to black and depletes the physical and mechanical properties of the polymer.
3. The final step is evolution of CO_2 due to the decomposition of the $CaCO_3$ filler, this step is of course not observed in a pristine PVC TG plot.

Other reactions of importance:

1. At higher temperatures, the polymer compound experiences partial carbonization with the elimination of benzene and other aromatics. Phthalates also thermally degrade from 200°C onward. Nevertheless, when incorporated in a polymeric compound the removal of plasticizers is shifted to elevated temperatures [79].
2. A portion of HCl generated in the second step can react with the calcium carbonate and forms $CaCl_2$, H_2O and CO_2.

For plasticizer evaporation

$$\Delta m = m_0 - m_0 \exp(-Kt)$$

The quantity of plasticizers in cable insulation varies between 20% wt to 45% wt depending on the manufacturer. In order to determine plasticizer removal kinetics, the original plasticizer concentration at the beginning must be known as per the kinetic equation. So, a method has to be developed to determine plasticizer amount of cable insulation and the jacket.

It was assumed that the plasticizer removal process occurs within the first degradation step in the TG spectrum around 250 ^{0}C. Thus the TG in the range from 150 ^{0}C to 330 ^{0}C was selected for the analysis.

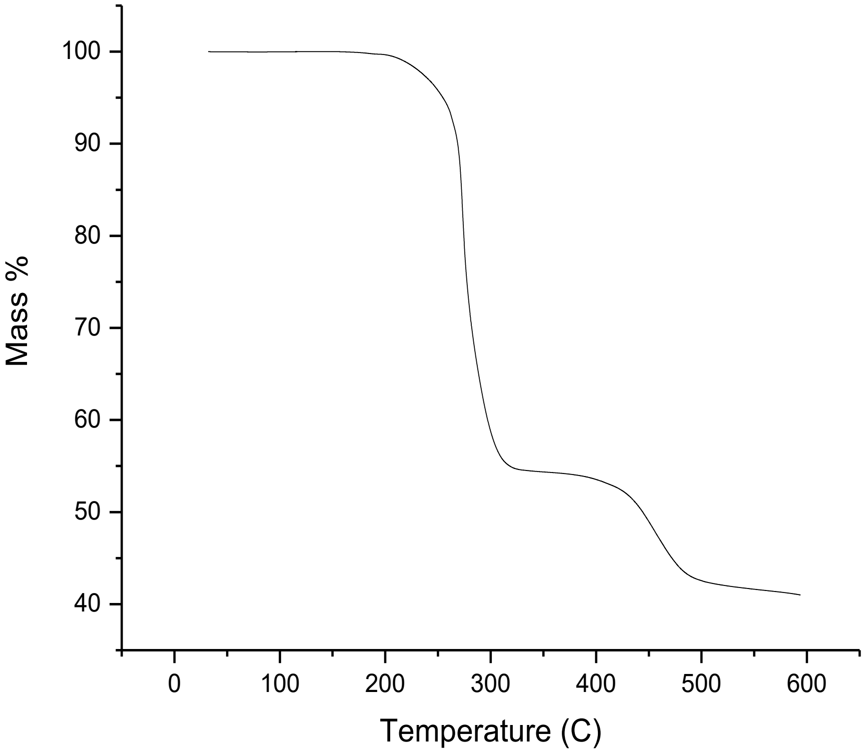

Figure 4.1: TGA of the cable insulation with unknown plasticizer percentage

Even though at first, the initial degradation step was seen as an individual event, when zoomed, it showed multiple unresolved events (Figure 4.2). This was confirmed by the DTG curve (Figure 4.3).

The first degradation event of the TGA can be attributed to three different processes. The first process is controlled by the removal of the plasticizer. This phenomenon arises in the three superimposed peaks in the area of study. Second process is dehydrochlorination or the removal of HCl. And the other process is the reaction of HCl and $CaCO_3$ filler.

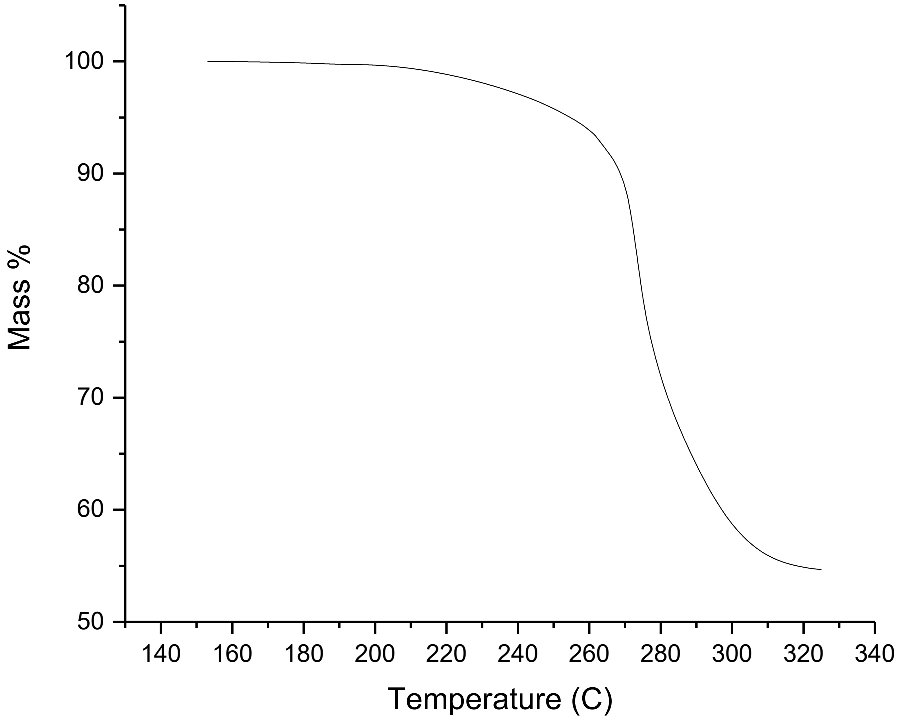

Figure 4.2: TGA of cable insulation in the range of 150 -330 ^{0}C

The temperature ranges for all three processes which are predominant could be identified. It could be observed that at temperature values lower than 275°C, the volatilization of plasticizer is the governing process while the dehydrochlorination is the governing process at temperature ranges higher than 275°C.

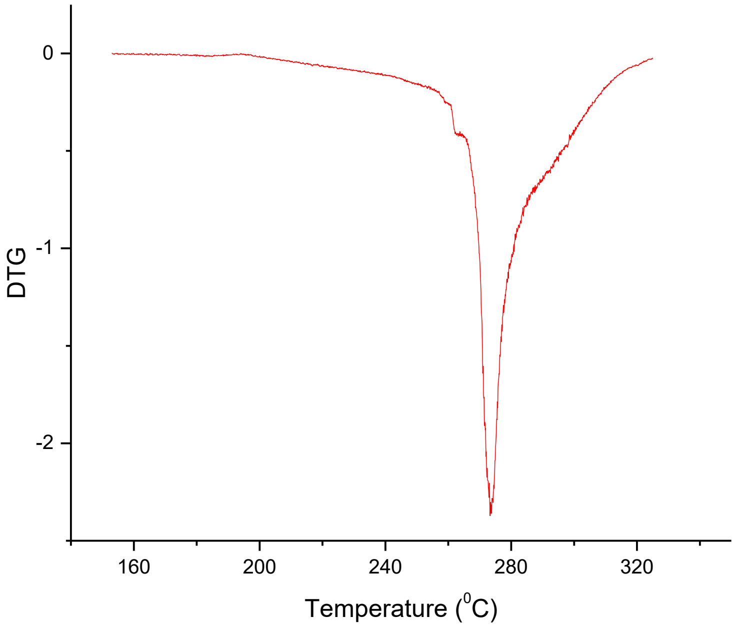

Figure 4.3: DTG curve between 150-325 ^{0}C

From Figure 4.3, it can be seen there are several events occur in the 150-325 ^{0}C region. As there are three peaks which are not resolved, nonlinear least square refinement with constraints using origin software was carried out to deconvolute this peak region into three Gaussian curves. Figure 4.4 shows deconvoluted DTF curve. The curve obtained has the R squared and Chi squared values 0.9952 and 0.0013 respectively.

According to literature plasticizer removal process, begins at lower temperatures and reach the completion temperature near to 330°C. It is well-indicated in the previous studies that dehydrochlorination is visible in the temperature region around 270 - 360°C. Removal of HCl activates the reaction of $CaCO_3$ with HCl. The DTG peak related to this reaction is around 300°C. So, the Gaussian (1) curve can be attributed to plasticizer removal process. The position of the peak and the area of the peak confirms the attribution. Moreover, the positions of the remaining two Gaussian peaks are also comply with the data of previous studies [34]

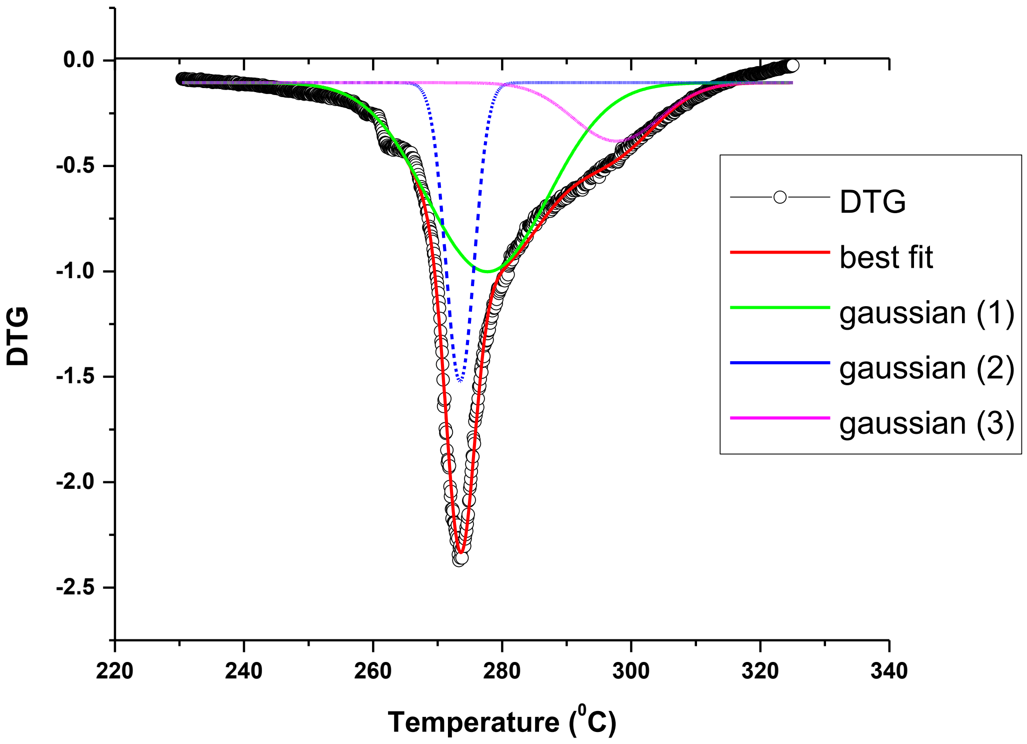

Figure 4.4: Deconvoluted DTG curves

Majority of thermal stages visible in the TGA are compacted to comparatively narrow temperature range. But the plasticizer removal event lies over wide temperature range, which overspread also in lower temperatures. Thus, the expansion of the Gaussian (1) curve up to room temperature is explained.

Part of the plasticizer removal process up to any temperature, T, can be derived from the area under the curve up to defined temperature. The percentage values of removed plasticizer at various temperature ranges are given in Table. The original amount of plasticizer at the beginning (M_0) was calculated by the area under the Gaussian (1) curve. The calculated amount of plasticizer is 32% which is an acceptable value for PVC cable insulation formation.

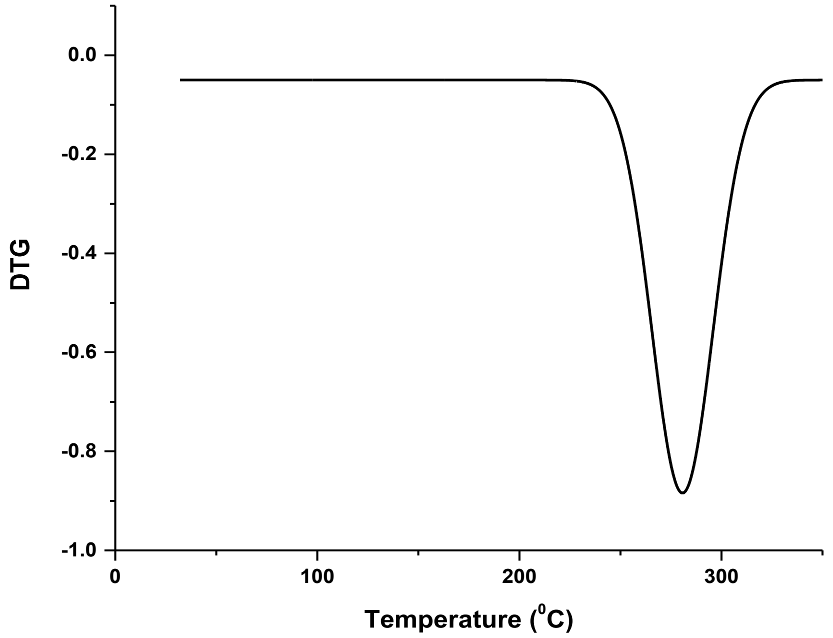

Figure 4.5: DTG curve for Plasticizer evaporation

Table 4.1: Plasticizer Evaporation using TGA

Temperature range	**Plasticizer evaporation (per 100g)**	**evaporation %**
32 °C-230°C	1.92	5.85%
230 °C-325°C	30.95	94.12%
above 325°C	0.01	0.03%
Total plasticizer amount	32%	

The calculated values from the table 4.1 indicate that 5.85% of plasticizers removed up to 230°C temperature and 94.12% removed above 230°C which is in a heating ramp of 10°C/min. Insulation at moderately temperatures emit plasticizers at very slow rates. So, it is not possible to study plasticizer removal process at lower temperatures using mass loss at isothermal conditions practically. Nevertheless, the model established from this study can aid with this situation. The developed model can be utilized to map higher temperature plasticizer removal kinetics to lower temperature values.

4.2 Representation of rate constant at 80-140 ^{0}C temperature range

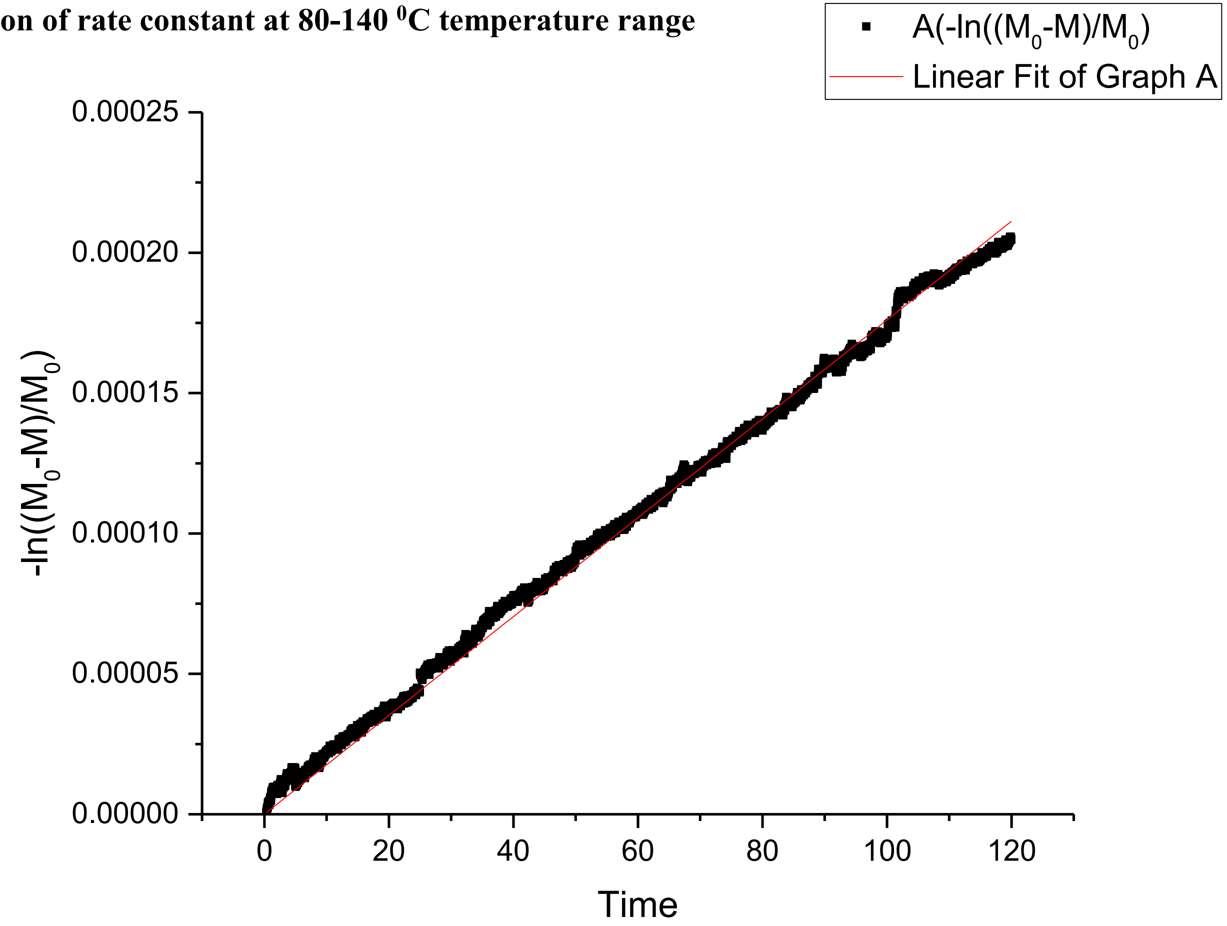

Figure 4.6: Graphical representation of the rate constant of evaporation at 80 ^{0}C

(R^2= 0.9991)

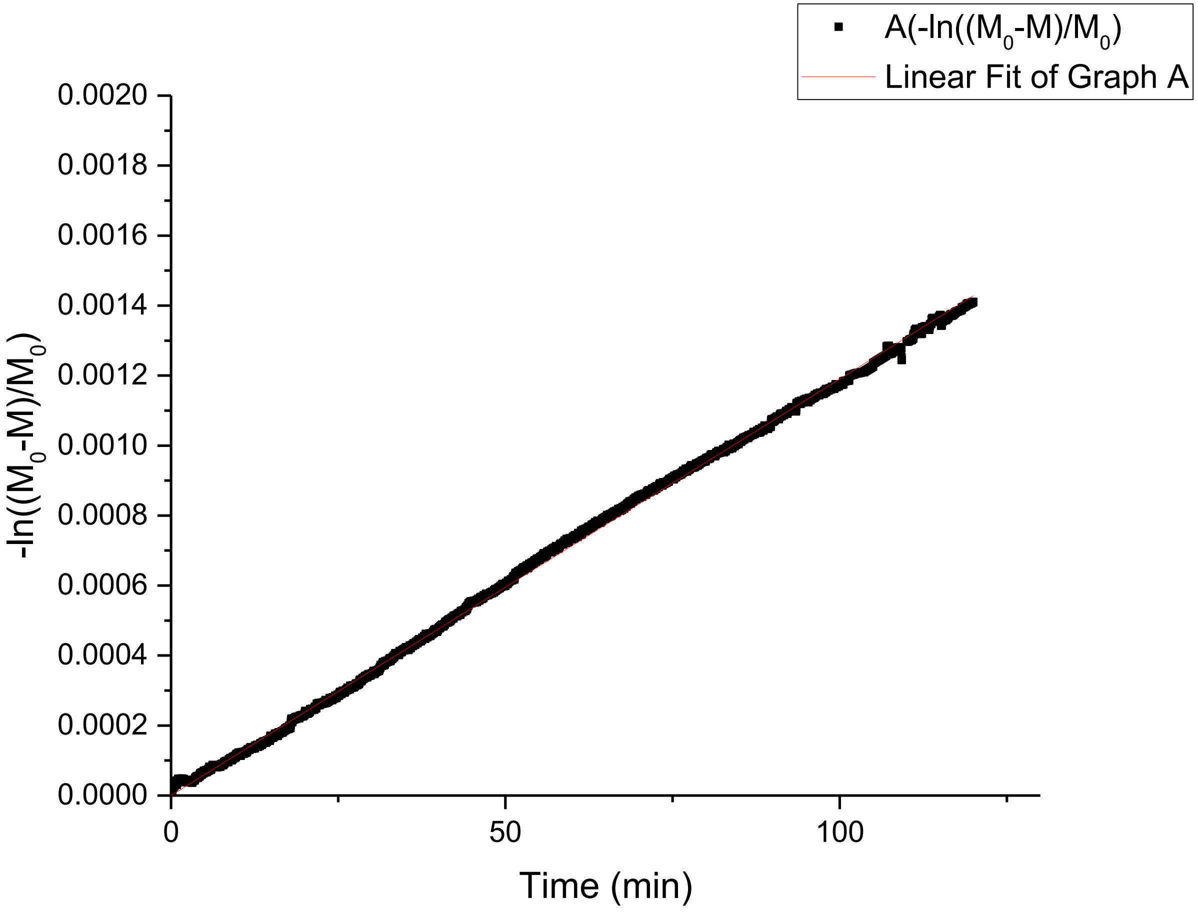

Figure 4.7: Graphical representation of the rate constant of evaporation at 100 ^{0}C

(R^2=0.9991)

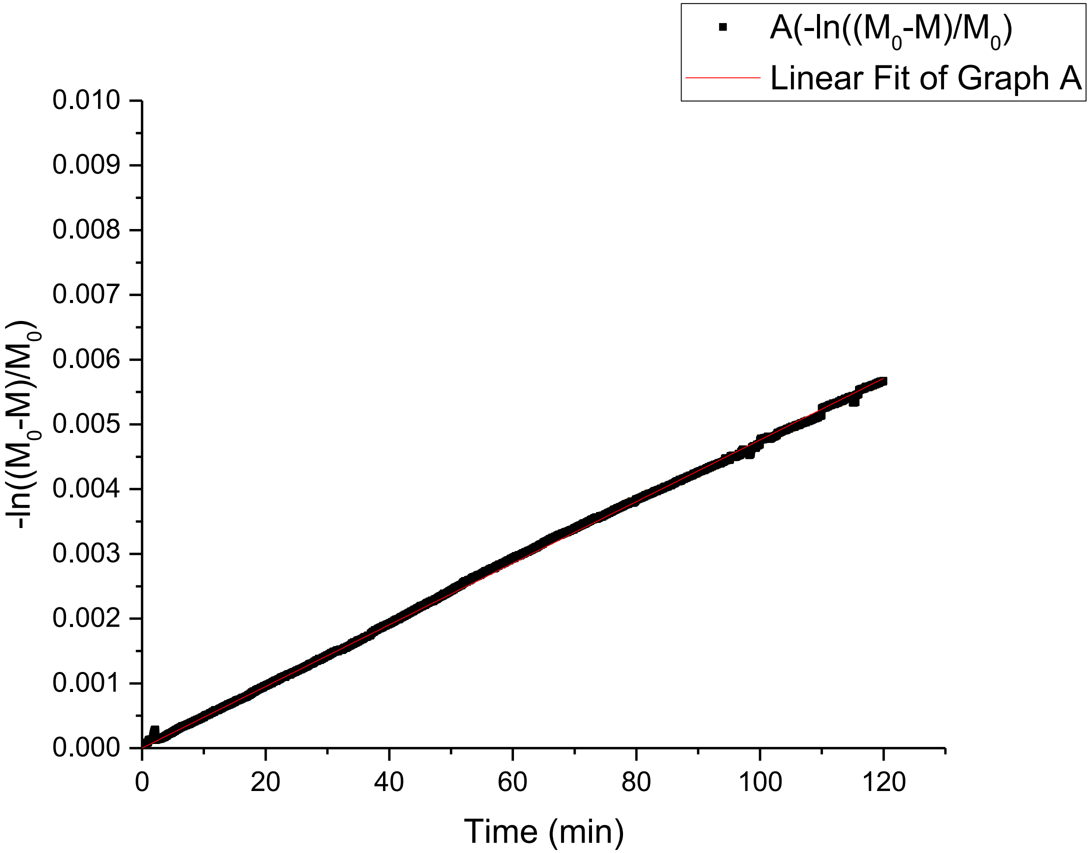

Figure 4.8: Graphical representation of the rate constant of evaporation at 120 ^{0}C

(R2=0.9995)

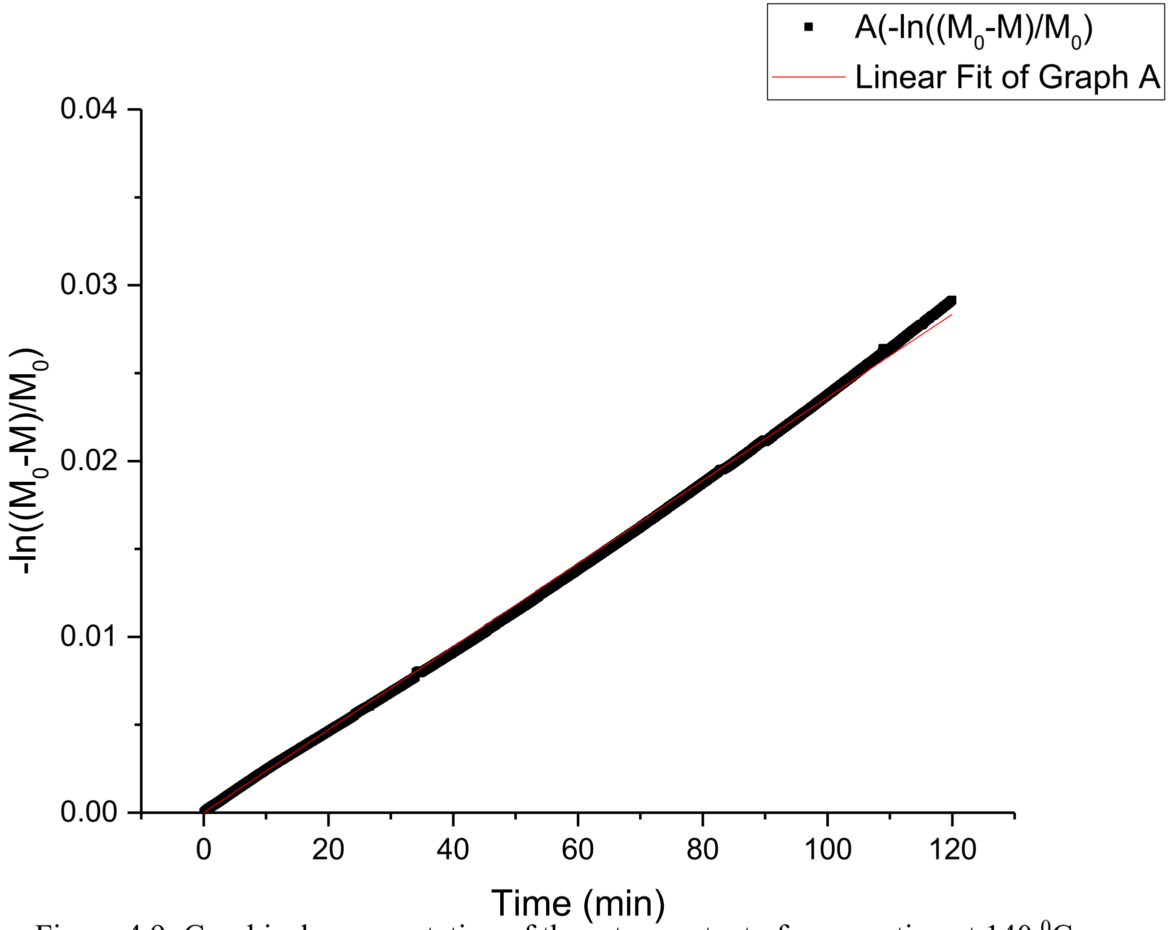

Figure 4.9: Graphical representation of the rate constant of evaporation at 140 ^{0}C

(R^2=0.9994)

Plasticizer evaporation data collected at 80^0C, 100^0C, 120^0C and 140^0C were analyzed and rate constant for each temperature were determined using and the derived equation.

4.2.1 Dependence of Rate Constant on Temperature

Table 4.2: Rate constant at different testing temperatures

Temperature (^{0}C)	Rate Constant(min^{-1})
80	1.76E-06
100	1.20E-05
120	4.76E-05
140	2.43E-04

Table 4.2 shows the rate constant is increasing with increasing temperature. Due to this behavior there's a tendency to show Arrhenius behavior of plasticizer evaporation.

4.2.2 Arrhenius Behavior

As the plasticizer evaporation reaction occur constantly over the temperature range considered and considerable physical transitions (e.g. crystallization or glass transition) is not present within the considered temperature span Arrhenius law can be used.

Arrhenius Equation

$$k(T) = ze^{-E/RT}$$

Where; z: Pre-exponential factor

E: Activation energy or the energy needed to plasticizer from the polymer surface

As assumed, the rate constant of plasticizer evaporation increases with the increasing temperature. Thus, Arrhenius equation showed linear behavior and liner regression analysis was conducted on the data obtained.

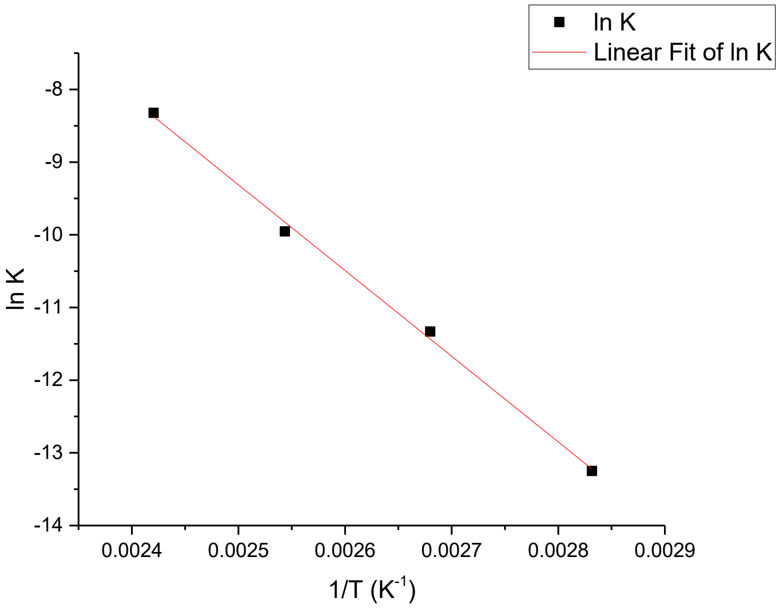

Figure 4.10: Arrhenius plot of rate constant for plasticizer evaporation (R^2=0.9977)

The graph plotted shows a linear nature. Even though there's a doubt in Arrhenius principle in accelerated temperature conditions as discussed in literature review this linear nature a of the Arrhenius plot with high R^2 resolve the that doubt. So, the kinetics of removal of plasticizers up to 140^{0}C follows Arrhenius principle. Thus, f (T, C_0) can be substituted with Arrhenius rate constant.

The activation energy and the pre-exponential factor for the evaporation process was calculated using regression analysis. The activation energy of the process is 98 kJ and the pre-exponential factor is 38638.3 min^{-1}. The values obtained are in accordance with the previous studies for plasticizer evaporation kinetics.

4.2.3 Mapping of Plasticizer Evaporation Data for Lower Temperatures

Since the evaporation process obeys Arrhenius law, the activation energy calculated can be used to model the plasticizer removal kinetics even at lower temperatures. The rate constants at 40 ^{0}C, 50 ^{0}C, 60 ^{0}C, 70 ^{0}C, 90 ^{0}C, 110 ^{0}C, 130 ^{0}C were determined depend on Arrhenius law and plasticizer removal at these temperature values were modeled depend on derived equation.

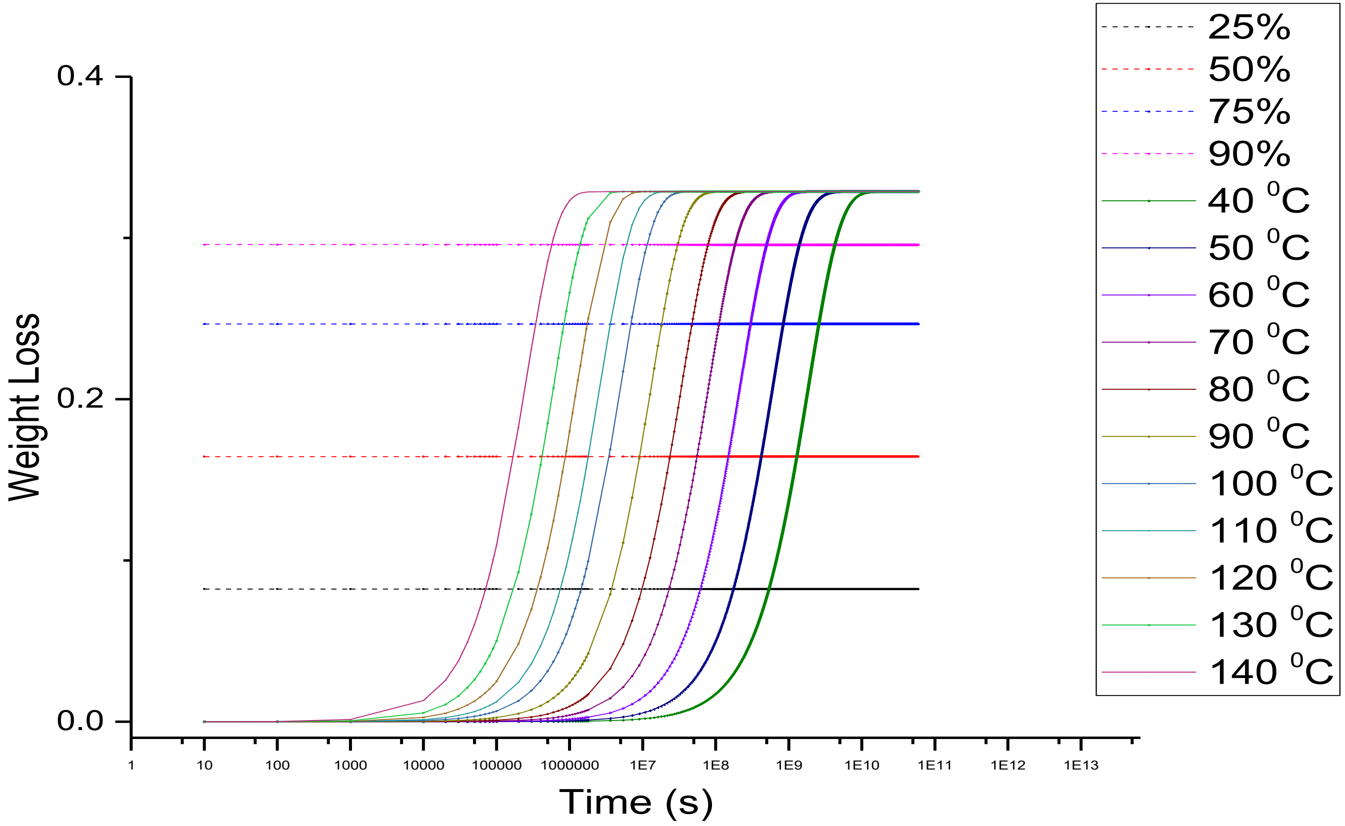

Figure 4.11: Plasticizer evaporation Mapping

The modeled plasticizer removal process at various temperatures was utilized to calculate the time to evaporate 25%, 50%, 75%, 90% plasticizer.

Table 4.3: Time Required to Evaporate 25%, 50%, 75% and 90% Plasticizer

Temperature	Time required to evaporate 25% Plasticizer	Time required to evaporate 50% Plasticizer	Time required to evaporate 75% Plasticizer	Time required to evaporate 90% Plasticizer
40 ^{0}C	16 yrs	42 yrs	84 yrs	137 yrs
50 ^{0}C	5.5 yrs	14 yrs	27 yrs	44 yrs
60 ^{0}C	2 yrs	5 yrs	10 yrs	16 yrs
70 ^{0}C	265 days	2 yrs	3.5 yrs	6 yrs
80 ^{0}C	114 days	270 days	1.5 yrs	2.5 yrs
90 ^{0}C	44 days	106 days	207 days	1 yrs
100 ^{0}C	16 days	41 days	81 days	132 days
110 ^{0}C	9 days	21 days	42 days	68 days
120 ^{0}C	4 days	10 days	20 days	35 days
130 ^{0}C	2 days	5 days	9 days	17 days
140 ^{0}C	20 hrs	32 hrs	4 days	6.5 days

4.3 Development of a rating index

This cable rating index matches the operating temperature of the cable to the remaining plasticizer amount.

Equivalent Temperature for the Time Varying Temperature

In domestic and factory environments all cables are subjected to cyclic temperature variations. So, it is important to calculate equivalent static temperature in order to determine the evaporated plasticizer amount and to rate the cable depending on remaining plasticizer amount.

$$-\frac{dC}{dt} = KC \; ; K = K_{\circ}e^{-\frac{E}{RT}}$$

$$-\frac{dC}{C} = K.dt$$

$$-\int_{C_{\circ}}^{C} \frac{dC}{C} = \int_{0}^{t} K_{\circ}\mathrm{e}^{-\frac{E}{RT}}\, dT$$

$$\text{But } T = T(t)$$

$$\therefore \ln\left(\frac{C}{C_{\circ}}\right) = K_{\circ} \int_{0}^{t} e^{-\frac{E}{RT(t)}}\, dt$$

$$y = \mathrm{e}^{-\frac{E}{RT(t)}}$$

$$\int_{0}^{t} y\, dt = \sum_{i=0}^{t} \frac{2yi(\Delta t)}{2} = \sum_{i=0}^{t} e^{-\frac{E}{RT(ti)}\Delta ti}$$

T(t$_i$): Temperature at time t$_i$

N: Number of hours of the day

$$\sum_{i=0}^{n} K_{\circ}e^{-\frac{E}{RT(ti)}}\, \Delta t = K_{\circ}e^{-\frac{E}{RT}}$$

$$\text{Equivalent Temperature } \boldsymbol{T} = \frac{-\boldsymbol{E}}{\boldsymbol{R}\boldsymbol{ln}\sum_{i=0}^{n}\frac{e^{-\frac{E}{RT(ti)}}}{n}\,\boldsymbol{\Delta t}}$$

4.3.1 Example of a cable performance under time varying temperature

Temperature fluctuates throughout the day. However, it is important to know temperature function in order to know evaporated plasticizer amounts. During the day time it shows maximum temperatures where during the night time temperature values are low.

For the investigation of the evaporated plasticizer amount equivalent temperature for the function must be known. To determine the equivalent temperature real time data was collected for a week and averaged. Then fitting curve for the plotted curve was drawn and temperature function was obtained (Figure 4.13).

The obtained temperature function is

$$T(t) = 303.2325\ 0.84553 - 1.27E{+}00t + 0.46053t^2 - 1.02E{-}01t^3 + 1.62E{-}02t^4 - 0.00151t^5 + 7.63E{-}05t^6 - 1.94E{-}06t^7 + 1.95E{-}08\, t^8$$

Maximum daytime temperature is in the range of 70^0C and it last for four hours.

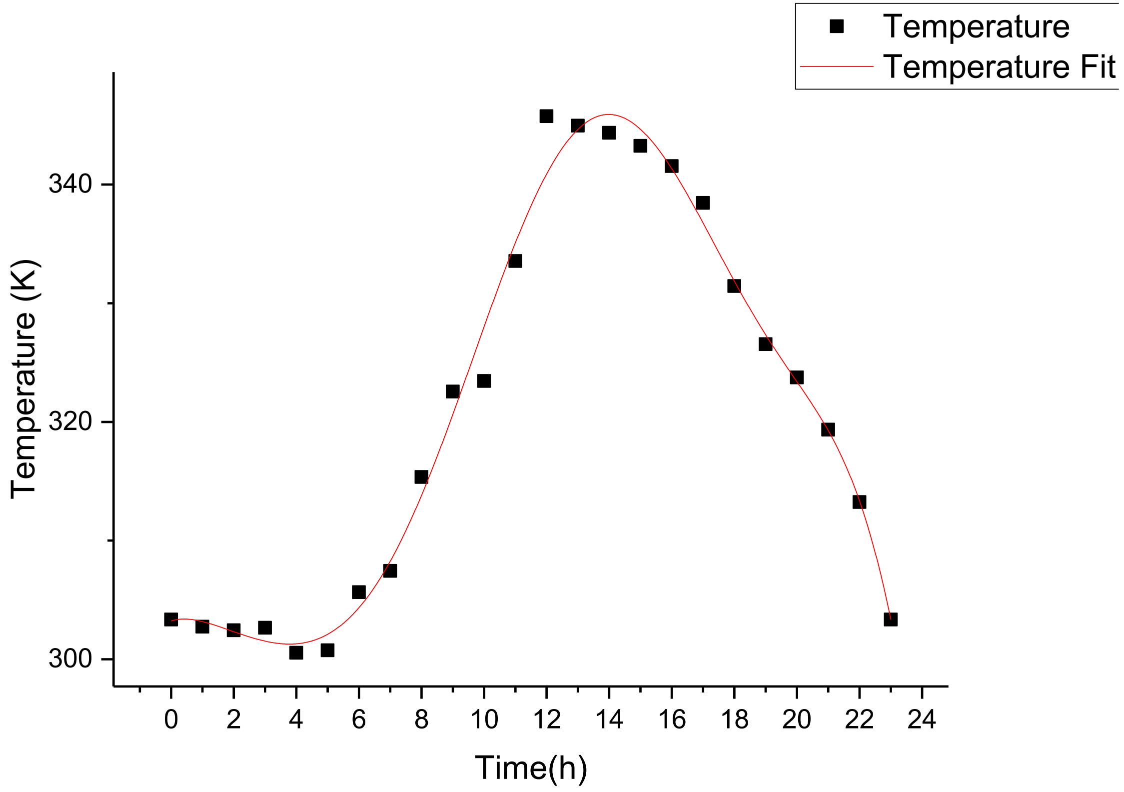

Figure 4.12: Temperature function of a roof throughout the day

$R^2=0.98225$

Equivalent Temperature

$$\boldsymbol{T = \frac{-E}{Rln\sum_{i=0}^{n}\frac{e^{-\frac{E}{RT(ti)}}}{n}\ \Delta t}}$$

$$\boldsymbol{T = \frac{-51000}{8.314ln\sum_{i=0}^{24}\frac{e^{-\frac{51000}{8.314T(ti)}}}{24}\ \Delta t}}$$

$T(t_i)$: = 303.2325 0.84553 -1.27E+00t+ 0.46053t2 -1.02E-01t3+ 1.62E-02t4 - 0.00151t5 + 7.63E-05t6 -1.94E-06t7+ 1.95E-08 t8

The calculated equivalent temperature for the temperature function is 54 ^{0}C. Then by considering that cable is exposed to this temperature throughout the day this evaporated plasticizer amount was calculated.

In order to calculate plasticizer amount, mapping of the plasticizer at 54 ^{0}C must be generated. For that rate constant values were calculate from the Arrhenius equation. The calculated rate constant for 54 ^{0}C is 1.27 x 10^{-7}. Then the amount of plasticizer lost with time is calculated and lost plasticizer amount over time was graphed.

However, this is a relatively moderate value. So, the cables which is under the celling is going to loses it plasticity within average lifetime of a house.

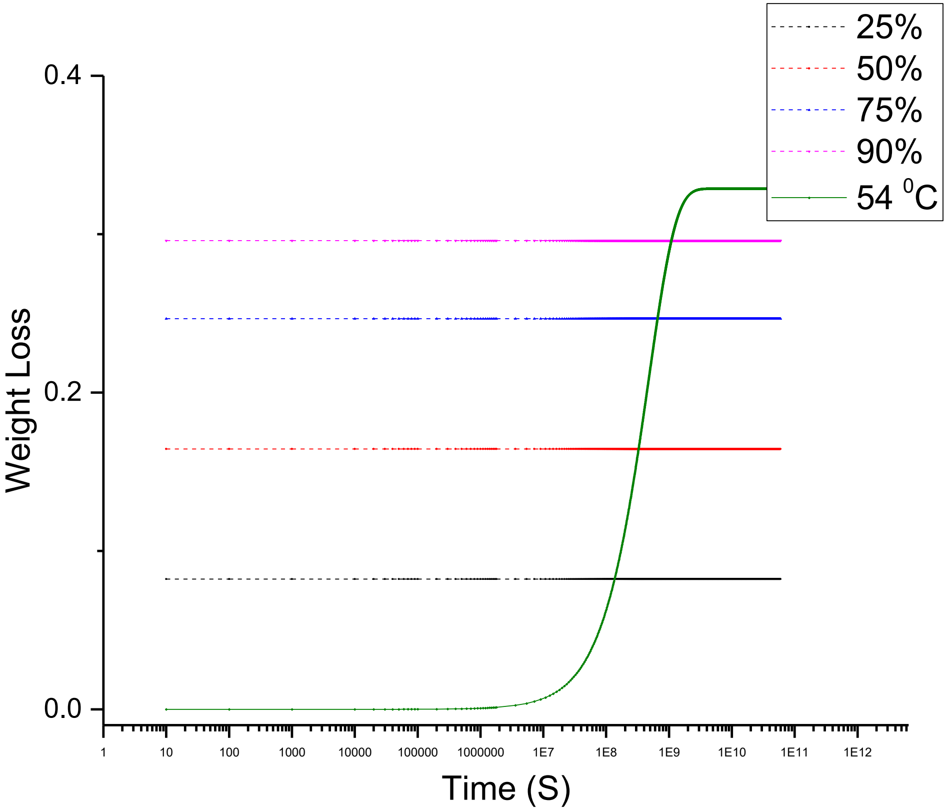

Figure 4.13: Weight loss of cable under a roof

Using the mapping made at 54^0C time required to evaporate 25% , 50%, 75%, 90% plasticizer. It shows that cable will take 32 years to evaporate 90% plasticizers under the temperature conditions.

Table 4.4: Time required to evaporate plasticizer at 54 ^{0}C

Weight %	**Time (years)**
25	4.5 yrs
50	10 yrs
75	21 yrs
90	32 yrs

CHAPTER 5

5. CONCLUSION

The study identified that the rate of the plasticizer evaporation from plasticized PVC cable insulation is a first order reaction and is in agreement with previous studies.

As initial plasticizer amount was needed to determine the evaporation kinetics of plasticizer from cable into surrounding medium thermo gravimetric analysis could be used and the of plasticizer was found using thermogravimetric analysis and it is equal to 32%.

Another finding of this study is increase of the rate constant of plasticizer evaporation process with the increasing temperature. From further analysis of this behavior it could be found that plasticizer evaporation shows Arrhenius behavior. From the Arrhenius behavior, activation energy for plasticizer evaporation from the surface of PVC cable insulation into surrounding was found to be 98 kJ/mol.

Plasticizer evaporation at different temperature profiles could be modeled using kinetic parameters found from the study. As cables are subjected to continuous temperature fluctuations, an attempt was made to find equivalent temperature for cable under a roof throughout the day and the equivalent static temperature rating found is 54^0C.

Thus, this research was successful in generating a rating index for the cable subject to cyclically varying temperature profiles

Recommendation for future works

1. Investigation of evaporation kinetics of the cable due to the combined effect of internal temperature profiles due to resistant heating and environmental temperature.
2. Investigation of the kinetics of evaporation considering the diffusion of plasticizer through the cable.

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