# CHARACTERIZATION OF CALCIUM CARBONATE FILLED NATURAL RUBBER- LOW DENSITY POLYETHYLENE BLENDS PREPARED WITH A TITANATE COUPLING AGENT

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Degree of Master of Philosophy

Department of Chemical & Process Engineering

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## DECLARATION

I certify that work described in this thesis was carried out by me under supervision of Dr. (Mrs.) S.M. Egodage and Dr. (Mrs.) D.G. Edirisinghe and the thesis has not been submitted to any university for any other degree. I also declare that this thesis does not include any material previously submitted for a degree, published, written or oral communicated by another person without acknowledgement to the best of my knowledge except where due references is made in the text.

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We certify that the above statement made by the candidate is true & that this thesis is suitable for submission to the university for the purpose of evaluation

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# Characterization of Calcium Carbonate Filled Natural Rubber-Low Density Polyethylene Blends Prepared with a Titanate Coupling Agent

## ABSTRACT

The aim of this study was to develop reactive blends from natural rubber (NR) and low density polyethylene (LDPE) with acceptable physico-mechanical properties. NR and LDPE blends at different blend ratios were produced in a Brabender Plasticorder by melt mixing at a temperature of 150 $^{o}$C, and rotor speed of 60 rpm. 20 parts per hundred parts of polymer (pphp) calcium carbonate was added as an inorganic filler. Physico-mechanical and chemical properties of the blends and composites were determined according to international standards. Thermal properties were determined using a differential scanning calorimeter. Morphology and structural characteristics were examined by a scanning electron microscope and fourier transform infrared analyzer, respectively. 50/50 NR/LDPE blends were prepared using three vulcanizing systems: sulphur, peroxide and mixture of sulphur and peroxide. NR/LDPE blend prepared with the mixed vulcanizing system showed the highest physico-mechanical, chemical, and ageing properties with a fine morphology. A series of simple blends was formulated by varying the LDPE loading from 10 to 90 pphp at 20 pphp intervals. The tensile strength, tear strength, and hardness increased with the increase of LDPE loading, while elongation at break decreased. The continuous phase of blends changed from NR to LDPE above 30 pphp LDPE loading. The optimum tensile and ageing properties were obtained for the composite prepared with 20 pphp calcium carbonate with or without titanate coupling agent (titanate CA) at 30 pphp LDPE loading. Further, 70/30 NR/LDPE composite prepared with 0.7 pphp titanate CA presented the highest physico-mechanical, chemical and ageing properties. Furthermore, the performance of the 70/30 NR/LDPE blends produced with 0.3 pphp peroxide was greater than that of the composites prepared without the peroxide and with a high amount of peroxide. Nevertheless, tensile properties, stress and strain of the 70/30 NR/LDPE composite improved with partial replacement of LDPE with recycled LDPE (rLDPE). The composite with 20 pphp rLDPE indicated the best improvement in all physico-mechanical properties.

**Keywords:** NR/LDPE blend, titanate coupling agent, peroxide, recycled LDPE, calcium carbonate

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# TABLE OF CONTENTS

**1. INTRODUCTION**

**2. LITERATURE REVIEW**

**3. MATERIALS AND METHODOLOGY**

**4. RESULTS AND DISCUSSION**

**5. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK**

**LIST OF FIGURES**

## LIST OF TABLES

# LIST OF ABBREVIATIONS

| **Abbreviation** | **Description** |
|---|---|
| A/O | Antioxidant |
| ASTM | American Society for Testing and Materials |
| BKF | (2, 2'-methylene bis (4-methyl-6-tert butyl phenol)) |
| BR | Polybutadiene rubbber |
| CA | Coupling agent |
| $CaCO_3$ | Calcium carbonate |
| CR | Polychloroprene rubber |
| CV | Conventional vulcanization |
| DCP | Dicumyl peroxide |
| DV | Dynamic vulcanization |
| DVs | Dynamic vulcanizates |
| EB | Electron beam |
| ENR | Epoxidized natural rubber |
| EPDM | Ethylene- propylene diene monomer |
| EPDM-*g*-MA | Ethylene- propylene- diene monomer-graft-maleic anhydride |
| EPR | Ethylene-propylene rubber |
| EV | Efficient vulcanization |
| EVA | Ethylene vinyl acetate copolymer |
| FTIR | Fourier transform infrared |
| GTR | Ground tire rubber |
| HDPE | High density polyethylene |
| HNBR | Hydrogenated nitrile butadiene rubber |
| IRHD | International rubber hardness degree |
| ISO | International standards organization |
| LDPE | Low density polyethylene |
| LLDPE | Linear low density polyethylene |
| MAH | Maleic anhydride |
| MDPE | Medium-density polyethylene |
| MW | Molecule weight |
| $M_1$ | Masses of before swelling |
| $M_2$ | Masses of after swelling |

|  |  |
|---|---|
| $M_i$ | Masses of the sample before water absorption |
| $M_f$ | Masses of the sample after water absorption |
| $m_1$ | Initial weight of the specimen |
| $m_2$ | Weight of the oven dried gel |
| NBR | Nitrile rubber |
| NR | Natural rubber |
| OENR | Oil extended natural rubber |
| PA | Phthalic anhydride |
| PE | Polyethylene |
| PFMs | polyfunctional monomers |
| PhHRJ-PE | Phenolic modified polyethylene |
| PP | Polypropylene |
| PS | Polystyrene |
| PVC | Polyvinylchloride |
| RH | Rice husk |
| rPE | Recycled polyethylene |
| RSS | Ribbed smoked sheets |
| S | Sulphur |
| SEV | Semi-efficient vulcanization |
| TBBS | N-tertbutyl1-2-benzothiazole sulfonamide |
| TEOs | Thermoplastic polyolefins |
| $T_g$ | Glass transition temperature |
| TPE | Thermoplastic elastomer |
| TPE-A | Thermoplastic polyamide elastomer |
| TPE-E | Thermoplastic polyester elastomer |
| TPE-O | Thermoplastic polyolefin |
| TPE-V | Thermoplastic vulcanizate |
| TPNR | Thermoplastic natural rubber |
| TPR | Thermoplastic rubber |
| wLDPE | Waste low density polyethylene |
| ZnO | Zinc oxide |
| $\Delta G\mathrm{m}$ | Gibbs free energy |
| $\Delta \mathrm{Hm}$ | Enthalpy |

## LIST OF SYMBOLS

| **Symbol** | **Description** |
|---|---|
| $\Delta G$ | Gibb’s energy |
| $\Delta H$ | Enthalpy |
| $\Delta T$ | Entropy |
| °C | Degree Celsius |
| µm | Micrometer |
| Cm | Centimeter |
| DC | Degree of crystallinity |
| $E_b$ | Elongation at break |
| F | Force |
| g | Grams |
| Kg | Kilograms |
| kGy | Kilo Gray |
| m | Meter |
| mA | Miliampere |
| MeV | Megaelectron volt |
| mg | Milligram |
| min | Minutes. |
| mm | Milimeter |
| MPa | Mega pascal |
| MT | Metric Tons |
| nm | Nanometer |
| Nm | Newton meter |
| php | Parts per hundreds plastics |
| phpp | Part per hundred of polymer |
| phr | Parts per hundreds rubber |
| rpm | Revolutions per minute |
| S | Seconds |
| Tg | Glass-transition temperature |
| $T_m$ | Melting point |
| V | Volt |

## LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1. Polymer Blends

A Polymer blend is a simple mixture or a combination of polymers obtained by various processing techniques. According to Sia et al. (2008), two or more polymers could be blended to make a range of random or designed morphologies to develop products that possibly offer desired combinations of features. Further, polymer blending is facilitated by mastication, which not only reduces viscosity but also under proper condition, provides opportunity for reaction (block or graft polymerization) (Parameswaranpillai et al., 2014).

Thermoplastic natural rubber (TPNR) blends are prepared by blending NR and particularly, polypropylene (PP) and polyethylene (PE) in various proportions. As the ratio varies, materials with a wide range of properties are obtained. Rubber-plastic blends are thermoplastic elastomers, while those with lower rubber content are impact–modified plastics (Soares et al., 2008). The soft phase, providing elastic properties, need not be continuous, is sufficiently small and adheres to the matrix under stress. The elastic properties of TPNR are considerably improved if the rubber phase is partially crosslinked during mixing, a process called dynamic vulcanization (Maziad et al., 2009). TPNR is more resistant to heat ageing than NR vulcanisates. Ozone resistance of TPNR is also very high (Maziad et al., 2009). The soft grades of TPNR can replace vulcanized rubber and flexible plastic namely LDPE for applications in footwear, sports goods, seals and mountings and a wide range of moulded and extruded goods. The automotive industry is the largest potential market for the hard grades in applications such as automotive bumpers and body protection strips.

Blends of both PP and PE with NR are immiscible in nature. Therefore, to make a more compatible blend, a block–copolymer compatibilizer can be introduced. Reactive blending is one of the effective ways to create such compatibilization at the interface. Further, a reactive blend would enhance properties through coupling of the two phases.

NR is a popular and vital material used in expensive applications. It is strong as a gum vulcanizate (cured, low hardness rubber, containing no fillers), but materially, soft with low dimensional stability (Raja, 2009). NR involves isoprene molecules that link into loosely twisted chains, and the monomer units along the backbone of the carbon chains are in a *cis* arrangement. This spatial configuration produces the high elastic character of rubber. Unvulcanized NR is soluble in many hydrocarbons, including benzene, toluene, gasoline, and lubricating oils (Potts et al., 2012), but water repellent and resistant to alkali and weak acids. Characteristics of NR such as elasticity, toughness, impermeability, adhesiveness, and electrical resistance makes it a valuable adhesive, a coating composition, a fiber, a molding compound, and an electrical insulator (Siong et al., 2008). Besides, NR has high resistance to tearing when hot and less heat build-up from flexing.

NR is one of the major plantation crops grown in Sri Lanka, which generates foreign exchange. Sri Lanka had around 132,693 ha under rubber in 2016. Sri Lanka has the potential to be one of the world leading rubber product manufacturing countries due to production of high quality raw materials such as Ribbed Smokes Sheet (RSS) rubber and crepe rubber to the world market and they are mainly used for pharmaceutical products, infant toys and food applications (Tillekeratne et al., 2003).

At present, Sri Lanka is the world's 13th largest producer of natural rubber. Rubber is the 2nd largest plantation crop in the country and it constitutes 8% of agricultural land use in Sri Lanka. Total export earnings from raw rubber and value-added products in 2016 were about Rs.98 billion (Anon, 2016). The growth in rubber smallholder sector, which consists of around 87,996 ha (66%) owned by the smallholders of total rubber extent in the country, largely reflects their quick response to higher natural rubber prices. Productivity of rubber land increased by 10% to 1,566 kg per ha in 2016 (Central Bank report, 2016). The rubber industry generates employment to a vast number of people mainly from rural areas, especially in the estate sector and provides employment to more than 200,000 persons. The BOI approved rubber industry consumes nearly 75% of Sri Lanka’s total domestic NR production. Domestic NR consumption of Sri Lanka has been reported as 111.8 million kilograms in 2016 (Anon, 2016). Nearly 60% of the NR production is used in Sri Lanka for manufacture of value added rubber products (http://www.irrdb.com). Export rubber production of Sri Lanka has been reported as 41.6 million kilogram in 2016 (Anon, 2016).

Linear low–density polyethylene (LLDPE) is a substantially linear polymer (Polyethylene), with many branches, made by copolymerization of ethylene with longer–chain olefins (Feng Luo et al., 2009). LLDPE is structurally different from conventional low–density polyethylene (LDPE) due to the absence of longer–chain branching (Feng Luo et al., 2009). The linearity of LLDPE is a result of various manufacturing processes of LLDPE and LDPE. Usually, LLDPE is produced at lower temperatures and pressures by copolymerization of ethylene, and higher alpha-olefins as butane, hexane, or octane (Yilmaz et al., 2008). The copolymerization process produces LLDPE polymer that has higher tensile strength, and higher impact and puncture resistance than LDPE. It is highly flexible and elongates under stress, and make thinner films with better environmental stress cracking resistance. It also possesses favorable electrical properties. However, LLDPE is difficult to process than LDPE and has a gloss and narrower range for heat sealing. Virtually LLDPE has entered all traditional polyethylene markets and used for plastic bags and sheets, plastic wraps, pouches, toys, covers, lids, pipes, buckets and containers, covering of cables, geomembranes, and primarily flexible tubing (Feng Luo et al., 2009).

A coupling agent forms an interface between an inorganic substrate (such as glass, metal or mineral) and an organic material (such as a polymer, coating or adhesive) to bond or couple, the two dissimilar materials (Stepek and Daoust, 1983). Further, a coupling agent is used in a blend of rubber and plastic and properties depend on the reactivity of the used coupling agent (Feng et al, 2009). Some benefits of coupling agents are better wetting of inorganic substrates, lower viscosities during compounding, smoother catalyst inhibition of thermoset composites, catalyst inhibition of thermoset composites, clearer reinforced plastics etc. (Reuvekamp et al., 2002).

Many researchers have achieved acceptable properties for various rubber / plastic blends by adding coupling agents (Feng et al, 2009). The effectiveness of coupling agents on LDPE/lignin blends was studied (Fung et al., 2009). Their work showed that ethylene-vinyl acetate and maleic anhydride are effective as coupling agents. The effect of titanate coupling agent on LDPE and polypropylene blends were also studied (Yilmaz et al., 2008). Further, a development of mixing conditions for reaction of tri ethoxy silyl propyl tetrasulphide (TESPT) silane coupling agent during rubber compound mixing with silica filler and tire rubber was reported (Reuvekamp et al.,2002).

Most of the silane coupling agents (vinyl trimethoxy silane, vinyl triethoxy silane, bis(3-triethoysilypropyl) tetra sulphide, (3-aminopropyl) triethoxy silane, etc.) have been used in the development of rubber blends. However, use of these coupling agents to produce NR and LDPE blends is not yet reported in detail with calcium carbonate ($CaCO_3$). Therefore, this research was focused on the development of reactive blends from NR and LDPE, modified with organophilic titanate agents.

## 1.2.NR/LDPE Reactive Blends

NR and LDPE simple blends are technically incompatible and thermodynamically immiscible. Hence, compatibilizer or coupling agent is used to blend immiscible materials during extrusion to achieve bonding between two dissimilar surfaces and develop their properties and improve the properties of the polymer blend and composite (Pracella et al., 2010). Thermoplastic elastomers (TPEs) are a class of polymeric materials that combine properties of elastomers with the ease of processability of thermoplastics. NR/LDPE blend is an example for TPEs, however, the two polymers are known to be incompatible (Nakason et al., 2006). Effects of filler namely dolomite, carbon black, silica and calcium carbonate on the physico-mechanical properties of NR / LLDPE blends have been studied (Ahmad, et al., 2004). NR/LDPE blends prepared with different types of fillers namely dolomite, clay, silica and calcium carbonate and investigated the effect of those fillers. As the new finding, agglomerate filler particle size and polymer- filler interaction are the issues influencing the physico-mechanical properties of NR/LLDPE blends (Ahmad, et al., 2004).

NR/LDPE blends were prepared with different liquid natural rubber (LNR) concentrations and studied. Enhancements in the physico-mechanical properties corresponded with the increase in gel contents of the blends. Additions of LNR in the blends decreased the surface and interfacial tension and improved the interaction between the phases of the blends (Dahlan et al., 2000) and LNR acted as the compatibilizer. NR/LDPE blends have been developed for light weight good quality microcellular soles (Srilathakutty et al., 1999), while NR/PE blends for roofing applications. (Wicramaarachchi et al., 2016).

Two series of NR/LDPE and NR/PS blends were prepared in the past at blend ratios; 100/0, 85/15, 70/30 and 55/45. The 70/30 NR/LDPE blend showed excellent chemical resistance and it was considered as the best blend ratio owing to its excellent tensile properties (Mohammed and Qusay, 2014). Further, the blend of 70/30 NR/LDPE prepared with N-isopropyl-N'-phenyl-p-phenylene (IPPD) indicated good thermal stability due to its good ageing properties (Bhowmick et al., 2002). Furthermore, 70/30 NR/PE blends have been developed as possible replacements for the conventional NR / HSR (high styrene resin) based soles (Srilathakutty et al., 1999). The above results from literature indicate that the NR/LDPE thermoplastic elastomer blend has remarkable properties and hence the same blend ratio was selected for this study.

## 1.3. Aim and Objectives

The scope of this study is to enhance physico-mechanical properties of rubber composites by incorporation of thermoplastics, while maintaining their elastic properties, to make them suitable for dry rubber applications such as flexible flow tiles, automobile components, roofing materials, playground mats, etc.

The aim of this study is to achieve compatibility between phases in $CaCO_3$ filled NR/LDPE composites through an organophilic titanate coupling agent, and a vulcanizing system, and to produce the composites with improved properties

Specific objectives of the study are:

- To find a suitable vulcanizing system for 50/50 NR/LDPE blend
- To design and prepare simple blends (without vulcanization agent) at different blend compositions
- To investigate the effect of titanate on rheological and physico-mechanical properties of the blends
- To study the loading of coupling agent/s on blend ratio
- To compare properties of NR/LDPE blends with those of NR/ recycled polyethylene (rPE) blends
- To study cost competitiveness of NR/rPE blends
- To propose suitable mechanism/s for reactive blending

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Principle of Polymer Blends

Combining polymers in various chemical compositions or structures and processing conditions are effective means of linking performance and economic relations with current materials. The interfacial behavior and equilibrium phase, phase morphology, physical and chemical interactions among constituents, blend ratio, and rheology are the fundamental problems influencing the properties of blends *(*Keskkula et al., 1996). All issues are related to blending compatibility, and an essential system of polymer blending is to incorporate a flexible period in a hard matrix to improve mechanical toughness.

The desired properties of surface morphology in a two phase system is difficult to achieve . As a majority of polymers are technologically incompatible and thermodynamically immiscible, such polymers construct a multi-phase composition that may damage the material performance while processing (Baker et al., 2000). They may be homogeneous or heterogeneous mixtures. As a result, the performance of the polymer blend depends on the type of polymers, the morphology of the blend ratio, and the effects of processing parameters. Further, polymer blend can provide a good combination of properties than that of a single component, which is referred to as a synergistic effect. (Chandra and Mishra, 2003)

Preparation of Polymer blends involves five techniques, i.e., melt blending, latex blending, partial block copolymerization, graft copolymerization, and synthesizing interpenetrating networks. Melt blending is a simple mechanical method to form a homogeneity in the polymer matrix (Brydson, 1995). The degree of miscibility between the components decides the functioning of a blend, and the fully-miscible blend is the most uncomplicated type. Many properties follow some additive relationship in amorphous polymers, and therefore, the miscible blends are comparable with random copolymers (Brydson, 1995).

When the components develop separate phases in blends, their properties are determined by how such phases are organized in-between and the type of the interface between phases. The behavior of blends that are immiscible is similar to composite materials in several ways. The performance of the constituent that develops the continuous phase dominates characteristics such as the softening temperature, young modulus, and permeation (Monte, 2005).

The interface behavior is connected to the thermodynamic interaction among the components. Subsequently, it directs morphology generation in the melt by interface interaction, interfacial tension, and adhesion in the solid state by the interfacial zone thickness and the degree to which chains from the two phases entangle. The blend shows a degree of toughness lower than component at very low thermodynamic affinity, and therefore deliberated as incompatible. Improvement of this property response is often called compatibilization. This important aspect of blend technology is described in the forthcoming part. Successful interaction between phases promotes obtaining additive properties without a compatibilization agent (Callaghan et al., 1993).

Polymer blending allows to reuse the recycled industrial and/or municipal plastic waste. Two extreme situations may occur while blending different polymers: (1) a gross phase separation and (2) a homogeneous mixture at the molecular level. It could be still more complicated due to the possibility of having various transitional situations such as increased separation limited to intermolecular level, the formation of co-continuous morphology, and dephasing into dispersed heterophase morphologies of increasing phase size (Daniel et al., 1994).

### 2.1.1 Classification of polymer blends

Basically, there are three different types of blends depending on the miscibility (Manson, 2012*)*

(i) Completely miscible blends

This type of blends shows one glass transition temperature ($T_g$), which remains between the glass transition temperatures of the blend components. This is closely connected to the blend composition. The complete miscible blends have $\Delta H_m < 0$ due to specific interactions.

(ii) Partially miscible blends

This blend has a fine phase morphology and suitable properties and is a compatible type. The two blend phases are uniform and have their own $T_g$. These $T_g$s deviate from the pure blend polymer component values towards the $T_g$ of the blend component. Here, the interface is wide with an effective interfacial adhesion.

(iii) Fully immiscible blends

This type of blend generates a coarse morphology, sharp interface and poor adhesion between the blend phases. Hence these blends are of no use without compatibilization agent. The blends will exhibit different $T_g$s corresponding to the $T_g$ of the component polymers.

### 2.1.2 Thermodynamics of miscibility

Most of the polymer blends are immiscible at the molecular level as expressed by the laws of thermodynamics. It has been reported that, given sufficient time, the internal disorder of the polymer system will eventually result in phase separation on a macroscopic scale (Gelos et al., 2014). The relative miscibility of polymers controls their phase morphology, which is of crucial importance for the final performance of polymer blend. The miscible behavior of polymer blends are understood in a thermodynamic sense through the Gibbs free energy of mixing ($\Delta G_m$). The free energy of mixing can be explained in terms of enthalpy and entropic contributions as given by Equation 2.1.

$\Delta G_m = \Delta H_m - T\Delta S_m$……………………………………………………………………..2.1

Where, $\Delta G_m$ is the free energy of mixing per unit volume, $\Delta H_m$ and $\Delta S_m$ are enthalpy and entropy of mixing, respectively. $\Delta H_m$ is independent of molecular weight and measures the energy change of intermolecular interactions. The binary mixture $\Delta G_m$ can vary with the composition as presented in Figure 2.1

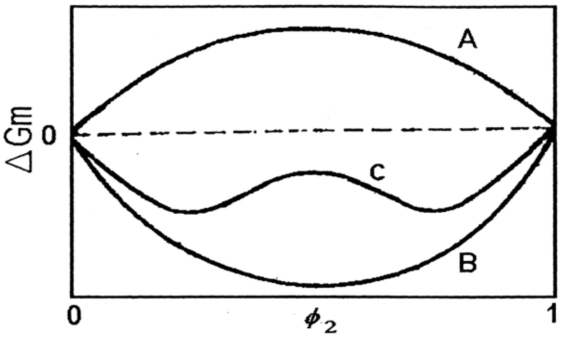


Figure 2.1. Gibbs free energy of mixing for binary mixtures (Gelos et al., 2014)

For a binary blend to be miscible, the following conditions should be satisfied:

(i) The $\Delta G_m$ of a binary mixer should be negative or zero

(ii) The second derivative of free energy function with respect to the volume fraction of major component should be positive.

$\Delta G_m < 0$…………………………………………………………………………2.2

$\frac{\partial^2 \Delta_{\max} G}{\partial \emptyset^2} > 0$ …………………………………………………………………….2.3

For all compositions, these principles happen by curve B. Curve A blends, which are fully immiscible, violate Equation 2.2. Systems pertaining to curve C are partially miscible. Here, one amorphous phase can be developed at compositions at the left and right sides of curve C. Molecular level mixing of the components happens in miscible polymer blends and they are distinguished by a single phase morphology. Immiscible blends do not comply with the settings in Equation 2.2 and Equation 2.3 and demonstrate a two-phase morphology, while the partially miscible blends do not satisfy the second criterion. It will then display a single- or a two-phase morphology. Nonetheless, the miscibility influences the appearance of superior properties.

## 2.2 Types of Polymer Blends

Polymer blends could be categorized according to different forms as the following. Most of the polymer blends are classified according to their surface behavior, some polymer blends are very soft, some are very hard and some are medium-hard.

i. Elastomer-elastomer blends
ii. Thermoplastic–thermoplastic blends
iii. Elastomer –thermoplastic blends

### 2.2.1 Elastomer- elastomer blends

Blending two or more different elastomers to gain desirable properties (technical or economical) has become common in the rubber industry. Also, elastomers or soft grade materials that are more or less incompatible are normally blended together to improve the processability of material. Further, it has been reported that the improvement may consist of lowering the stock viscosity or producing a material that is less prone to fracture or crumbling when subjected to flow (Zeid, 2007). The improved behavior of such blends of different elastomers is attributed in part to the limited degree of dispersion of one rubber component in the other. Furthermore, normal stress function and the related phenomena of die swell and shrinkage can also be altered by blending (Zeid, 2007).

Mohamed, 2011 has reported that CR/NR blends prepared with varying blend ratios and physico-mechanical properties have been evaluated. The blends have been prepared with different doses of gamma rays up to 250 kGy to induce by ionizing radiation. Physico-mechanical performance, namely impact strength, tensile strength, young modulus, modulus at 300% elongation and elongation at break have been studied as a function of irradiation dose concentration and blend composition. Gel content and swelling index have been studied as a function of irradiation dose using toluene as the solvent. NR/CR blend was found to be thermally stable than pure NR compound (Mohamed, 2011).

In addition, Goyanes et al. (2008), vulcanized blends of NR/SBR with sulfur and n-t-butyl-2-benzothiazole by varying the amount of each polymer in the blend. The thermal results have been explained on the basis of the structure formed during the vulcanization of the blends considering the variation of the crosslink density of each phase.

### 2.2.2 Thermoplastic-thermoplastic blends

Improving physico-mechanical properties such as stiffness is usually the reason for the development of novel thermoplastic blends. Other reasons for blending two or more thermoplastics together include (Le et al., 1993):

i. Improving the processability of the polymers
ii. Enhancing the physico-mechanical properties of the blends, making them more desirable than those of the single polymers
iii. Plastic recycling process where blending technology may be the means of driving desirable properties from recycled product

Polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) constitute a huge proportion of the total capacity of plastic currently used for non-load bearing applications. The blends of these plastics organize one of the most rapidly evolving areas of engineering plastic for improving mechanical properties such as impact strength as it is usually the main reason for the development of the plastic-plastic blends (Ghosh et al., 1998).

Banghua et al. (1996), developed morphological behavior of PVC/ high-density polyethylene (HDPE) blends by using compatibilizers such as acrylonitrile butadiene rubber (NBR) and hydrogenated acrylonitrile butadiene rubber (HNBR). SEM analysis indicated that NBR and HNBR enhanced the adhesion and reduced the phase separation between PVC and HDPE. Additionally, morphological behavior of blends or composites were affected by different factors (i) type of compatiblizing agent (ii) amount of compatibilizing agent (iii) blend ratios of the polymers (iv) concentration of compatibilizing agent.

### 2.2.3 Thermoplastic-elastomer blends

Elastomer-thermoplastic blends consist of two polymeric materials having elastomeric behavior at room temperature and thermoplastic behavior at processing temperature (Montoya et al., 2004). If the elastomer is the major phase and the plastic is the minor phase, this blend will have the properties of reinforced elastomer which will make a soft blend. If plastic is the major phase, the obtained blend will be a hard plastic blend. They are prepared by mixing a thermoplastic and an elastomer under high shearing action. Elastomers such as EPDM (ethylene propylene diene monomer), NR, NBR, SBR etc. and plastics such as PP, PE, nylon, etc. are usually used as blend components (Petrovic et al., 1996).

Further, the soft grades of blends can replace vulcanized rubber and flexible plastic for applications in footwear, sports goods, seals and mountings and a wide range of molded and extruded goods. Furthermore, NR/LDPE blends have been developed for light weight good quality microcellular soles (Srilathakutty et al., 1999), where as hard grades of NR/LDPE or high density polyethylene blends for roofing applications. (Wickramaarachchi et al., 2016). The elastomer-thermoplastic blends weight ratio diverges in a broad array to modify many characteristics, i.e., hardness, tensile strength, modulus, elongation at break, compression set, brittleness temperature, and oil resistance, etc.

#### 2.2.3.1 Thermoplastic elastomer (TPE)

TPE is a different category of material that combines the characteristics of vulcanized rubbers and thermoplastic materials. Further, it is known that TPEs can be produced from polymer blends consisting of unvulcanized rubber and plastic polymers such as polyolefins namely PE, PP, etc. (Kim et al., 1995). TPEs exhibit rubbery properties while maintaining the thermoplasticity of the matrix. They generate the properties of both plastics and rubbers. The unique properties of both materials exist because TPE materials are created only by the physical mixing of plastic and elastomer and no covalent or chemical bonding exists between the two (Kim et al., 1995). This behavior has created a new field of polymer science. Thermoplastic elastomers have become an important part of the polymer industry. They are used in different applications such as adhesives, medical devices, footwear, automobile parts household goods, etc.

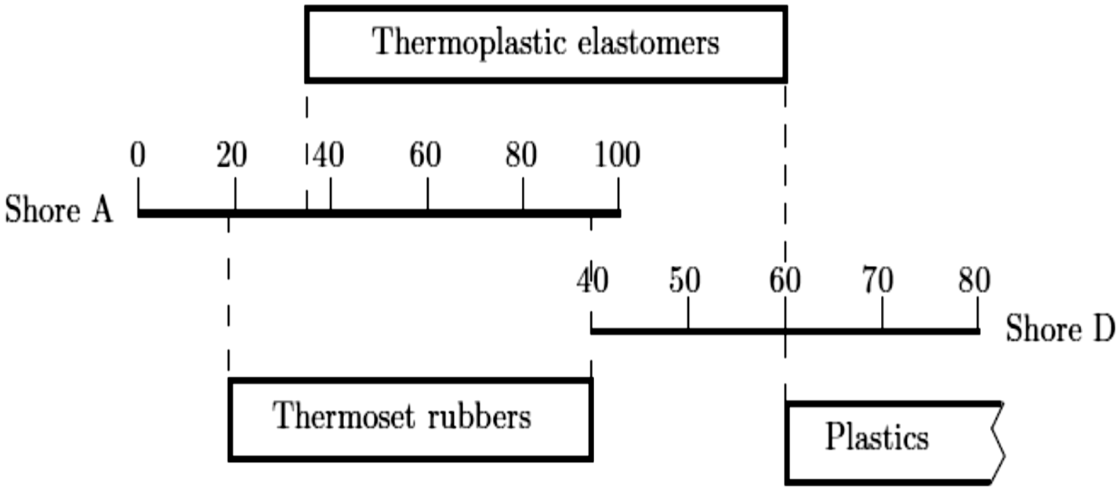
“Thermoplastic natural rubber” (TPNR), which is a TPE having a base of NR and thermoplastic blend, is a category of materials made by blending NR and thermoplastics. TPNR blends have two markedly different product classes as ‘simple blend’ which is known as thermoplastic elastomeric olefins (TEOs) or thermoplastic polyolefins (TPOs), and thermoplastic vulcanizates (TPVs) or dynamic vulcanizates (DVs). NR is considered to be a good component for blending with the plastic due to it has excellent elastic, flexible and impact resistance properties.

Zeid et al. (2008) investigated the properties of TPE, which are physical, thermal and physico-mechanical properties as a function of irradiation dose and blend composition in composites of EPDM and HDPE and ground tire rubber (GTR). NR/LDPE blends were used to fabricate small electrical wire insulators by creating radiation cross-linking among NR/LDPE by utilizing phthalic anhydride (PA) as a compatibilizer (Upathum et al., 2007). Physical properties of the 50/50 NR/LDPE blend were prepared by varying the loading of starch and properties were evaluated (Carvalho et al., 2003). The composites were prepared in an intensive batch mixer at 150 °C, by varying the starch content from 2.5 to 20%.

Further, blends were prepared with oil extended natural rubber (OENR) and HDPE with different percentage of oil extended NR and HDPE varying from 0 to 100 at 10% intervals by melt mixing at 160 °C (Pechurai et al., 2008). Properties of former composite were investigated in terms of rheological, morphological, and physical features, of composites using compatibilizing agent. Phenolic-modified polyethylene (PhHRJ-PE) was used as a compatibilizing agent and a constant amount of PhHRJ-PE was used to improve the surface adhesion and physical performance of OENR/HDPE.

Furthermore, Koshy et al. (1993) found an improvement of impact resistance at low temperature and flex cracking resistance of NR after blending it with ethylene-vinyl acetate (EVA), as well as an increase of melt processing and an enhancement of aging properties. Hence, EVA was used as an anti-degradation agent.

TPEs take an intermediate position between rubbers which are soft, flexible and with elastic characteristics, and thermoplastics which are hard, rigid; in fact, they correspond both domains



(O'Connor et al., 1981). The positions of TPEs, thermoset rubber and plastics in terms of Shore A and D hardness are given in Figure 2.2.

Figure 2.2. Shore A and D hardness scales for thermoset rubbers, plastics, and thermoplastic elastomers (Rader et al., 2004).

Classification of TPEs

TPEs must have three necessary characteristics.

i. The ability to be stretched to reasonable elongations and, after releasing of the stretch, to return to its original shape
ii. The processability as a melt at prominent temperature
iii. The absence of significant creep (Grady et al., 1994)

The classification of the TPEs of commercial importance is given in Figure 2.3. Also, the structure of three main classes of TPE systems is shown in Figure 2.4

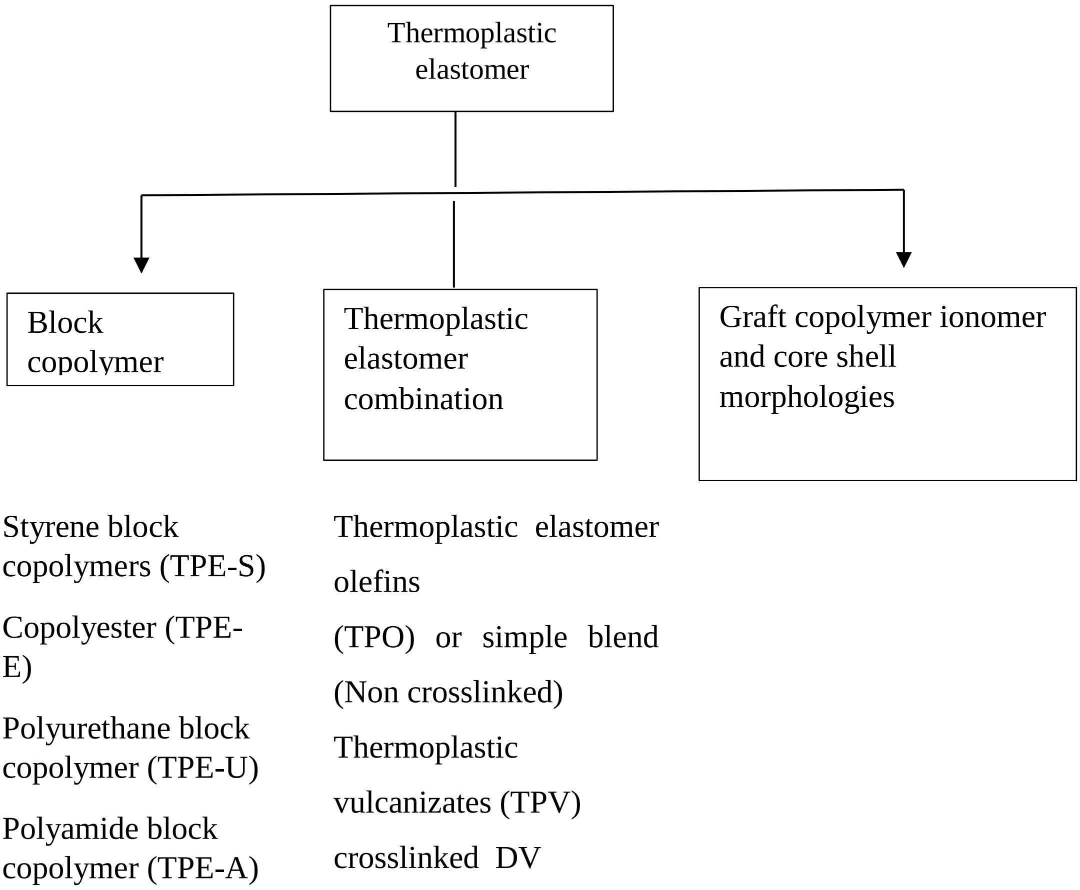
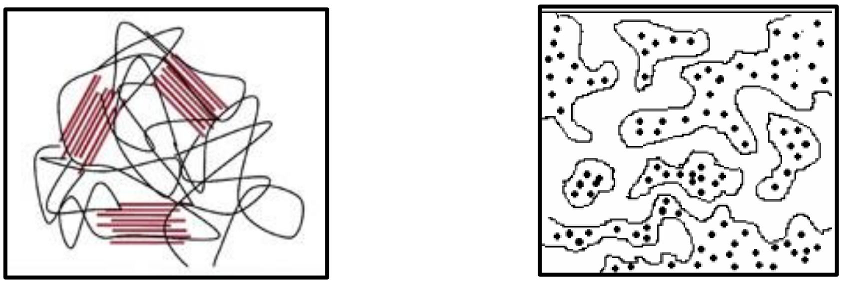


Figure 2.3 Classification of TPEs.



(a) (b)

Figure 2.4 TPE structures: (a) segmented block copolymer (b) hard polymer/elastomer blends (Holden, 2000)

Segmented block copolymers (Figure 2.4 a) generally contain soft elastomeric segments and crystallizable or hard segments. It was reported that, due to incompatibility between the soft and the hard segments, phase separation occurs (Ibrahim et al., 1998). The soft phase provides the material with elastomeric behavior, while the crystallized hard segments serve as physical crosslinks, providing the shape stability and reinforcement of the soft phase (Naderi et al., 1999).

The blends containing hard and soft polymers (Figure 2.4b) are produced by mixing the hard polymer such as plastic and a soft or flexible polymer such as rubber together at a temperature higher than the melting temperature of plastic (Holden, 2000). TPEs based materials are among the most interested materials and probably the fastest growing sector in TPE commercial market (Ibrahim et al., 1998) due to the properties, simple processing and practical productivity, recyclability, and cost effectiveness. TPOs are used at lower temperatures without exposition to high mechanical stress. Further, the TPVs are widely used in the automotive industry and outdoor applications namely ground mat, roofing sheet with high application temperature (wickramaarachchi et al., 2016).

#### 2.2.3.2 Thermoplastic vulcanizates (TPVs)

One method of making a TPE material named TPV was developed by dynamically vulcanizing during the blending process. The dynamically vulcanized rubber phase provided the material which has good physico-mechanical strength, ageing performance and recovery properties (Anandhan et al., 2003). The improvements of various properties of TPVs are:

i. Greater melt strength
ii. Improved physico-mechanical properties
iii. Improved fatigue resistance
iv. Improved high temperature utility
v. Greater stability of phase morphology in the melt
vi. More reliable thermoplastic fabricability (Abdou-Sabet et al., 1996).

*Dynamic vulcanization (DV)*

According to Figure 2.5, the morphology of the system gets more stable due to the DV process. This process gives a consistent and finer distribution of rubber particles to the thermoplastic matrix (Antunes et al., 2012). Some outstanding features of TPVs are, its ability to melt-process as thermoplastic and exceptional elastic recovery after mechanical deformation. It is possible to co-inject or co-extrude TPVs with a thermoplastic to produce complex articles developed from solid and hard components.

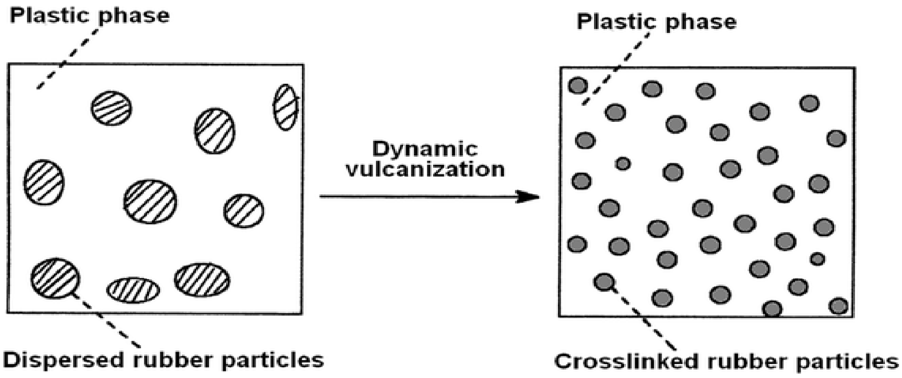


Figure 2.5. Phase morphologies of TPE blends before and after DV (Antunes et al., 2012).

The overall physio-mechanical performance of the TPEs is enhanced upon DV. DV is used to make 'semi-rigid' rubber-plastic compositions containing minor proportions of vulcanized rubber. TPV technology is based on the crosslinking of a rubber (with sulphur, peroxide or both) during its intimate melt blending with a thermoplastic to form a discontinuous micro gel of vulcanized rubber, suspended in a continuous matrix of a thermoplastic (Naskar et al., 2003). Wang et al., 2003 has reported new cross-linking agents for dynamic vulcanization of PP/EPDM system, which does not cause degradation of the PP phase. Further, it was reported that, TPVs contained fully vulcanized rubbers in plastic phase according to former blend performance (Coran et al., 1994).

*Morphological development of dynamic vulcanizates*

Chung et al., 2001 and Goharpey et al., 2001 reported that, construction of cross-links into the polymeric network increases the viscosity due to increasing crosslinking density of the elastomer phase, deviations the interfacial performance, deviations the surface tension, the viscosity and blend ratio of polymer blend and thus significantly affects the morphology improvement of rubber and thermoplastic blend through TPVs. All through this DV procedure, the crosslinked elastomer is changed into a dispersed phase and the thermoplastic minor phase turns into the matrix. This morphology change is called "phase reversion" where two phases individually trade their action or capacity. In this phase conversion stage the objective is to identify and govern the affecting parameters namely processing temperature, blending rate, etc.

Furthermore, the viscosity mismatch between the elastomer and plastic phases occurs and elongation flow is dominant in the flow regime. Hence, the dynamic vulcanizing elastomer phase tends to break up into smaller rubber particles dispersed in the thermoplastic matrix (Figure 2.5) under shear stress and morphology transforms as shown in Figure 2.6. Radusch. (2006) explained that, initially co-continuous phase could be seen of simple blend vulcanization system. Thereafter, it was regularly, modified for dispersion of vulcanized rubber particles in the plastic matrix. The formation of the performance of polymer matrix-particle morphology is essentially influenced by the kinetics of vulcanization reaction, resulting in a difference in crosslink density and crosslink formation of the elastic phase. If the crosslink density of the elastomeric phase is very low, it undergoes large deformation under low level of stress. In contrast, if the crosslink density is high, the rubber phase deforms under high shear stress (Radusch, 2006).

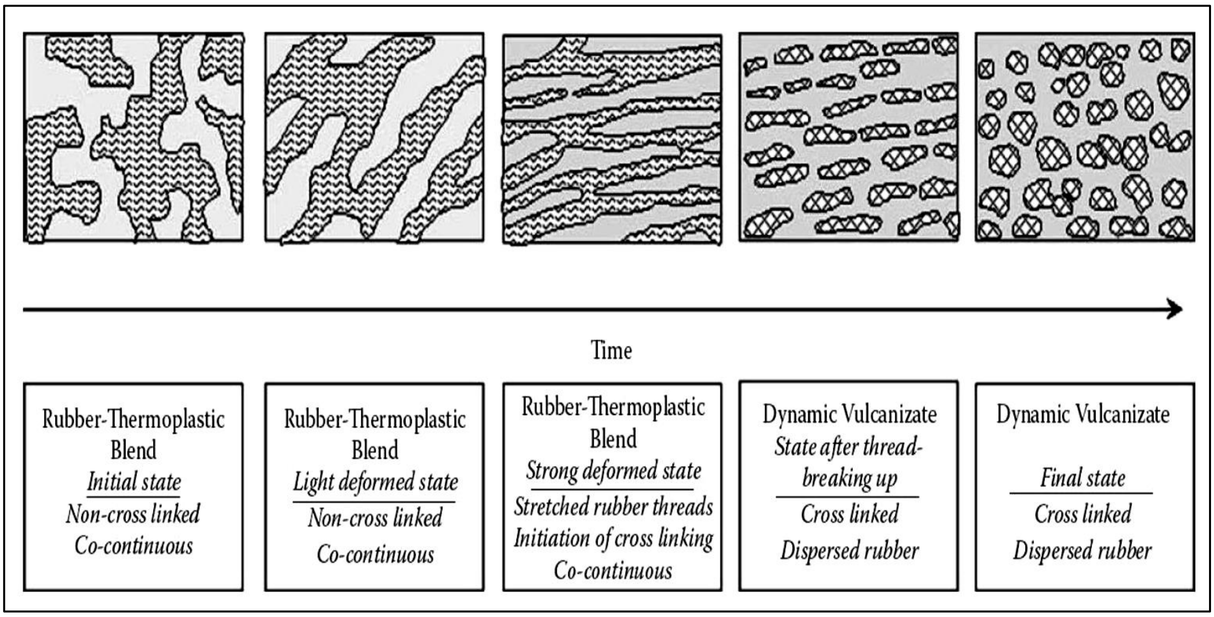


Figure 2.6. Schematic diagram of phase morphology transformation during the DV process. (Radusch, 2006)

## 2.3 Polymer Composites

Polymer composites are made by blending with different types of polymers and different types of filler and they could achieve remarkable physico-mechanical properties more than that of individual constituent materials. They might have special advantages over single phase materials such as high tensile strength, high thermal stability, high stiffness, long fatigue life, high corrosion, etc. Besides the above, another advantage is reduction in life cycle cost (Daniel et al., 1994).

Alger (1989), has classified polymer composites into three main categories to get a clear picture of the various classes of polymer composites. These classes of polymer composites are:

i. polymer – polymer combinations
ii. Polymer gas combinations
iii. Polymer –filler combinations
    - Polymer – fiber combinations
    - Polymer – particulate combinations

Further, composites are mixtures of materials differing in components such as type of polymer, fillers, other ingredients, etc., where individual ingredients preserve their features. These individual ingredients interact to provide the required mechanical strength or toughness to the composite phase (Shaw et al., 2010). The composite material has two or more phases as matrix and dispersed phases. Their characteristics considerably vary from the features of any of the constituents. The matrix phase is the 'primary phase' with a continuous character, and the matrix is typically more elastic and a soft phase. The matrix phase embraces and shares a load with the secondary phase, i.e., dispersed phase or reinforcing phase. The dispersed phase has a discontinuous arrangement and remains embedded in the matrix. The dispersed phase is stronger than the primary phase, and hence, it occasionally defines the reinforcing phase (Mayer et al., 1998). In the previous study, structural applications of composites were characterized as follows:

i. They generally consist of two or more physically distinct and mechanically separable materials.
ii. They are made by well mixing the separate materials in such a way as to achieve uniform dispersion of the constituents.
iii. They have remarkable mechanical properties and in some cases uniquely different from the properties of their components (Mayer et al., 1998).

Polymers are the popular matrix material for the development of composites. The polymer matrix composites have a higher potential for industries because they can be easily fabricated into any large complex shape (Akovali et al., 2001). Composites consist of thermoplastic or elastic polymer matrices, and the elastic and thermoplastic matrix composites are superior materials than the typical metals and ceramic substances. Composite selection is performed based on chemical, electrical, thermal, flammability, environmental, cost, performance and manufacturing requirements (Mazumdar, 2002). Further, polymer composites are named after their type of reinforced filler such as carbon black composites, hybrid fiber composites, and glass fiber composite material. Physico-mechanical properties of the reinforced fibers are much higher in comparison to the normal polymer material, which makes polymer composites a better load bearing component.

### 2.3.1. Properties of polymer composites

The characteristics of various polymers decides their application. The main advantages of polymer composites are easy processability, low cost, good chemical resistance, better ageing performance and low specific gravity. Further, Huang et al. (2006) have reported that polymer composites exhibit less surface tension, low modulus, and low operating temperatures. Accordingly, thermoplastic polymers, thermosetting polymers, elastomers, and their blends are the polymer variations for composites.

#### 2.3.1.1. Thermoplastic polymer composites

Thermoplastics have branched or linear chain molecules with firm intra-molecular bonds. These bonds are structurally semi crystalline or amorphous and get restructured with the application of heat and pressure (Sriramula et al., 2009). Different thermoplastic polymer composites are prepared for different industrial applications with polyethylene, nylon, polypropylene, polystyrene, etc. Further, thermoplastic composites prepared with thermoplastic polymer with different fillers namely $CaCO_3$, carbon black, dolomite, etc. have essential advantages as follows,

i. Highly recyclable
ii. Aesthetically superior finishes
iii. Hard crystalline
iv. High-impact resistance
v. Reshaping capabilities
vi. Chemical resistance

#### 2.3.1.2. Thermosetting polymer composites

The structure of thermosets is a cross-link or a network, facilitated by covalent bonds with all molecules. After solidified by cross-linking, they will not reshape. They may decompose on heating but do not become softer. Some typical examples are polyesters, epoxies, phenolics, silicone, and polyimides. Thermoset plastics significantly improve the material's mechanical properties, providing enhanced chemical resistance, and ageing resistance. Thermoset plastics are resistant to deformation and possess some of the high impact resistant properties of plastics; hence, they are utilized in sealed products. The thermoset plastic polymers are the epoxies, phenolics, silicones, and polyesters (Sriramula et al., 2009). Thermosetting plastics are used for different industrial applications and hence, they have essential advantages as follows.

i. More resistant to high temperatures
ii. High levels of dimensional stability
iii. Cost-effective
iv. Highly flexible design
v. Thick to thin wall capabilities

## 2.4 Natural Rubber (NR)

Natural rubber (NR) from the isoprene monomer (2-methyl-1, 3-butadiene) is an elastomeric type polymer, which can revert to its original shape upon stretching or deforming. Natural rubber is also a polymer obtained from the rubber tree as a milky white fluid form known as 'latex.' The latex is obtained by tapping (making a cut in the tree bark), and coagulated by an acid treatment, washed, and dried.

NR is a significant material commonly used in expensive applications. Despite its high strength as a gum vulcanizate (cured, low hardness rubber, containing no fillers), materially, NR is soft with low dimensional stability. NR is made of isoprene molecules connected with loosely twisted chains. The monomer units along the backbone of the carbon chains are in a cis arrangement and it is this spatial configuration that gives rubber its highly elastic character. Further, while at room temperature NR exhibits considerable strength, appreciable elasticity and resilience it is sensitive to temperature variation, thus sensitive to hot and cold conditions. It is liable to oxidize, to sticky products. These factors impose restrictions on the usefulness of the material. It has been recognized that the chemical modification can change the physical properties of natural rubber and these extend its scope of application. (Cohan et al., 1948)

To enhance the physical properties, alter vulcanization, prevent long-term deterioration, and increase processability, the typical rubber compound formulations are incorporated with ten or more ingredients, in which the amounts are given as parts per (a total of) hundred parts of rubber.

NR is cheaper and has high resilience (elasticity) and strong tensile and tear properties, which make them a suitable material for shock and vibration isolators. Massive quantities of natural rubber are used in rubber manufacturing to produce quality rubber end products.

Compounding rubber with additives is the best procedure that fulfills the given application with respect to properties, cost, and the process involved. This formulation of rubber leads to end-products such as tires, belting, engine, and other mechanical goods (Sethuraj and Ninan, 2012). During rubber compounding, when rubber or elastomeric materials are subjected to the vulcanization process, they react with sulphur and accelerators at a higher temperature. Hence, vulcanization is a critical process that forms a cross-linked molecular network and converts rubber from plastic temperature-sensitive materials to technologically-useful elastic materials (Sethuraj and Ninan, 2012; Mark, 1996; Roberts, 1988). Furthermore, rubber compounding via combining with additives, fillers, and a small volume of oils helps to protect rubber compounds from ozone, heat, and oxygen, increase modulus and strength and reduce the processing cost (Sethuraj and Ninan, 2012).

The blends have been prepared with NR and different types of synthetic rubbers, compatible with NR blends are decided according to physico-mechanical performance of blends (Goldthorpe, 2015). Excellent reports exist in the literature on the diffusion and sorption processes in elastomer and their various blends. Thus, transport studies have been conducted on natural rubber/epoxidized natural rubber (Koshy et al., 1993), NR/PS (Johnson et al., 1999), nitrile rubber/polypropylene (Asaletha et al., 1998), and ethylene-propylene rubber/nylon blends (George et al., 2000).

### 2.4.1 Vulcanization

During vulcanization, the rubber molecules are converted into a network by crosslink formation, using vulcanizing agents. Usually, Sulphur or peroxide or both (mixer) act as vulcanizing agents, and occasionally, other special type vulcanizing agents or high energy radiation may be used. During the vulcanization process, the gum-elastic raw material converts into the rubber-elastic end product. Hence, the vulcanization determines the final characteristics such as hardness and elasticity.

### 2.4.2 Vulcanization system

Vulcanization systems, which are known as chemical crosslinking systems or cure systems, are very important in the rubber industry. Vulcanization of the rubber phase during mixing or dynamic vulcanization has been used to improve physical properties of thermoplastic elastomers (Coran and Patel, 1983; Fischer, 1973; Stricharzuk, 1977; Goettler et al., 1982). The vulcanizates crosslink the rubber molecule and enhance the mechanical strength and elasticity of rubber. The vulcanization system can be classified into:

i. Sulfur system
ii. Sulfur donor system
iii. Non-sulfur vulcanization systems

Before combining, rubber and thermoplastic are pre-mixed with the curative and other additives in dynamic cross-linking. The rubber cross-links typically produce a semi-interpenetrating polymer type network that could be molded or extruded.

#### 2.4.2.1 Sulphur vulcanization

Sulphur has been used as a main vulcanizing agent. In addition, accelerators are used to increase sulfur reactivity and reduce the vulcanization time. Senzothiazoles, amines, sulfonamides and dithiocarbamates are used as the accelerates for rubber vulcanization. Zinc oxide and stearic acid, are used as the activators. Further, antioxidants are used to minimize thermal and oxidative degradation of the rubber and IPPD, 6IPPD, WSP are used as antioxidants for rubber vulcanization. Figure 2.7 shows the scheme of the crosslinking reaction of rubber molecules by sulphur vulcanization system. Reactions of accelerator and activator (i.e., ZnO) causes opening of cyclic molecular sulphur

i. This complex is self-destroyed, and react with rubber chains leading to a sulphur- bound rubber intermediate
ii. The sulphur-bound rubber intermediate thereafter reacts with other rubber chains and affects their crosslink
iii. The polysulphide links between the rubber chains are consequent

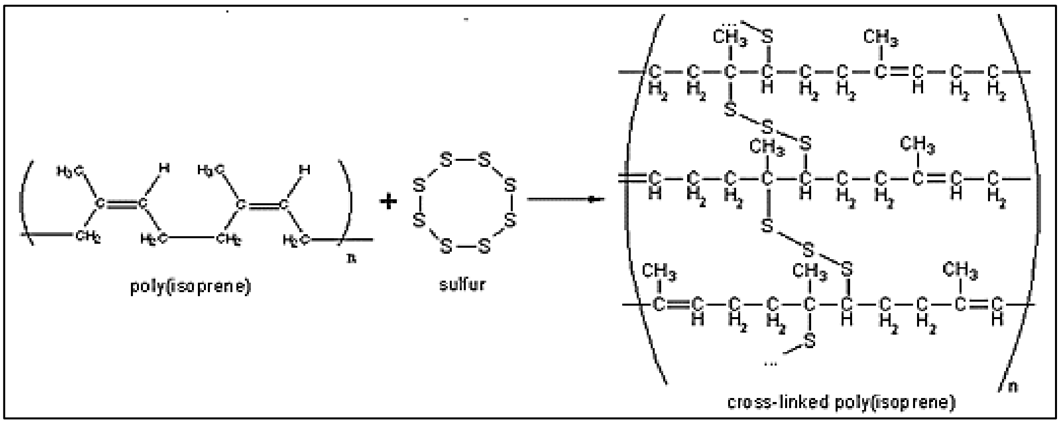


Figure 2.7 Crosslinking of diene rubbers using sulphur system

Sulfur bonds generally exist as mono, di and polysulfide. It has been found that proportion of each type of crosslinking can be altered by varying sulfur to accelerator ratio in the vulcanization system (White, 2001). Vulcanization systems are categorized as follows.

i. Conventional vulcanization system (CV) - sulfur to accelerator ratio is greater than one. The cross links formed are predominantly poly sulfidic type

ii. Efficient vulcanization system (EV) -sulfur to accelerator ratio is less than one, equal in proportion of mono sulfide and polysulfide type

iii. Semi-efficient vulcanization (SEV)- sulphur to accelerator ratio is equal

In a previous study, the HDPE and EPDM compositions were fixed at 50/50 by weight, and the ratio of accelerators to sulfur was varied from 0.4 to 6.34 by weight. As per the outcome, the polymer EPDM/HDPE contained cure agents sulfur in a ratio of cure accelerators/sulfur = 6.34 and 1.85, respectively. This revealed improved physico-mechanical properties (Moldovan et al., 2008). In another study, TPVs based on NR/HDPE blends with various types of blend compatibilizers were prepared by different vulcanization systems namely sulphur, peroxide and mixed. The mixed vulcanization system showed the highest shear stress and tensile strength, whilst the sulphur curing system gave the lowest values, and the peroxide curing system exhibited intermediate values (Nakason et al., 2006).

### 2.4.2.2 Peroxide vulcanization

Peroxides are vulcanizing agents generally used for vulcanization of elastomers that do not contain reactive sites. Some examples of elastomers that are vulcanized by peroxide such as NR, ethylene-propylene rubber (EPR), ethylene-vinyl acetate copolymers (EAM), and silicone rubbers. Elastomers such as polyisoprene and polybutadiene can also be readily crosslinked by peroxides, but the properties of the vulcanizates obtained are found to be lower compared to those of sulphur vulcanizates (Nakason, et al., 2006). In contrast, peroxide vulcanizates coming from diene rubbers show better thermal ageing performance and compression set. Further, lower vulcanization temperature and poorer concentration of peroxides were found to be better reasons, showing a proper equilibrium between the degree of cross-linking of the rubber and degradation of the macromolecular chains by side reactions in relation to the crystallization of NR, which communicates vulcanizates based on NR outstanding properties (Kruželák et al., 2014). Hence, in this study, peroxide with low concentration was used to prepare NR/LDPE blends and composites. The mechanism of crosslinking reaction using peroxides is shown in Figure 2.8. At the initial stage of the vulcanization using peroxides, the organic peroxide is decomposed into two organic radicals that can abstract hydrogen atoms on the rubber chains and then convert them into macroradicals (Kruželák et al., 2014). The macroradicals can react together with the formation of carbon-carbon intermolecular bridges.

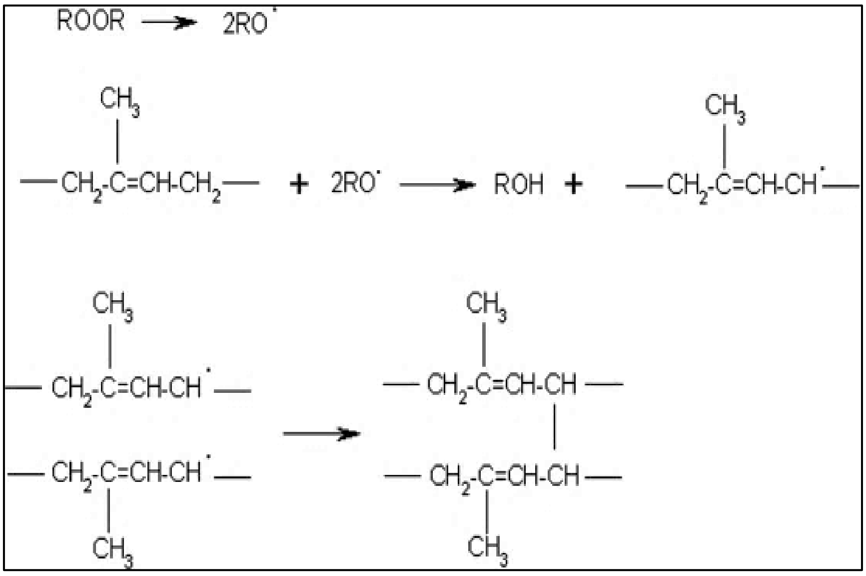


Figure 2.8 Crosslinking of diene rubbers using peroxide systems (Kruželák et al., 2014)

The most common types of curing systems such as sulphur system, peroxide system, and sulphur/peroxide mixed systems, were used for the preparation of TPVs (Sampath et al., 2013). Both NR and LDPE can be cross-linked with peroxides such as dicumyl peroxide (DCP). However, the ability of DCP to form crosslinks in LDPE has been reported as more efficient than that to form crosslinks in NR (Maziad et al., 2009). The 25/75 NR/LDPE blends vulcanized with DCP loading of 2 phpp has shown improved tensile strength and is associated with crosslinking of the LDPE phase (Maziad et al., 2009). Further, these blends did not show any phase separation after boiled xylene extraction. In addition 60/40 NR/LDPE blends were prepared with DCP loading of 0.3 phpp at different temperatures, and the effect of viscosity on properties of the blends were studied (Poolsawat et al., 2011). The 20/80 NR/LDPE blends grafted with grafted maleic anhydride (MAH) and acrylic acid, and with DCP loading of 0.3 phpp revealed that the grafting as a proper route to obtain enhanced properties (Patel et al., 2006). All these NR/LDPE blends showed that DCP is a promising curing agent to use in the blends. However, these blends were prepared at a constant DCP loading, and the effect of DCP loading was not studied. Rice husk (RH) filled NR/LDPE composites in different compositions were also prepared using DCP as the curing agent and MAH as a compatibilizer (Maizad et al., 2009). The 25/75 NR/LDPE blend with DCP loading of 1 phpp indicated expanded Young's modulus and hardness, but decreased impact strength, tensile properties and swelling properties.

#### 2.4.2.3 Radiation vulcanization

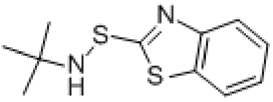
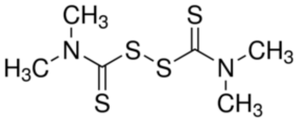
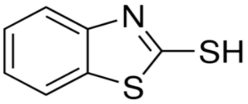
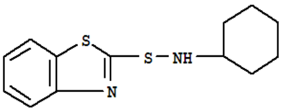
The radiation is a famous technique for the modification of polymer blends. In most, Co-60 radiation is used to initiate the polymerization and cross linking reaction in rubber and plastic. Irradiation causes a rubber or plastic molecule to become ionized and excited. The excited molecules can then break up into two radical chains. The radicals formed, are stabilized by recombination leading to cross linked structure of the molecules. Hemmerich, (2000) reported that**,** rubbers that can be successfully cross linked by radiation are BR, SBR, NR and NBR. Radiation vulcanized articles, particularly based on latex, show high clarity and purity with good surface finish. Ahmed et al., (2000) reported on radiation vulcanization based on NR latex. The combination of sulfur vulcanizing and irradiation –induced crosslinking when applied to solid NR compound can reduce nitrosoamine level in the factory atmosphere. Further, the compound prepared with NR crosslinked by the electron beam , mechanical properties and crosslink density on irradiation dose was determined from a dose range of 50 to 200 kGy. The results showed an increase in physico-mechanical properties and crosslink density due to the introduction of polyfunctional monomers (PFMs) (Manaila et al., 2014).

### 2.4.3 Accelerators

The accelerator is generally an organic chemical and as the name denotes, it speeds up the rate of vulcanization. Accelerating agents increase the rate of the cross linking reaction and lower the sulfur content necessary to achieve the best vulcanizate properties. Further, accelerator also decreases the quantity of sulphur necessary for vulcanization and thereby improve thermal ageing properties of the rubber vulcanizates. Furthermore, accelerators are also classified as primary and secondary accelerator due to balance the curing rate of vulcanization reaction.

Sulfonamide and thiazole act as primary accelerators. They have a proper processing safety, a wide vulcanization plateau, optimum crosslink density, and the desired reversion delay (Amin, 1997). Most rubber based compounds or composites have a dosage of approximately 1.5 phr added primary accelerators. The primary accelerators are activated by using basic accelerators such as aniline, guanidines, thiurams, and dithiocarbamates as secondary accelerators. In above study, secondary accelerators used increased the rate of vulcanization but affected scorch safety. The dosages of the secondary accelerators normally range between 10-40% of the primary accelerator. Table 2.1 illustrates commonly used accelerators for TPE composites (http://www.nocil.com/Downloadfile/DTechnicalNote-Vulcanization-Dec10.pdf).

Table 2.1 Accelerators for TPEs

| Chemical name | Chemical structure | Applications |
|---|---|---|
| N-tert-Butyl-2-benzothiazolesulfenamide (TBBS) |  | NR composites, NR/LDPE blends |
| Tetramethylthiuram disulfide (TMTD) |  | EPDM/HDPE blends |
| 2-Mercaptobenzothiazole (MBT) |  | NR composites |
| N-Cyclohexyl-2-benzothiazolesulfenamide (CBS) |  | EPDM/LLDPE blends |

### 2.4.4 Antioxidants

The degradation of the end product can be initiated by heat, light, impurities such as catalyst residue, or mechanical stress; hence, the application of antioxidants in almost all synthetic and natural rubbers and plastics prevent polymer degradation and increase the durability of the end product. Synthetic rubbers are also particularly susceptible to degradation from ozone and atomhosperic oxygen, and antiozonants are used as well. There is a wide range of rubber and plastic that use antioxidants. The synthetic rubbers analyzed include BR, SBR, polybutadiene and EPDM. The antioxidants are categorized into two types, primary and secondary, depending on the mechanism used to stop the degradation process (Sundaram, K., 1982).

Industrial polymers are issued to degradation due to mechanical, heat, ozone and light stresses (Jorgensen et al., 2008). A main cause of the degradation has been accepted to be an autocatalytic process due to the generation of free radicals following the mechanical action, temperature, or light stress. The free radical oxidation process in a polymer material is known to be in regard of the mechanism showed in Figure 2.9. In terms of mechanism of action antioxidants can be categorized as three major types.

i. Carbon radicals ($R^{\cdot}$) that are generated by the external stress or the interaction of the alkoxy ($RO^{\cdot}$) and hydroxyl ($HO^{\cdot}$) radicals generated in the degradation cycle
ii. Primary antioxidants that trap the peroxy radicals ($ROO^{\cdot}$) generated by the reaction of the carbon radicals with oxygen.
iii. Secondary antioxidants that avoid the formation of $RO^{\cdot}$ and $HO^{\cdot}$ by the decomposition of the hydroperoxide (ROOH) formed when the $ROO^{\cdot}$ abstract a labile hydrogen from the polymer backbone (Sundaram, K., 1982).

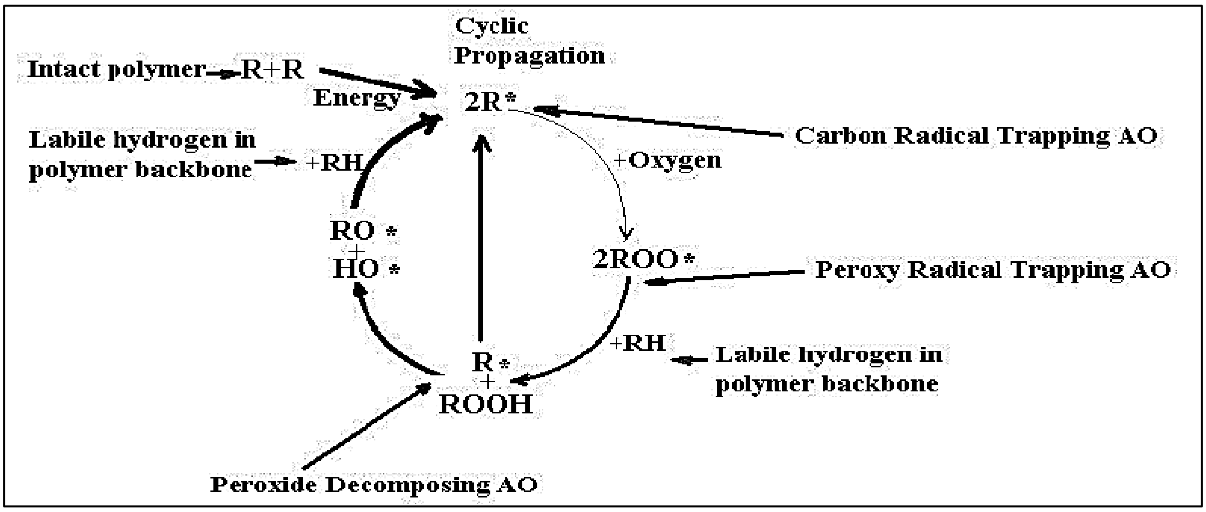


Figure 2.9. The free radical mediated oxidation/degradation process in a polymer system

## 2.5 Polyethylene (PE)

PE is used as the highest volume plastic based polymer in the world (World Plastics Production 1950 – 2015 - ISO). PE which has the simplest basic structure among all over polymers is a follower of polyolefins. Its high ductility, toughness, excellent chemical resistance, excellent electrical insulating properties (Gorter et al., 2012) and ageing resistance, low organic solvent absorption and minimal water absorption, and the ease of processing allows different density grades of PE a good selection for many goods. The limitations of PE are its comparatively low modulus, yield stress, and melting point (105 to 115°C). PE is used to make soft and medium hard containers, plastic bags, film, and pipes, among other things. It is an incredibly versatile polymer with almost limitless variety due to copolymerization potential, a wide density range, a molecular weight (MW) which ranges from very low to very high (approximately 6x$10^6$), and the ability to vary MW distribution (Baker et al., 2000).

Structure of PEs are arranged with carbon and hydrogen atoms, and various grades of PE have wide-ranging thermal, aging, chemical, and mechanical properties. PE is a white and translucent (Gorter et al., 2012) polymer, but available in different grades of PE in term of density that range from 0.91 to 0.97 g/$cm^3$. The density of a grade is governed by the morphology of the backbone long, linear chains with very few side branches can assume a much more three-dimensionally compact, regular, crystalline structure (Baker et al., 2000). According to its density and branching, PE is classified into four major groups: (1) low-density PE (LDPE), (2) linear low-density PE (LLDPE), (30 medium-density PE (MDPE), and (4) high-density PE (HDPE).

Table 2.2. Types of Polyethylene (Gorilovskii et al., 2005)

| Name | Density range (g/$cm^3$) | Degree of branching |
|---|---|---|
| Low density PE (LDPE) | 0.910 – 0.940 | high degree of short and long chain branching |
| Linear low density PE (LLDPE) | 0.915 – 0.925 | significant numbers of short branches |
| Medium density PE | 0.926 – 0.940 | relatively low branching |
| High density PE | » 0.941 | no branching |

Figure 2.10 illustrates the chain configuration variances that manage the degree of crystallinity, which decides final thermo mechanical characters along with MW. The yield strength (or hardness) and the melt temperature increases due to material density, while elongation decreases with increased density caused by the crystallinity of material (Baker et al., 2000).

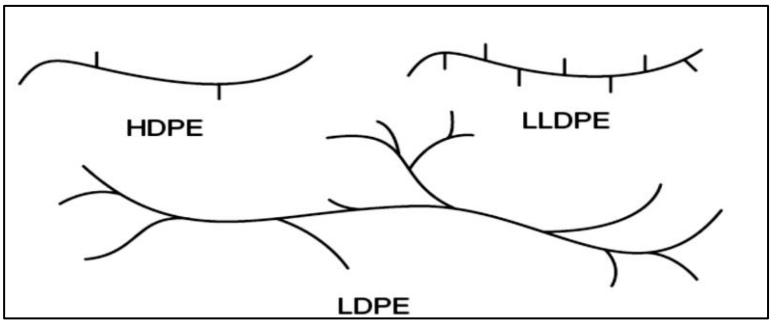


Figure 2.10 Chain configurations of polyethylene (Baker et al., 2000).

Gases and some lower hydrocarbons evolve once PE is exposed to high-energy irradiation, and there is an increase in unsaturation. Most importantly, C-C bonds form via cross-linking of molecules. Crystallization and cross-link point formation intervene with each other, and progressive radiation will ultimately produce an amorphous but cross-linked polymer. Excessive exposure can cause color development, and the presence of air surface may lead to oxidation (Gorilovskii et al., 2005).

### 2.5.1 Low-Density Polyethylene (LDPE)

LDPE is a long-chain thermoplastic polymer with many branches, with a density of 0.915-0.925 g/cm$^3$ , molecular weight up to $4 \times 10^6$ (Rubin, 1990), and a melting range of 105-120 °C (thermal properties of LDPE). The relatively low melting point and the broad melting range facilitate process applications. The glass transition temperature of LDPE lies below the room temperature (~ -120 °C), resulting in soft and elastic nature of polymers.

LDPE merges high impact strength, toughness, and ductility to make it the most appropriate material for packaging films and soft grade applications, where it is vastly applied. In different applications of films such as shrink film, the thin film for automatic packaging, heavy sacking, and multilayer films, LDPE behaves as a seal layer or a water vapor barrier (Baker et al., 2000).. Hence, LDPE was chosen for this research to make flexible material by blending with NR. LDPE is made via free-radical polymerization, with alkyl branch groups of two to eight carbon atom lengths, though four carbons are the frequent branch length. The high reaction pressures induce crystalline regions (Baker et al., 2000). Figure 2.11 presents the reactions to form LDPE.

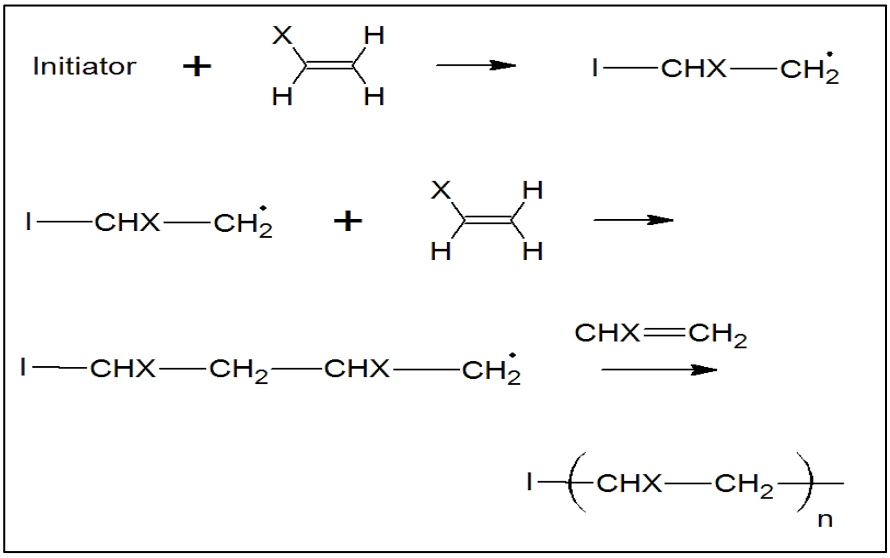


Figure 2.11 Radical polymerization of LDPE (Rubin, 1990)

The 70/30 NR/LDPE blend showed excellent chemical resistance and it was considered as the best blend ratio owing to its excellent tensile properties (Mohammed and Qusay, 2014).

### 2.5.2 Blend with recycled polyethylene (rPE)

It can be seen in the literature, composite prepared with rHDPE/NR/KP by varying KP loadings and physico-mechanical performance were evaluated. As the results, the tensile strength and elongation at break decreased, however, the stabilization torque and the tensile modulus increased. SEM pictures of fracture surface demonstrated that fibrillation because of increase of rHDPE loading (Cao et al., 2012). Generally, we know that rLDPE is used material and also, it is cured material, hence properties do not improve properly and it would be effected to make weak interface (Rector, 2006). This study suggests that rLDPE could also be blended with NR to prepare TPEs. Further, TPEs from waste PE and recycled rubber (RR) were prepared and it was found that tensile performance and impact strength improved with the increase of RR proportion. With Si-69 treatment, tensile and flexural strength were increased (Nando et al., 2010). RR consisted of vulcanized rubber and filler. Furthermore, this study was focused to improve the properties of NR/LDPE composite via partial replacement of LDPE with rLDPE and also to reduce the cost of final composite.

## 2.6 Simple and Reactive Blends of Natural rubber and Low-Density Polyethylene

The reactive blends prepared with the compatibilizer showed improved physical properties compared to simple blends, prepared without the compatibilizer (Gajanayake et al., 2012). Gajanayake et al. (2012) have reported that NR/LLDPE blend prepared without compatibilizer, showed poor solvent resistance with the increase of NR loding. Further, the microscopic image of a simple NR/LLDPE blend, at a particular blend composition, illustrated relatively high agglomerates of LLDPE phase and voids at the interface. Reactive NR/LLDPE blend at a similar composition showed small LLDPE agglomerates uniformly distributed in the NR phase. Therefore, Some properties such as the rheological, interfacial surface and thermodynamic are needed to develop the morphology in the reactive polymer blends. The reaction occurs at the interface between the polymeric components such as in reactive compatibilization (Dufaure et al., 2005).

Blends prepared with rubber and thermoplastic, dispersed rubber phase in thermoplastic continuous phase generally exhibits increased stiffness , strength and decreased flexibility. Low level of homogeneity of blends may also result in rapid decrease in elongation at break of blends (Sombatsompop et al., 2001). Further, in LLDPE/ GRT blend prepared with EOC (ethylene-1-octene copolymers), physico-mechanical performances of LLDPE/GRT blends increases due to addition of EOC compared to simple LLDPE/ GRT blend (Rocha et al., 2014). Besides, the addition of EOC in the 50/50 LLDPE/GRT blend, leads to a major increase of tensile properties and fine phase morphology. As the results, EOC was selected as the best compatibilizing agent for LLDPE/GRT blends (Rocha et al., 2014).

Blend prepared with reactive compatibilizer named dicumyl peroxide showed good improvement of mechanical properties of the waste rubber/LDPE blends, than the simple waste rubber/LDPE blends (Hrdlicka et al., 2010). Ahmad et al., (2004) prepared 30/70 NR/LLDPE blends with different fillers namely carbon black N110, silica and calcium carbonate. The physico-mechanical properties of the blends depend on filler characters. The degree of swelling index and elongation at break revealed a decreasing trend with a rising volume percent of filler loading in the blend. Other significant changes in physical properties were the gel content, and bound rubber of the samples indicating a strong chemical interaction between filler particles and the polymer matrix. Accordingly, agglomerate particles size and polymer-filler interaction determine the physical and chemical properties of NR/LLDPE blends (Ahmad et al., 2004). A progression of ternary polymer mixes of polybutadiene elastic (BR)/LDPE/PVC was prepared with peroxide and sulfur as compatibilizing agents and indicated remarkable mechanical properties.

## 2.7 Fillers Used in Composites

Fillers are defined as materials incorporated to a polymer formulation for reducing the cost of the compound and improve properties. Fillers retain their inherent characteristics, yet, massive differences are usual. Depending on the molecular weight, compounding fillers are merged with both rubbers and thermoplastics to reduce the cost by increasing volume, to reinforce the polymer, and thereby improve the performance of the final product. $CaCO_3$, silica, talc, and alumina hydrates frequently used non-black particulate fillers or mineral fillers in thermoplastics and rubbers. Dispersion of inorganics in polymers and adhesion of a polymer to an inorganic filler is challenging because of the non-polar nature of many thermoplastics and rubbers such as olefin-based polymers. Hence, $CaCO_3$ does not show property enhancement when incorporated either into rubbers or to thermoplastics. $CaCO_3$ is a natural product from sedimentary rocks and is separated into chalk, limestone, and marble. In some cases, $CaCO_3$ is treated to improve bonding with thermoplastics (Bosshard et al., 1987). $CaCO_3$ can exist in a number of crystallographic modifications: calcite, aragonite and vaterite (Betinngyte et al., 2012). Ground natural calcite is usually micron-sized with a broad size distribution and irregular shape and is used as filler extender. It is known that $CaCO_3$ is the most widely used non-reinforcing filler in natural rubber composites. It is inexpensive and can be used at high loadings.

According to literature, owing to the dissimilar nature of polyolefin and $CaCO_3$, it is important to achieve a good dispersion of $CaCO_3$ particles in polyolefin in order to obtain optimum performance of the composites. However, $CaCO_3$ does not disperse easily in LDPE and it tends to agglomerate. Further, interactions of polyethylene with polar substances is at a low level due to its crystallinity and polarity (Doufnoune et al., 2008). Hence, low loadings of LDPE such as 30 phpp is blended with 70 phpp loading of NR. Nevertheless, properties of 70/30 NR/LDPE composites filled with $CaCO_3$ are not at an acceptable level due to poor dispersion of $CaCO_3$ in the LDPE phase as well as compatibility of the two polymer phases NR and LDPE. Coupling agents could be used to increase dispersion of $CaCO_3$ in LDPE and to develop compatibility between NR and LDPE phases. Also, it was reported in literature that the dispersibility and compatibility of the inorganic phases of HDPE/$CaCO_3$ composite can be improved through surface treatment of the amorphous $CaCO_3$ filler with stearic acid (Croitoru et al., 2017).

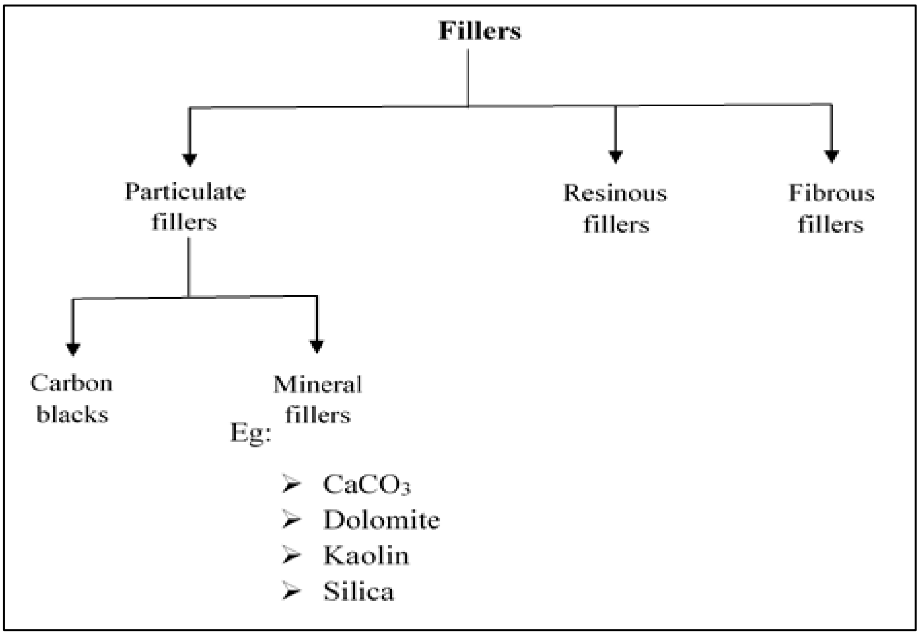


Figure 2.12 Classification of Fillers

### 2.7.1 Particulate fillers

Particulate fillers are divided into two types, inert fillers and reinforcing fillers. The term inert filler is something of a misnomer as many properties may be affected by incorporation of such filler (Rothon et al., 1990). Each type of filler may differ in the following ways:

- Particle size and dispersion
- Particle structure and permeability
- Morphology on the surface
- Contaminations such as metal ions and other different fillers

### 2.7.2 Calcium carbonate ($CaCO_3$)

Calcium carbonate occurs widely in nature and has many suitable properties and it is extensively used as filler. Calcium carbonate is an example for a nonreinforcing filler. Three types of calcium carbonate fillers are used in rubbers (Subramanium, 2012).

- Naturally occurring calcium carbonate

Ground lime stone or chalk of particle size in the range 0.5 to 3 µm can be incorporated into rubbers to obtain low cost, light color articles. The filler increases hardness and gives only little reinforcement in rubbers.

- Precipitated calcium carbonate

This is produced from the following reaction as a precipitate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

The filler has fine particle size as low as 0.1 nm and confers rubber with improved strength properties.

- Activated calcium carbonate

This is produced by treating precipitated calcium carbonate with up to 3% stearic acid or stearate. The filler shows better dispersion and can be used in higher grade coloured products.

### 2.7.3 Fillers used for NR/LDPE blends

NR/LLDPE blends were prepared by different types of fillers namely different grade of carbon black, types of clays, silica, dolomite and calcium carbonate and physico-mechanical and chemical properties releasing (Ahmad et al., 2004). As the previous study, fillers were incorporated into the NR/LDPE blends in the range 10-60 phpp. Ahmad et al. (2004) reported that, physico-mechanical properties of the blends are dependent on filler characterization. The swelling index and elongation at break revealed a decreasing trend with increasing volume percent of filler loading in the blend. The changes in other physical properties were the gel content, and the sample's bound rubber had a substantial collaboration between the filler particles and NR/LLDPE blends (Ahmad et al., 2004).

The NR/LDPE filled silica composites preparation involved three mixing routes. The investigation comprised of testing the effects of filler incorporation routes on the morphological and tensile properties of prepared composites. Morphologies of phases in LDPE/NR/Silica composites strongly depended on the filler incorporation routes (Ying et al., 2014).

Physico-mechanical properties of two blend series were studied. Two blend series were prepared with NR/PE and NR/PS and properties were evaluated with two different types of fillers, carbon black and nanocarbon particles (Mohammed et al., 2004). Tensile properties had been increased of the NR/PE, NR/PS blends with the increased carbon black and nanocarbon particles. It was found that the integration of PE and PS in the blend compositions leads to a decrease in the degree of swelling. As expected, when the PE and PS were increased in former composites. Hence, the ratios of 70/30 NR/PE, 85/15 NR/PS blends showed in better tensile properties ((Mohammed et al., 2004)).

Performance of kenaf powder (KP) as filler for rHDPE)/NR composites was prepared with different filler loadings (Cao et al., 2012). In former literature, LDPE molded pieces have been prepared with two natural fillers which are wheat bran and pumpkin seeds and evaluated physico-machanical properties of composites. Also, these natural fillers generate as waste products (Głogowska, et al., 2017). The polymer blends were examined in respect to their basic mechanical properties and microstructure (Głogowska, et al., 2017).

### 2.8 Compatibilization of Polymer Blends

Compatibilization is a method which is used to modify the interfacial properties of the immiscible polymer blends. It causes a reduction of the interfacial surface tension and coefficient and stabilizes the desired blend morphology (Utracki, 2003). Most polymer blends are incompatible and categorized by two-phase morphology, constricted interface, less physical collaborations via the phase boundaries, and weak mechanical properties (George et al., 1995). These problems can be alleviated by addition of a third component into the incompatible polymer blends in order to enhance the degree of compatibility between the components (Bonner and Hope, 1993). The third part is called as a blend compatibilizer or compatibilizing agent that is a macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Generally, the compatibilizers have a block polymer structure, one block being miscible with one blend component and a second one miscible with the other blend component (Koning et al., 1998). The physico-mechanical properties would be evaluated of its polymer components, then also by the phase interface via phase morphology and surface tension via interfacial adhesion. The phase morphology and the interface interaction are significant from the standpoint of stress transference (Bonner and Hope, 1993).

#### 2.8.1 Type of compatibilizer

A compatibilizer offers a chemical interaction via the covalent, hydrogen or other types of bonds among two or more different polymer materials, generally compatibilizers are an inorganic and an organic.  In polymer composites, compatibilizing agent is used as intermediate agent between the inorganic and organic materials to obtain significat improvement of properties (Padhiyar et al., 2008). The main polymer based applications are in filled polymer blends, including both elastomer and different plastic, such as immiscible blend (NR/LDPE, NR/PP etc.), phenolics, etc. and most of rubber applications where silanes (Si-69) are used as filler managements as well as for make crosslinking polyolefin based polymer.  Developing novel technologies in polymer material applications also apply silane type compatibilizing agents. In previous literature, research have been done with different type compatibilizing agents, the LLDPE/GRT blends prepared with ethylene-1-octene copolymers (EOC) compatibilizing agent. The 50/50 LLDPE/GRT blend prepared with EOC and evaluated the physico-mechanical properties. As the new finding, elongation at break and tensile strength remarkably improved additionally of 5 w/w% EOC in the LLDPE/GRT blend in compared to simple blend (Rocha et al., 2014). NR/LLPE reactive blends were prepared with diallyl malateas and physico-mechanical properties were evaluated. As the result, diallyl malateas react as a good compatibilizer for NR/LLDPE blends (Gajanayake et al., 2012).

Further, organosilane compatibilizing agents can develop a durable bond between organic and inorganic materials. Organo-functionality could be directly integrated into silanes, and Amino, epoxy, methacrylate, mercapto, and vinyl are the popular functionalities (Wypych, 2006). Inorganic compatibility initiated by alkoxy groups are attributed to the silicon atom. This bond is hydrolytically unstable and hydrolyzes to an intermediate Si-OH bond in the presence of moisture, which then condenses with surface-bound OH groups on inorganic surfaces to form stable Si-O-M bonds (Nakamura et al., 2012).

NR/LDPE/GRT blends were prepared in the past with different types of compatibilizing agents, namely phenolic and peroxide (Radheshkumar et al., 2002). The detected improvements in mechanical performance were attributed to chain entanglement and co-crosslinking in the interphase between the GTR particles and the surrounding matrix. Phase morphology, which was assessed using SEM on the etched surfaces of cryogenically fractured thermoplastic dynamic vulcanisate compositions, has been discussed (Radheshkumar et al., 2002).

### 2.8.2 Coupling agents (CAs)

A coupling agent (CA) is a complex chemical component which provides a chemical interaction through the different stable bond between two or more dissimilar materials namely polymer-filler or polymer-polymer.

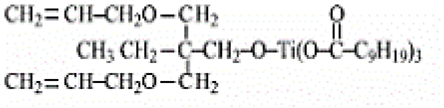
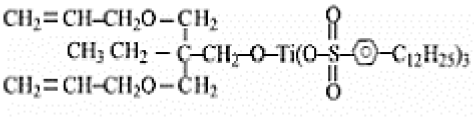
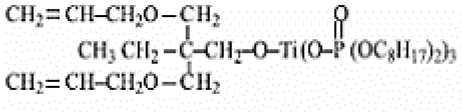
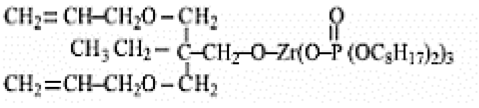
### 2.8.2.1 Titanate coupling agents

Titanate CAs are organometallic (present as the metal complex) interphase bond stability dependent on basically titanium or zirconium. Titanate based CAs bolster expanded number of interaction on fillers in various types of thermoplastics material such as LDPE, HDPE, PP, PS ect. The many types of response ways that these types of titanate such as Lica 12 and work in filled polymeric material such as filled $CaCO_3$ plastic could be clarified by separating the diverse components of the titanate particle into six functionalities (Pocius., 1997). The titanate structure would be created to generate astounding performance via the six functionalities on the essential compound structure appeared in Figure 2.13. Table 2.3 shows a commercial name, description and structures of four basic CAs.

$$(RO)_n\text{-Ti-}(\text{-O X R' Y})_{4-n}$$

Figure 2.13. Basic chemical structure of a titanate molecule

Table 2.3 Chemical description and structure of some titanate coupling agents

| Commercial name | Chemical description | Chemical structure |
|---|---|---|
| Lica 01 | Neopentyl(diallyl)oxy, trineodecanonyl titanate |  $CH_3CH_2-\underset{CH_2=CH-CH_2O-CH_2}{\overset{CH_2=CH-CH_2O-CH_2}{C}}-CH_2-O-Ti(O-\overset{O}{\overset{\|}{C}}-C_9H_{19})_3$ |
| Lica 09 | Neopentyl(dyallyl)oxy,<br>tri(dodecyl)benzene – sulfonil titanate |  |
| Lica 12 | Neopentyl(diallyl)oxy, tri(dioctyl)phosphato titanate |  $CH_3CH_2-\underset{CH_2=CH-CH_2O-CH_2}{\overset{CH_2=CH-CH_2O-CH_2}{C}}-CH_2-O-Ti(O-\overset{O}{\overset{\|}{P}}(OC_8H_{17})_2)_3$ |
| NZ 12 | Neopentyl(dyallyl)oxy, tri(dioctyl)phosphato zirconate |  $CH_3CH_2-\underset{CH_2=CH-CH_2O-CH_2}{\overset{CH_2=CH-CH_2O-CH_2}{C}}-CH_2-O-Zr(O-\overset{O}{\overset{\|}{P}}(OC_8H_{17})_2)_3$ |

As per the schematic illustration in Figure 2.14 shows reactivity of titanate CAs with hydroloze filler such as $CaCO_3$ of $MgCO_3$. Titanate based CA was reacted with free protons at the surface of polymeric matrix incorporate inorganic filler as in Figure 2.16 component and structure natural monomolecular layers superficially. Kattas et al. (2000) expressed that "titanate-treated inorganic fillers are mentioned different characteristic, they are hydrophobic, organophilic, and organofunctional, and, subsequently, show upgraded dispersibility and bonding with the polymer network."

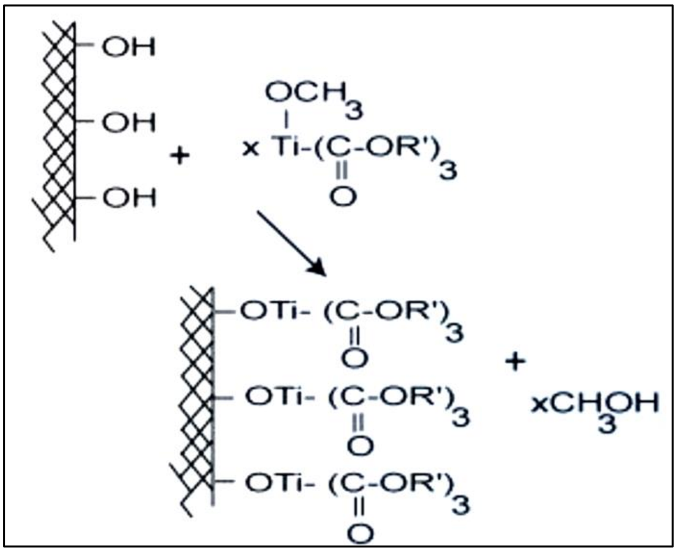


Figure 2.14. Schematic diagram of the monomolecular layer formation by titanate CA (Pocius, 1997)

Ester type titanate CAs are used to make a chemical bridge between two different polymeric phases such as an inorganic filler and organic polymer. Titanate CAs reaction is unique and it reacts with free protons on the polymer surface through the inorganic filler. Pocius. (1997) reported that, an excess amount of titanate CAs do not react with polymer network at the surface of the polymer interface, hence it would be a reason to make the weak interface and degrade the polymer. Therefore, the concentration and amount of ester type coupling agent are a significant parameter for polymer blending.

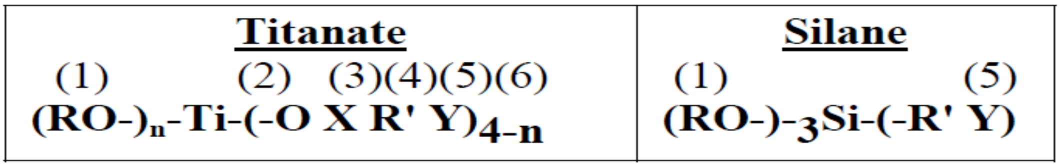
Physico-mechanical properties improved with titanate CAs due to better filler dispersion, reduction of interface tension etc. (Elshereksi et al., 2017). Further, titanate CAs are delivered remarkable hydrolytic stability and hence, it could be imported to produce dental composites. Elshereksi et al. (2017) reported that, development of the resistance of moisture of the polymer composite due to adding a little amount of ester type titanate CAs. Furthermore, most of the researches have used titanate CAs to improve the filler- plastic interaction. Hajian et al. (2011) reported that the composite prepared with PVC and different types of nanofillers such as Zinc oxide, $CaCO_3$, $TiO_2$ etc. The properties of nanofillers filled composites were evaluated by DSC, thermogravimetric analysis and physico-mechanical properties. Glass transition temperature of nanofillers filled PVC composites increased due to better dispersion of nanofillers through titanate CA. Furthermore, thermal stability and impact strength of nanofillers filled PVC composites improved due to better compatibility and stability (Hajian et al. 2011).

Although, properties of asphalt binder prepared with addition LLDPE-$CaCO_3$ modifier and titanate CA significantly increased (Hasan et al., 2018) the composite stiffness that added to bring down rutting potential, the protection from low-temperature splitting of black-top cover was not unfavorably influenced. The asphalt composite prepared with different titanate CA loadings and properties were evaluated. Hence, 1% titanate coupling agent loading composite was showed best performance in term of resistance to moisture damage and rutting compared to other counter parts (Hasan et al., 2018).

It is reported that, fly ash filled chloroprene rubber (CR) composite was prepared with different amount of titanate CA. The composite prepared with 1% titanate coupling agent showed better physico-mechanical properties compared to other counterparts (Alkadasi, et al., 2006). Also, the impact strength of composite has been increased under the above titanate loading. As the final results, fly ash filled CR composites prepared with titanate CA show remarkable properties in term of tensile strength, young’s modulus, hardness ect. Alkadasi, et al. (2006) reported, all these properties were improved by 1000%.

### 2.8.2.2 Functions of titanate coupling agents

A comparison of the six different types of active sites of basic structure of titanate CA and silane is shown in Figure 2.15 (Nakamura et al., 2012). Also it illustrated different functionalities according to the Figure 2.15



$$\overset{(1)}{(RO\text{-})_n}\text{-}\overset{(2)}{Ti}\text{-}(\text{-}\overset{(3)}{O}\ \overset{(4)}{X}\ \overset{(5)}{R'}\ \overset{(6)}{Y})_{4-n} \qquad \overset{(1)}{(RO\text{-})}\text{-}_3Si\text{-}(\text{-}\overset{(5)}{R'\ Y})$$

Figure 2.15. Basic structure of titanate coupling agent and silane coupling agent

As shown in the Figure 2.15, titanate coupling agent has 6 functional sites according to relevant parts on the molecular structure where:

*Function (1)* RO = Hydrolyzable group or substrate-reactive group with surface hydroxyls or protons

*Function (2)* Ti (Zr), Si = Tetravalent titanium, zirconium, or silicon. The Ti–O (or Zr–O) link can separate and permit trans esterification, trans alkylation, and other catalyzed reactions such as ‘repolymerization’; the Si–C bond is more stable and unreactive.

*Function (3)* X = Binder functional groups, i.e., phosphato, pyrophosphato, sulfonyl, and carboxyl that may impart intumescence, burn rate control, anticorrosion, quaternization sites, and dissociation rate/electron-transfer control.

*Function (4)* R’ = thermoplastic-specific functional groups, i.e., aliphatic and non-polar isopropyl, butyl, octyl, isostearoyl groups; naphthenic and mildly polar dodecylbenzyl groups; or aromatic benzyl, cumyl or phenyl groups. Provide tangles with long hydrocarbon chains and bonding via Van der Waals forces.

*Function (5)* Y = thermoset (but also thermoplastic)-specific functional groups such as acrylyl, methacrylyl, mercapto, and amino. Provides a thermoset reactivity that chemically bond the filler to the polymer.

*Function (6)* 4–n = mono-, di- or tri-organofunctionality. Hybrid titanate (or zirconate) coupling agents, such as those containing 1 mole each of a carboxyl [function (3)] and aliphatic isostearoyl [function (4)] ligand and 2 moles of carboxyl [function (3)] and acrylyl [function (5)] ligands are possible.

Therefore, function (1) relates to filler/fiber substrate reaction mechanisms, while functions (2) to (6) are polymer/curative reactive (Monte, 2005).

### 2.8.2.3 Effects of titanate coupling agents

There are six functional sites of titanate CA which are shown in Figure 2.15. Functional site 1 is most important for proper dispersion, enhance the good adhesion among the polymer and filler and generate hydrophobicity impacts. These impacts are additionally identified with increment filler polymer association.

Dispersion effect of titanate CA - Dispersion capacity of inorganic fillers depends on different factors such as; surface tension, phase morphology, interface of the inorganic filler, etc of polymer blends and composites. Otherwise, it will cause total agglomeration to the original filler molecule, for example, elastic and plastic, complete expulsion of air voids and furthermore the making of a genuine nonstop inorganic or organic composition (Monte., 2005). According to former literature, Monte. (2005) reported that titanate based CA has better hydrophobicity characters. Hence, Figure 2.16 illustrates effect of titanate CA with inorganic filler. Further, it clearly shows titanate CA helps to disperse filler on polymer matrix without keeping space among the polymer and filler.

Adhesion Effect – This effect refers to the dispersion capability of inorganic particles in different types of polymers such as types of thermoplastics and types of rubber . Also, adhesion of a thermoplastic to an inorganic particles are very difficult because many plastics , natural and synthetic rubbers are olefin based polymer and they are non-polar. In the previous studies, titanates type CAs are well recognized as adhesion promoters. According former findings, experiment has been mentioned bonding polyolefins to metals and adhesion of polyolefins to foil (Monte, 2005).

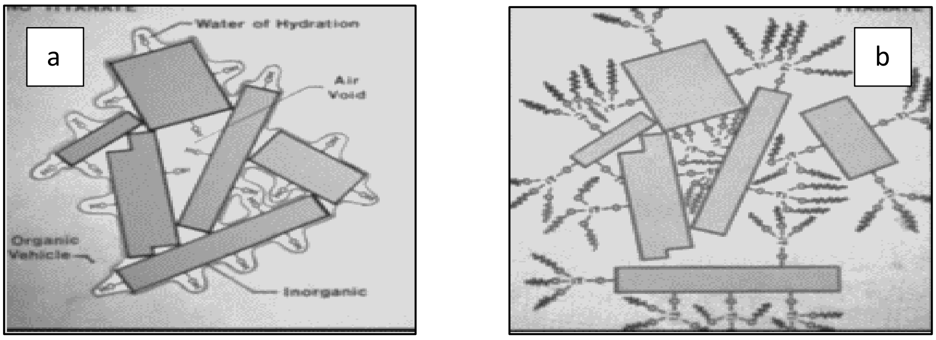


Figure 2.16. Dispersion effect on an agglomerated inorganic in an organic phase (a) without a titanate CA (b) with titanate CA (Monte, 2005)

### 2.8.2.4 Surface modification of fillers with titanate coupling agents

The organic titanates respond with surface hydroxyl groups to produce a polymer network at the surface of fillers. This reaction results in formation of monomolecular coating on the surface of the filler. In Figure 2.17 coating of filler by titanates is illustrated schematically.

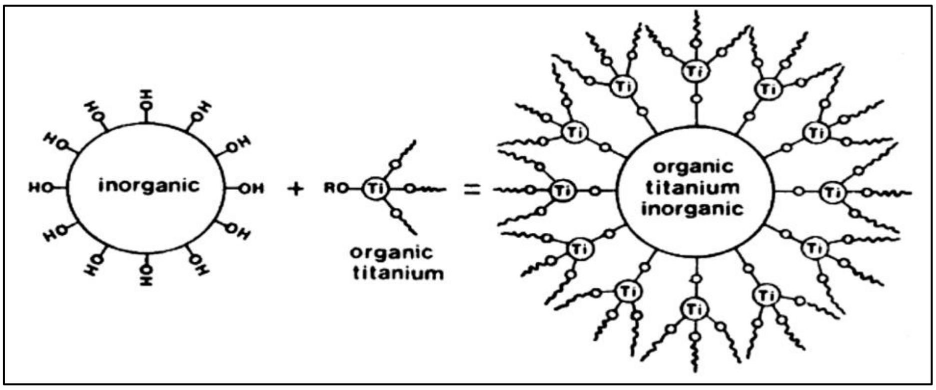


Figure 2.17. Schematic diagram of coating of filler by titanates (Monte, 2005)

Use of organic titanates for surface change relies upon their capacity to hydrolyze to an exceptional coating. The physico-mechanical properties of polymer composite directly affect the type of polymer/s, polymer blend proportion, the amount of organometallic CA utilized (Elshereksi et al., 2017). Figure 2.17 shows how to make a hydrolyze coating on filler surface through the titanate coupling agent and hence, filler surface would be modified and generate the following properties (Hajian et al., 2011).

i. The organometallic interface improves dispersability of filler in polymer matrix and reduces viscosity

ii. It could modify frictional characteristics of the polymers

iii. It could modify surface characteristics of the final composite

iv. Reductions water-vapor transmission

# CHAPTER 3

# EXPERIMENTAL

## 3.1 Materials

In this study natural rubber and low-density polyethylene were utilized as polymeric materials. $CaCO_3$ was utilized as inorganic filler and titanate (Lica 12) was utilized as the coupling agent. This section describes the properties of these materials and also, explains the origins.

### 3.1.1 Low-density polyethylene (LDPE)

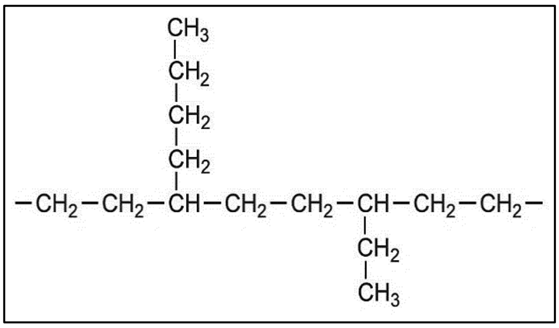


Figure 3.1. Chemical structure of LDPE

LDPE was purchased from Qatar Petrochemical Company Ltd. The commercial name of the LDPE is "Lotrene FD 0274" and it is bundled as pellets in 25 kg white coloured PE bags. Table 3.1 shows physical characteristics of LDPE obtained from the supplier.

Table 3.1 Physical Properties of LDPE used

| Properties | Value | Test method |
|---|---|---|
| Melt Flow Index, g/10 min | 2.4 | ASTM D-1238 |
| Density @ 23 °C , $g/cm^{-3}$ | 0.923 | ASTM D-1505 |
| Crystalline melting point, °C | 115 | ASTM D-2117 |
| Softening point, °C | 96 | ASTM D-1525 |
| Tensile strength, MPa | 12 | ASTM D-882 |
| Elongation at break, % | 400 | ASTM D-882 |

### 3.1.2 Natural rubber (NR)

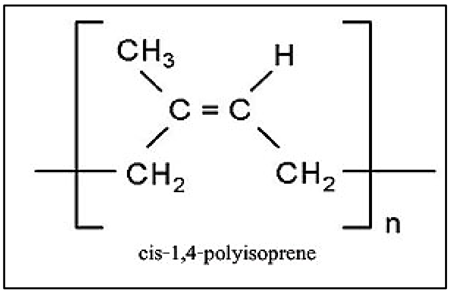


Figure 3.2. Chemical structure of NR.

Natural rubber (RSS-2) was supplied by Rubber Research Institute of Sri Lanka. The technical specifications of RSS-2 grade are shown in Table 3.2.

Table 3.2. Properties of natural rubber

| Property | Value |
|---|---|
| Dirt content, % | 0.019 |
| Volatile matter, % | 0.72 |
| Nitrogen content, % | 0.487 |
| Ash content, % | 0.4 |
| Initial plasticity number ($P_0$) | 49.4 |
| Plasticity retention index | 64 |

### 3.1.3 Calcium carbonate ($CaCO_3$)

$CaCO_3$ used in this study was supplied from Lanka Minerals & Chemicals (Pvt.) LTD, Sri Lanka. Its trade name is "*LAKCARB 2*". The chemical composition and physical properties of this filler are given in Table 3.3 and Table 3.4, respectively.

Table 3.3.Chemical composition of $CaCO_3$

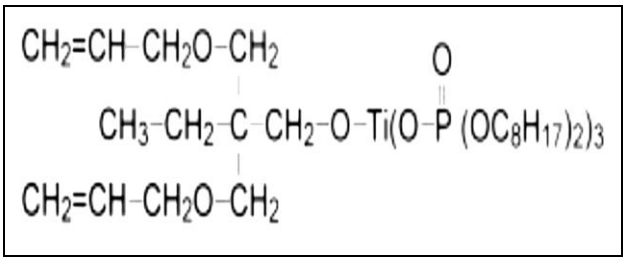
| Material | Composition, w/w % |
|---|---|
| Calcium carbonate | 98 |
| Magnesium carbonate | 1.5 |
| Aluminum oxide | 0.18 |
| Silica | 0.2 |
| Iron oxide | 0.03 |
| Loss on ignition | 43±1% |

Table 3.4. Physical properties of $CaCO_3$

| Property | Value |
|---|---|
| Average particle size | 3.0 µm |
| Density | 2.7 g/cm$^3$ |
| pH | 9.0 |
| Moisture | 0.5% |

### 3.1.4 Titanate coupling agent

In this research, titanate based coupling agent (titanate CA) was used to investigate its effects on physico-mechanical, thermal, ageing, dynamic and morphological properties of LDPE and NR blends and composites. In this study, neoalkoxy organo-titanate, which is appropriate for these polymers and was used and it was supplied by Pheonix Industries, Sri Lanka. The trade name of the titanate CA is “Lica 12” having chemical name of Titanium IV 2,2 (bis 2-propenolatomethyl) butanolato, tris (dioctyl) pyrophospato –O and its structure is shown in Figure 3.3.



$$CH_3{-}CH_2{-}\underset{\underset{CH_2{=}CH{-}CH_2O{-}CH_2}{|}}{\overset{\overset{CH_2{=}CH{-}CH_2O{-}CH_2}{|}}{C}}{-}CH_2{-}O{-}Ti(O{-}\overset{\overset{O}{\|}}{P}(OC_8H_{17})_2)_3$$

Figure 3.3. Chemical structure of titanate coupling agent

Titanate CA has three physical forms that can be used for many polymer industrial purposes in many areas, liquid, powder and pellet forms. In this study pellet forms of Lica 12 were used. This is the pellet form of Lica 12 and its name comes from the abbreviation of “CA pellet system form of Lica 12”. It has a chemical composition of 20 w/w% Lica 12, 69 w/w% LLDPE as binder and 11 w/w% hydrated amorphous silica. Lica 12 was used in NR/LDPE blends by direct addition into melt blending.

### 3.1.5 Chemicals

Sulphur and dicumyl peroxide (DCP) were used as the vulcanizing agents. Sulphur could vulcanize NR, however, DCP would vulcanize both NR and LDPE phases. DCP loading in a range 0.1 – 0.9 parts per hundred parts of polymer (pphp) was selected since flexibility of the

NR/LDPE composites would decrease at higher loadings. Efficient vulcanizing system was used to suit for the applications mentioned in the scope of the study. Stearic acid and zinc oxide (ZnO) as the activators, N-tert-butyl-2- benzothiazolesulfenamide (TBBS) as the accelerator and BKF (2, 2'-methylene bis (4-methyl-6-tert butyl phenol)) as the antioxidant were used and were and were purchased from the Sri Lanka. All the chemicals were industrial grade and were used without further purification.

## 3.2 Methodology

### 3.2.1 Preparation of blend and composite compounds

The composites were prepared by melt mixing using a Brabender plasticorder operated at a temperature of 150 °C, and at a rotor speed of 60 rpm. Total mixing time was kept constant according to the type of blend or composite.

#### 3.2.1.1 Study on vulcanization system

To identify the best vulcanizing system, four 50/50 NR/LDPE blends were prepared with and without vulcanizing agents and the formulations are given in Table 3.5. The mixing cycle used in the preparation of NR /LDPE blend compounds is also given in Table 3.5. NR/LDPE blend compounds were compression moulded in an electrically heated hydraulic press at 150 $^{o}$C under 3.5 bar pressure for 12 minutes.

Table 3.5 Formulation and mixing cycle of 50:50 NR/LDPE blends

| **Ingredient** | **Loading (pphp)** | | | | **Total mixing time (min.)** |
|---|---|---|---|---|---|
| | **Control-1** | **Sulphur system** | **DCP system** | **Mixed system** | |
| LDPE | 50 | 50 | 50 | 50 | 0 |
| NR | 50 | 50 | 50 | 50 | 4 |
| ZnO | 05 | 05 | 05 | 05 | 5 |
| Stearic acid | 02 | 02 | 02 | 02 | |
| BKF | 1 | 1 | 1 | 1 | |
| TBBS | 0 | 1 | 0 | 0.5 | 6 |
| Sulphur | 0 | 1 | 0 | 0.5 | 8 |
| DCP | 0 | 0 | 1 | 0.5 | 10 |
| Dumped | | | | | 12 |

### 3.2.1.2 Preparation of simple blend compounds

A series of simple NR/LDPE blend compounds, i.e. without filler was prepared at different blend ratios by varying LDPE loading from 10 pphp to 90 pphp. The compounds were prepared according to the compositions shown in Table 3.6. At the start of mixing, LDPE was introduced into the plasticorder and was mixed for 4 minutes. NR was then added to molten LDPE and mixed for another 3 minutes.

Table 3.6 Formulations of NR/LDPE simple blends

| **Ingredient** | **Loading (pphp)** | | | | | |
|---|---|---|---|---|---|---|
| LDPE | 90 | 70 | 50 | 30 | 10 | 0 |
| NR | 10 | 30 | 50 | 70 | 90 | 100 |

### 3.2.1.3 Preparation of composites with and without titanate CA

$CaCO_3$ is the commonly used filler in rubber/thermoplastic blends, and the loading in a range 20-30 pphp showed acceptable properties in previous studies. Two compound series of $CaCO_3$ filled NR/LDPE composites were prepared. One series prepared with titanate CA and another series prepared without titanate CA. Two series of $CaCO_3$ filled NR/LDPE composites prepared by varying LDPE loading from 10 pphp to 90 pphp. The formulation of the composite with the CA is given in Table 3.7. Complete blending time was kept steady at 14 minutes. Blending cycle is given in Table 3.8.

Table 3.7. Formulations of NR/LDPE composites with titanate CA

| **Ingredient** | **Loading (pphp)** | | | | | |
|---|---|---|---|---|---|---|
| LDPE | 100 | 90 | 70 | 50 | 30 | 10 |
| NR | 0 | 10 | 30 | 50 | 70 | 90 |
| BKF | 2 | 2 | 2 | 2 | 2 | 2 |
| $CaCO_3$ | 20 | 20 | 20 | 20 | 20 | 20 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 | 2 |
| CA | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| TBBS | 1 | 1 | 1 | 1 | 1 | 1 |
| Sulphur | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| DCP | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |

Table 3.8. Mixing cycle of NR/LDPE composites with titanate CA

| **Total time, min** | **Ingredient** |
|---|---|
| 0 | Added LDPE |
| 4 | Added NR |
| 6 | Added ZnO + Stearic acid +A/O |
| 7 | Added ½ $CaCO_3$ |
| 8 | Added ½ $CaCO_3$ |
| 9 | Added CA |
| 11 | Added TBBS |
| 12 | Added Sulphur + DCP |
| 14 | Dumped |

### 3.2.1.4 Preparation of composites at different mixing routes

50/50 NR/LDPE composites were prepared by varying the addition stage of titanate CA, The three mixing routes that were used to identify the best route are given in Table 3.9.

Mixing I - Titanate CA was added after mixing LDPE and NR.
Mixing II - Titanate CA was added after mixing LDPE, NR, and activators
Mixing III - Titanate CA was added after mixing LDPE, NR, activator, and $CaCO_3$

Table 3.9 Mixing routes of 50/50 NR/LDPE composites with titanate CA

| **Mixing route** | **Time (min.)** | | | | | |
|---|---|---|---|---|---|---|
| | **1** | **3** | **4** | **5** | **6** | **8** |
| Mixing I | LDPE | NR | **CA** | Activators | $CaCO_3$ | Vulcanizing system |
| Mixing II | LDPE | NR | Activators | **CA** | $CaCO_3$ | Vulcanizing system |
| Mixing III | LDPE | NR | Activators | $CaCO_3$ | **CA** | Vulcanizing system |

### 3.2.1.5 Preparation of composites at different titanate CA loadings

It was found that the continuous phase of the composites were changed from NR to LDPE when the LDPE loading was above 30 pphp, In order to fulfill the scope of the study, the composition of the composites were selected as 70/30 NR/LDPE. A series of 70/30 NR/LDPE composites was formulated by varying the titanate CA loading from 0.3 to 1.5 pphp at 0.2 pphp intervals. The NR/LDPE composite prepared without titanate CA was taken as the Control-3. The formulations of the composites are given in Table 3.10. The composites were prepared by melt mixing using a Brabender plasticorder operated at a temperature of 150 °C, and at a rotor speed of 60 rpm. Total mixing time was kept constant at 14 minutes.

Table 3.10. Formulations NR/LDPE composites with different loadings of the titanate CA

| **Ingredient** | **Loading (pphp)** |
|---|---|
| LDPE | 30 |
| NR | 70 |
| Zinc oxide | 05 |
| Stearic acid | 02 |
| A/O | 01 |
| $CaCO_3$ | 20 |
| CA | 0 , 0.3 ,0.5, 0.7, 0.9 , 1.2 , 1.5 |
| TBBS | 01 |
| DCP | 0.5 |
| Sulphur | 0.5 |

### 3.2.1.6 Preparation of composites at different DCP loadings

A series of 70/30 NR/LDPE blends was formulated by varying the DCP loading from 0 to 0.9 pphp. The formulation of the composites with the DCP loading is given in Table 3.11. The blends were prepared by melt mixing using a Brabender plasticorder operated at a temperature of 150 °C, and at a rotor speed of 60 rpm. Total mixing time was kept constant at 14 minutes. Mixing cycle used in preparation of NR /LDPE blend compounds is given in Table 3.12.

Table 3.11. Formulations of 70/30 NR/LDPE composites at different DCP loadings

| **Ingredient** | **Loading (pphp)** |
|---|---|
| NR | 70 |
| LDPE | 30 |
| Zinc oxide | 05 |
| Stearic acid | 02 |
| A/O | 01 |
| $CaCo_3$ | 20 |
| DCP | 0  0.1  0.3  0.5  0.7  0.9 |
| Sulphur | 0.5 |
| TBBS | 0.5 |

Table 3.12. Mixing cycle of 70/30 NR/LDPE composites at different DCP loadings

| **Total time, min** | **Ingredient** |
|---|---|
| 0 | Added LDPE |
| 4 | Added NR |
| 6 | Added ZnO + Stearic acid +A/O |
| 7 | Added ½ $CaCO_3$ |
| 8 | Added ½ $CaCO_3$ |
| 9 | Added TBBS |
| 11 | Added Sulphur + DCP |
| 12 | Dumped |

### 3.2.1.7 Preparation of composites with recycled LDPE (rLDPE)

A series of NR/LDPE/rLDPE blends was formulated by varying the ratio of LDPE: rLDPE loading from 30:0 to 0:30 by weight. The formulation and the mixing cycle of the composites with the LDPE:rLDPE loading is given in Table 3.13.

Table 3.13. The formulations and the mixing cycle of NR/LDPE composites at different LDPE : rLDPE ratios

| Ingredient | Loading (pphp) | Total mixing time (Min.) |
|---|---|---|
| LDPE | 30 25 20 15 10 0 | 0 |
| rLDPE | 0 05 10 15 20 30 | |
| NR | 70 | 3 |
| Zinc oxide | 05 | 4 |
| Stearic acid | 02 | 5 |
| A/O | 01 | 6 |
| $CaCO_3$ | 20 | 7 |
| CA | 0.7 | 7 |
| TBBS | 01 | 11 |
| DCP | 0.3 | 12 |
| Sulphur | 0.5 | 13 |
| Dumped | | 14 |

### 3.2.2 Preparation of vulcanizates

Vulcanization was carried out according to ISO 2285, using the laboratory hydraulic press operated under 35 MPa pressure and temperature of 150 °C for 15 minutes. Then the test specimen was cooled by passing water through the cooling channel of the hydraulic press and it was removed from the mold once the temperature reached 40-30 °C. All the test specimens were kept at ambient conditions for 25 hours and then the properties were evaluated according to the standards.

### 3.2.3. Determination of properties

#### 3.2.3.1 Tensile stress-strain properties

International standard ISO 37-2011 was followed to determine the tensile stress-strain characteristics of the blends and composites on an intron tensile testing machine (model 3365) at cross-head speed of 50 mm/min. All tests were carried out at a temperature of 26 ± 2 °C. Test specimen were punched out from 2mm thick compression moulded sheets using a dumbbell die. The thickness of the narrow portion was measured by a bench thickness gauge

(Wallace Instruments, UK). The sample was held tightly by the two grips of which the upper grip was fixed.

#### 3.2.3.2 Tear strength

The test consists of measuring the force required to tear a specified test piece. ISO 34-2011 was used to determine the tear strength of prepared NR/LDPE blends and composites. Thickness of the test specimen was measured by a bench thickness gauge (Wallace Instruments, UK) in the region in which tearing is expected to occur in accordance with ISO 3529. The test piece was mounted on the universal testing machine and it was extended at 50 mm/min grip separation rate. The tear strength which was expressed in newtons per meter of thickness is given by equation 3.1.

$\text{Tear strength} = \text{F}/\text{d}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$3.1.

Where F is the maximum force in Newton

d is the median thickness of the test specimen in millimeters.

#### 3.2.3.3 Hardness

Hardness is defined as the resistance to elastic deformation of the surface for materials. Standard test method for the determination of hardness is ISO 48:2010 and IRHD is the measuring unit which stands for International Rubber Hardness Degrees. Initial contact force was applied to a spherical indenter and the penetration was set to zero. Then the force was increased to a specified total load and the depth of indentation was measured. Three test pieces of 10 mm thickness were tested using Bareiss BS 06 hardness tester. The readings were taken after 10 seconds and the mean values were calculated.

#### 3.2.3.4 Ageing properties

The test specimens were subjected to control deterioration by air at an elevated temperature and at atmospheric pressure after which specified properties were measured and compared with those of unaged test pieces. ISO standards ISO 37:2010 (E) and ISO 34-1:2010 (E) were followed for calculate retention of tensile property. Air oven (Venticel 222) was used at 70 °C temperature for 72 hours and thereafter kept for 48 hours at room temperature. Dumbbell shape test specimens were tested for tensile stress-strain properties and compared according to the following equation 3.2.

$$\text{Retention of tensile property, \%} = \frac{\substack{\text{Tensile property obtained,}\\ \text{after ageing}}}{\substack{\text{Tensile property obtained,}\\ \text{before ageing}}} \text{ X100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

### 3.2.3.5 Degree of swelling

ISO 1817:2011 describes methods of evaluating the resistance of vulcanized and thermoplastic rubbers to the action of liquids by measurement of properties of the rubbers before and after immersion in test liquids. Three test specimens of (30mm x 10mm x 2mm) for each treatment were tested. The test specimens were immersed in p-xylene for 72 hours in closed lid bottles and weighed the final weight and calculated the degree of swelling (Q) as a percentage according to the equation 3.3.

$$Q\ (\%) = \frac{(\mathrm{M_2 - M_1})}{\mathrm{M_1}}\ X\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3.$$

Where, $M_1$ and $M_2$ are masses of the sample before and after swelling.

### 3.2.3.6 Gel content

Test specimens having dimensions of 1 cm x 3 cm x 0.2 cm were placed in specimen holders and immersed in boiled p-xylene for 16 hours. It was found that during this period all soluble materials in the composites were able to be extracted into p-xylene. The specimens were oven dried at 70 °C until constant weight was obtained (Zhu et al., 2016). Weights were measured to the nearest 0.1 mg. Gel content ($Q'$) as a percentage was calculated according to the equation 3.4 (Bengtsson et al., 2005).

$$\mathrm{Q'}(\%) = \mathrm{m_2/m_1} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4.$$

Where, $m_1$ is the initial weight of the specimen and $m_2$ is the weight of the oven dried gel

### 3.2.3.7 Water absorption

Water absorption was obtained by immersion of test specimens having dimensions of 30 mm x 10 mm x 2 mm for 72 hours in water at room temperature. Increase in weight to the initial weight of the specimen, as a percentage, was reported as the degree water absorption (Q") according to the following equation 3.5.

$$\mathrm{Q''}\ (\%) = \frac{(\mathrm{M_f - M_i})}{\mathrm{M_i}}\ \mathrm{X}\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5.$$

Where, $M_i$ and $M_f$ are masses of the sample before and after water absorption.

### 3.2.3.8 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is an effective analytical tool for screening and profiling polymer samples; a powerful technique to qualitatively identify organic materials and to determine molecular structure. The test pieces obtained from the gel content test were used to obtain the FTIR spectra. A Nicolet 380 FTIR spectrometer was used for the testing. The spectrometer was operated with a resolution of 4 cm$^{-1}$and the scanning range was 400 – 4000 cm$^{-1}$.

### 3.2.3.9 Analysis of thermal properties

The thermal properties of the NR/LDPE composites were examined by different scanning calorimetry (DSC) using NETZSCH-DSC 204 F1 calorimeter. Appoximatly 10 mg was placed in an aluminum pan with a cover and scanned under a nitrogen atmosphere from room temperature to 150 °C. The melting temperature ($T_m$) was determined as the peak temperature of the melting endotherm, and the enthalpy of fusion ($\delta H_m$) was determined as the area of the melting endotherm. The degree of crystallinity ($X_C$) was calculated via the total enthalpy method, according to equation 3.6.

$$X_c, (\%) = \frac{\delta H_m}{\delta H_m^0} \times 100 \ldots\ldots 3.6.$$

Where $\delta H^0$m is the enthalpy of fusion for 100% crystalline LDPE was taken as 288 kJ/kg (Saci et al., 2016).

### 3.2.3.10 Dynamic mechanical properties

Dynamic mechanical properties of the NR/LDPE blends and composites were evaluated using a Dynamic Mechanical Analyzer, DMA Q 800 TA (USA). The dual cantilever mode of deformation was used. Rectangular test specimens having dimensions 40 mm x 12 mm x 2 mm were heated over the temperature range -130 °C to 100 °C, at a rate of 2 °C/min. Liquid nitrogen was used as the cooling medium. Storage modulus (E'), loss modulus (E'') and tan δ of each composite were recorded in temperature sweep mode at a frequency of 1.0 Hz.

### 3.2.3.11 Analysis of morphology using scanning electron microscopy

Surface morphology of tensile fracture surfaces of NR/LDPE blends and composites was examined by Scanning Electron microscopy (SEM) using a ZEISS EVO LS 15 microscope. The specimens were cut and mounted on aluminum stubs. The specimens were sputter coated with a thin layer of gold to avoid electrostatic charging during examination. This analysis was made to study the effect of titanate CA on dispersion and performance of fillers in the polymer matrix for LDPE and NR composites and compatibility of NR/LDPE blends.

### 3.2.3.12. Optical microscopy

Slices of composites having uniform thickness around 0.1 mm were carefully separated from the test specimen using a microtome cutter. The test specimens were maintained at -80 °C using liquefied nitrogen in order to reduce the flexibility of the test specimen during the cutting. Images were obtained at 400 times the level of magnification. The polarized visible light was used as the light source. Images of each sample under the above condition were recorded using the universal software.

## 3.3. Statistical Analysis

One-way ANOVA method was used to evaluate the significance change of tensile strength of blends and composites at a 95% confidence interval and Minitab 17 version was used as a statistical analysis software. It was designed to find whether there is a significant difference in tensile strength in blends and composite (alternative hypothesis) or no any significance difference (null hypothesis) in the blends and composite.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Effect of the Vulcanization System on Properties of 50/50 NR/LDPE Blends

50/50 NR/LDPE composites were prepared with three different vulcanization systems namely sulphur, peroxide and mixed to identify the best vulcanization system.

### 4.1.1 Physico- mechanical properties

Stress-strain curves are an extremely important graphical measure of a material's mechanical properties such as tensile strength, modulus, elongation at break and help in calculating Young's modulus, and explaining material deformation behavior. Stress-strain curves for NR/LDPE blends with and without vulcanization system are shown in Figure 4.1. Stress-strain curves for 50/50 NR/LDPE blends with and without vulcanization system show behavior of a semi-crystalline thermoplastic material. According to the results, the mixed vulcanization system shows the best elongation property and the peroxide vulcanization system shows the best tensile property. The highest stress value exemplify in the peroxide method this means it has the highest degrees of crystallinity compared to the other vulcanization system (Dluzneski., 2001).

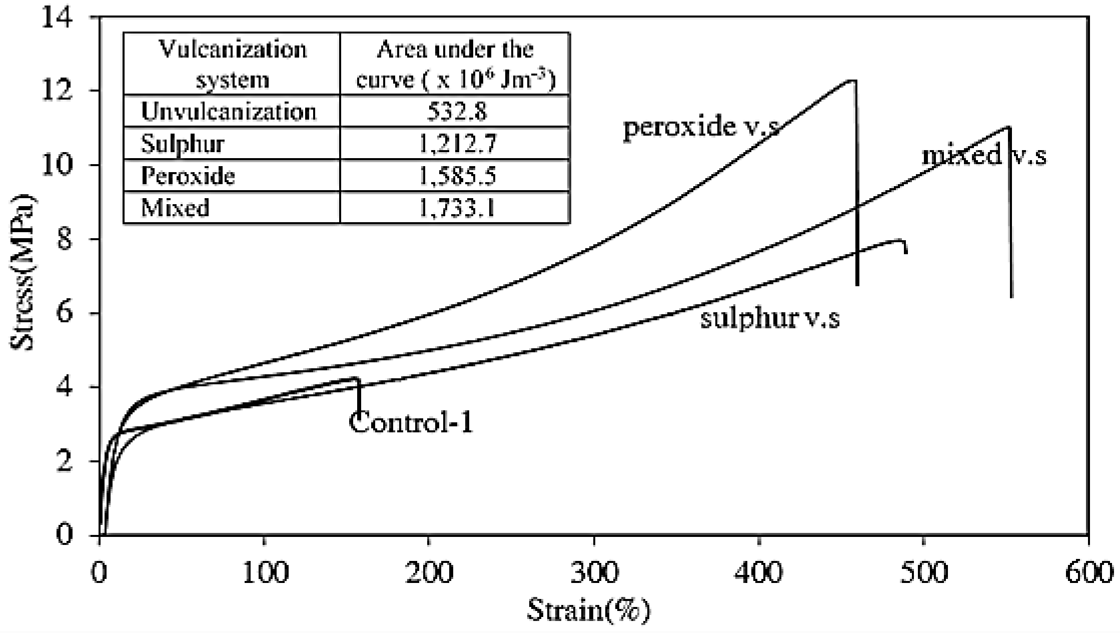


Figure 4.1: Stress-strain curves of 50/50 NR/LDPE blend prepared with different vulcanization systems

The blend prepared with mixed and peroxide vulcanization systems showed good tensile strength compared to Control-1 and sulphur vulcanization system. Therefore, peroxide and mixed composite indicate good inter molecular interactions and a lower surface tension (Rector., 2006). In previous litteratrure, NR/HDPE blends with various types of blend compatibilizers were prepared by different vulcanization system namely sulphur, peroxide and mixed vulcanization systems. It reported that, mixed vulcanization system showing the highest shear stress and tensile strength, whilst the sulphur vulcanization system gave the lowest values, and the peroxide vulcanization system exhibited intermediate values (Nakason, C et al., 2006).According to the statistical analysis (one way ANOVA) at 95% confidence interval there is an Effect of vulcanization system on properties of 50/50 NR/LDPE blends (p=0.000). Control-1 indicates the lowest tensile value while it has not added curatives that mean it has not illustrate fine phase morphology according to Figure 4.13.

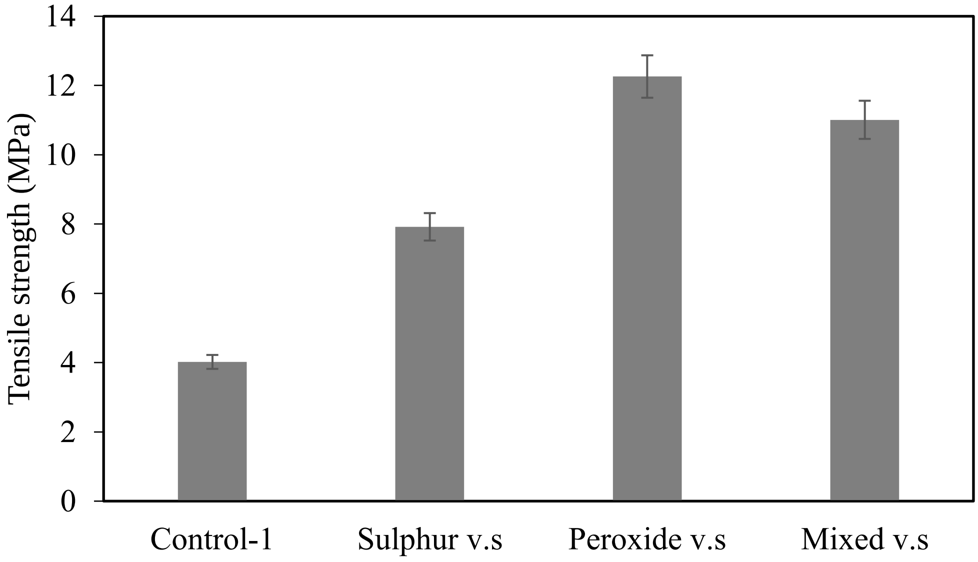


Figure 4. 2: Tensile strength of 50/50 NR/LDPE blends prepared with different vulcanization systems

Elongation is an interesting result to explain elasticity and amorphous behavior of a material. The Control-1 shows the lowest elastic properties than the other blends, as it does not contain any vulcanization agents and it has no phase interaction. Crystalline materials show low elongation properties (Monticelli., 2012) and Figure 4.3, indicates the presence of a crystalline phase in the Control.

Two different types of network structures are formed during dynamic vulcanization using sulphur and peroxide systems (Ghosh et al., 1992). The mono-, di- and poly-sulphidic linkages in sulphur system impart high chain flexibility to the polymer network. In the peroxide vulcanization system, only rigid C-C linkages are present. Figure 4.4 provides evidence that sulphur to increase elongation property of a material and peroxide helps to increase strength of a material. Due to presence of C-C, C-S and S-S linkages in NR phase of the blend, the blend with the mixed vulcanization system became more flexible, and less strength compared to the blend with peroxide vulcanizing system.

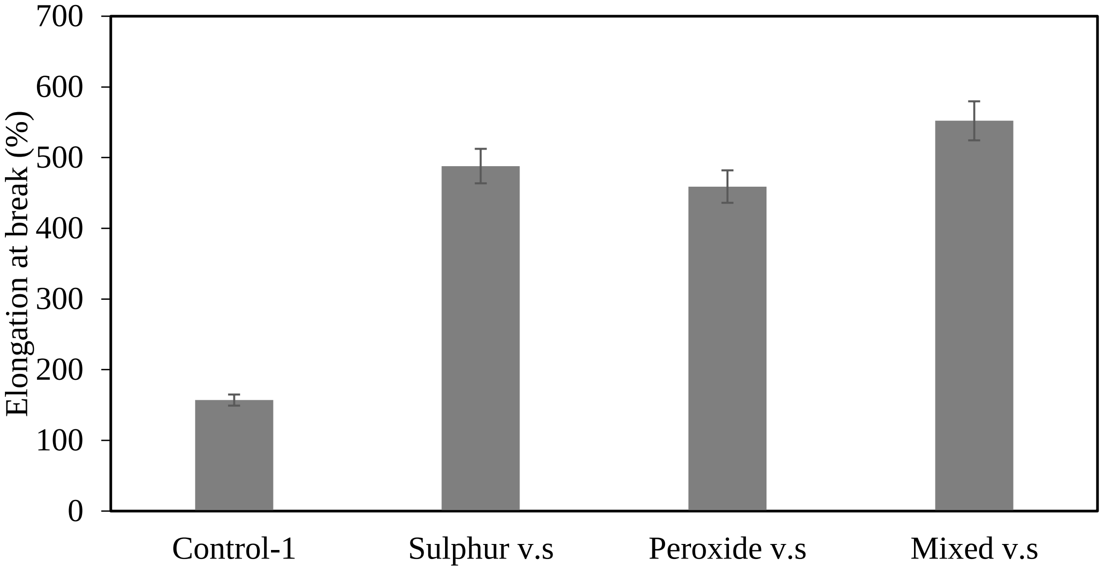


Figure 4.3: Elongation at break of 50/50 NR/LDPE blend prepared with different vulcanization systems

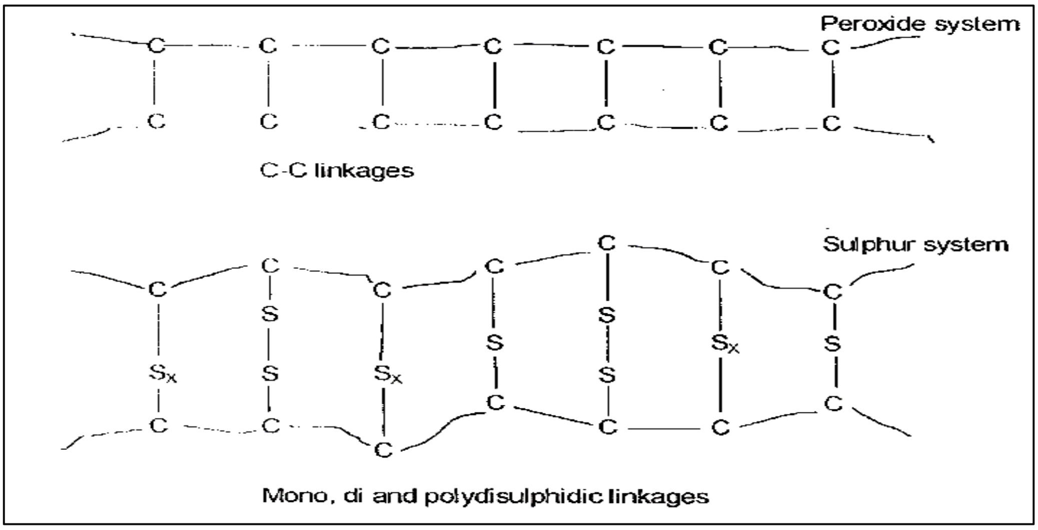


Figure 4.4: Structure of the network formed by different cross-linking systems: peroxide (DCP), and sulphur systems (Ghosh et al., 1992).

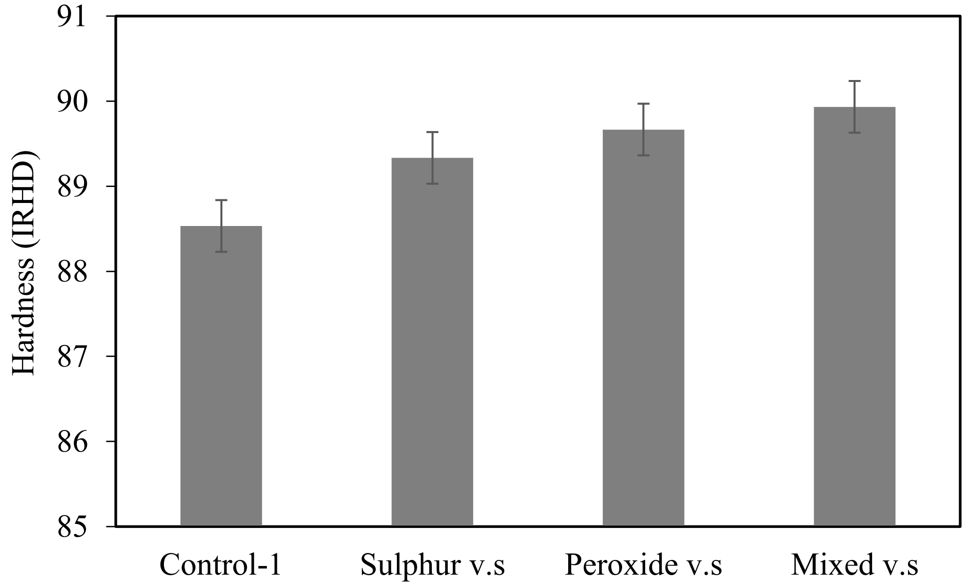


Figure 4.5: Hardness of 50/50 NR/LDPE blends prepared with different vulcanization systems

Hardness is referred to as a measure of modulus at low elongations and reflects the cross-link density of a material. The lowest hardness was obtained for the Control-1 where the crosslinking agent was not included. The highest value was from the blend with mixed vulcanization system. According to the Figure 4.5, hardness of all blends was higher than 88 IRHD and it indicates that the continuous phase of the compounds were LDPE. The blend with sulphur vulcanization system showed higher hardness than the Control-1 and is due to formation of sulphur crosslinks in the NR phase. DCP forms crosslinks in both phases and hence the blends with the peroxide vulcanization system, and with the mixed vulcanization system, showed increased hardness compared to that with the sulphur vulcanization system. Further, the area under the stress-strain curve is helped to explain elastic potential energy of polymeric materials. The blend prepared with mixed vulcanization system showed the highest elastic potential energy (1733.1x $10^6$ $Jm^{-3}$) according to Figure 4.1. Hence, the highest toughness is shown by the blend with the mixed vulcanisation system compared to other counterparts.

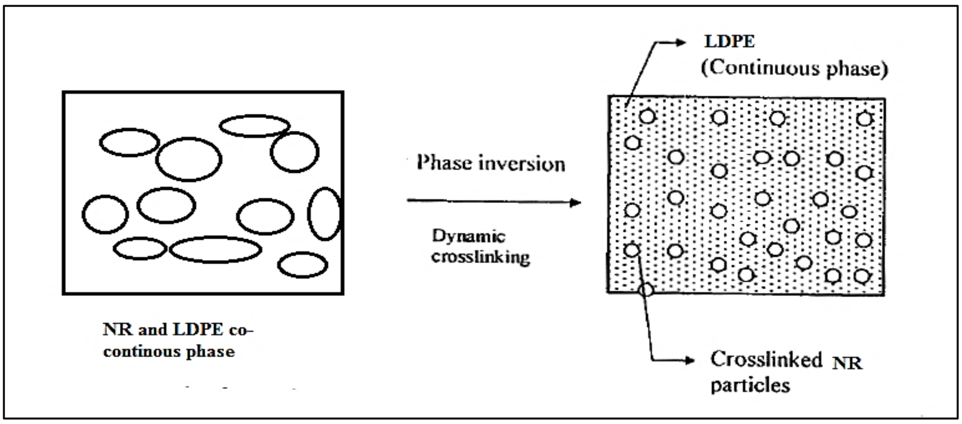


Figure 4.6: Phase morphology of dynamically vulcanized 50/50 NR/LDPE blends

Tear strength indicates the crack propagation property of a material. If the tear strength is high, the material has a good adhesion and finer phase morphology between the NR and the LDPE phases, Hence it would be helped to improve tear properties of NR/LDPE blends. According to Figure 4.7, blend prepared with vulcanization systems showed improved tear strength than Control-1. Further, homogenous phases are illustrate better tear strength due to increase of interaction between two polymer phases. Hence the mixed vulcanization system indicates good less heterogeneity between the NR and the LDPE phases.

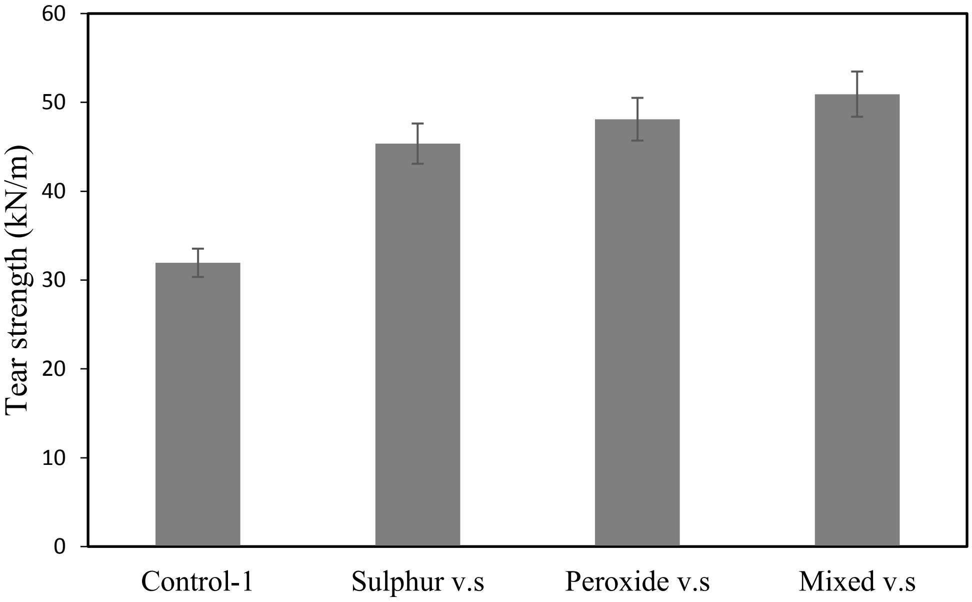


Figure 4.7: Tear strength of 50/50 NR/LDPE blends prepared with different vulcanization systems

### 4.1.2 Ageing properties

Stress – strain curves Figure 4.8, show a similar behavior (semi crystalline) to those obtained for the NR/LDPE blend, before aging. The blend prepared with the mixed vulcanization system showed better ageing properties compared to the other counterparts. The observed improvements in mechanical and ageing performance were attributed to chain entanglement and co-crosslinking in the interphase between the GTR particles and the surrounding matrix, i.e. with the virgin rubber and/or LDPE (Radheshkumar et al., 2002).

In addition, the highest strain value elucidates from the mixed vulcanization system as in the before aging stress strain curve in (Figure 4.1). Further, the mixed vulcanization system indicates good thermal stability and good heat resistivity compared to the counterparts.

All the vulcanization system and Control-1 show good retention of elongation at break and tear strength. In contrast, all the vulcanization system and Control-1 show low retention of tensile strength. Therefore, these blends are not at the required level in regard to resistance to thermal degradation in terms of retention of tensile strength. It was reported that, oxidative thermal ageing of a polymer blend or composite is a free radical oxidative degradation process due to molecular oxygen and thermal energy. Development of free radical on NR and LLDPE is the rate determining step of the thermal oxidative degradation process for NR and LDPE and it depends on bond dissociation energy of C-H bond (Gajanayake., 2014).

According to Table 4.1, peroxide vulcanization system shows very low retention of tensile strength properties (physical ageing) and indicates the initiation of radical reaction between C-C under the ageing condition. Carig. (2006) has reported that the changes in the polymer properties under the different environmental and processing conditions are termed ageing. Polymers have been known to demonstrate two kinds of ageing: chemical and physical ageing. Chemical ageing is thermal degradation, photo oxidation, etc. and the changes are connected with degradation and lead to molecular chain scission and/or crosslinking. The result is cracking and chemical disintegration of polymers. Therefore, percentage retention of properties after ageing is generally less than 100.

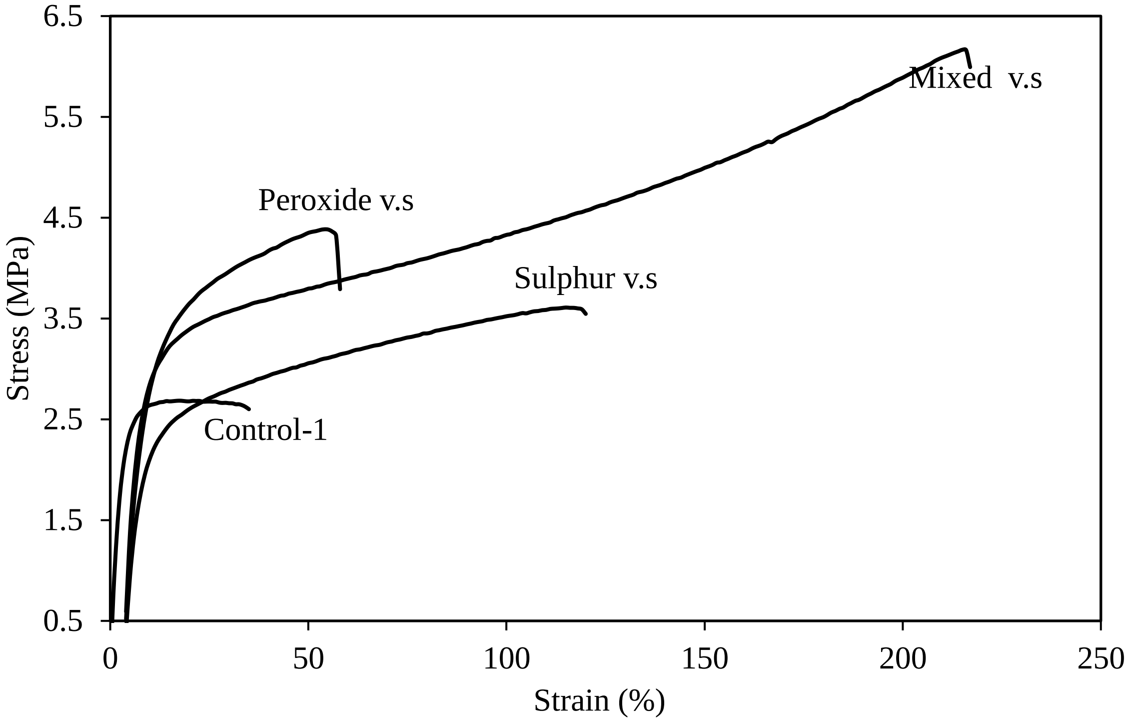


Figure 4.8: Stress – strain curves of 50/50 NR/LDPE blends after ageing

Table 4.1: Retention percentage of mechanical properties of 50/50 NR/LDPE blends

| **Vulcanization system in the blend** | **Retention of tensile strength (%)** | **Retention of elongation at break (%)** | **Retention of tear strength (%)** |
|---|---|---|---|
| Control | 65 | 42 | 82 |
| Sulphur | 44 | 88 | 87 |
| Peroxide | 35 | 96 | 85 |
| Mixed | 54 | 102 | 90 |

### 4.1.3 Degree of swelling and gel content

The swelling behaviour of a thermoplastic material defines the chemical or liquid absorption capacity of it or its compound. If the compound shows a higher percentage of swelling it can absorb a high amount of liquid without dissolving in the same. The mobility of the penetrant through the polymer chains depends upon the free volume in the matrix. According to free volume theory (Harogoppad, 1991), the rate of diffusion depends upon the ease with which polymer chain segments exchange their positions with penetrant molecules.

The degree of swelling of the 50/50 NR/LDPE blends with the peroxide vulcanization system and with the mixed vulcanization system is shown in Figure 4.9. Control-1, which was prepared without any vulcanization system, and the blend with sulphur vulcanization system, were greatly dissolved in p-xylene and hence it was difficult to conduct the swelling test for the said blends. The LDPE continuous phase in the blend with the sulphur vulcanization system was not cross-linked by sulphur and hence it was also dissolved. C-C crosslinks formed with a peroxide vulcanization system are more rigid and stable under heat compared to C-S crosslinks formed with a sulphur vulcanization system (Dluzneski., 2001). Also, C-C crosslinks are shorter than sulphur crosslinks and hence penetration of solvent molecules through a peroxide vulcanized network would be difficult than through a sulphur vulcanized network and this results in a higher degree of swelling for the latter. A higher degree of swelling reflects lower gel content. According to the Figure 4.9, blends prepared with peroxide and the mixed vulcanization system have good solvent resistance compared to the blend prepared with sulphur vulcanization system and the Control-1.

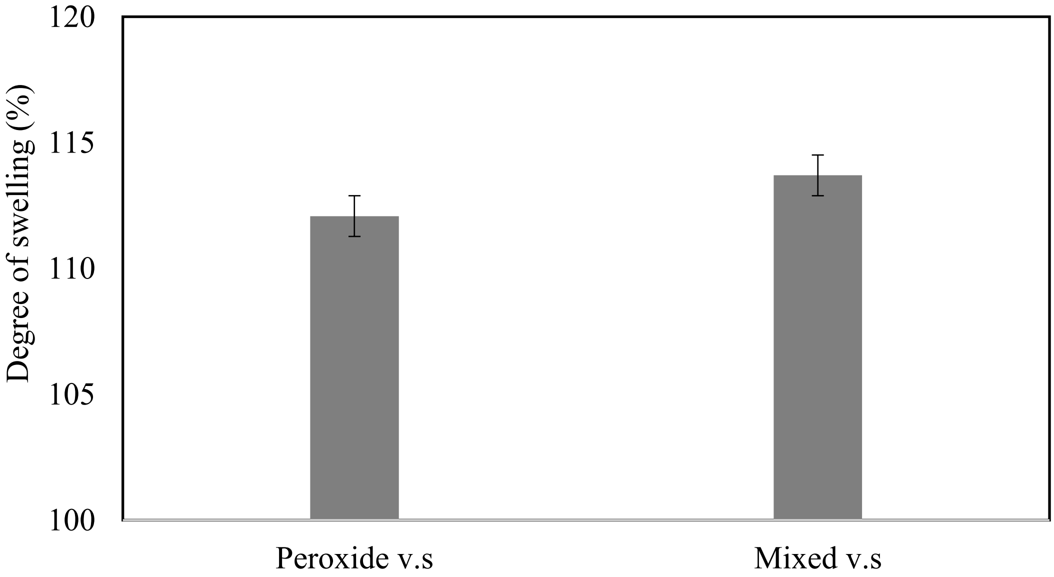


Figure 4.9: Degree of swelling of the 50/50 NR/LDPE blends prepared with the peroxide and the mixed vulcanization systems

The gel content test is used for defining the solvent resistance of a thermoplastic or rubber compound. Crosslink density of a material is directly proportionate to the gel content. When the gel content is high, percentage swelling will be reduced. Figure 4.10 shows that the gel content of the blend prepared with the peroxide vulcanization system is markedly higher than that of the blend prepared with the sulphur vulcanization system. The blend prepared with the mixed vulcanization system has the highest gel content and indicates the highest crosslink density due to good chemical interaction with NR and LDPE. Further, vulcanization system prepared with sulphur shows the lowest gel content due to more interaction of sulphur with bound rubber compared to other blends (Ahamed, 2004).

Figure 4.11, shows the FTIR spectra of the NR/LDPE blends which were prepared with the peroxide vulcanization system and the mixed vulcanization system. Both these NR/LDPE blends have a strong stretching absorption around 1376 cm$^{-1}$ (see Appendix A). This peak confirms the presence of LDPE and it is evidenced for the amount of crosslinks present in the LDPE phase of the blend. In addition, the peak at 840 cm$^{-1}$ (see Appendix A) corresponding to NR appears in both blends. Hence, both sulphur and peroxide vulcanization systems are presented crosslinked LDPE and crosslinked NR phases. Therefore, this is evidence for the high gel content of NR/LDPE blend prepared with the mixed vulcanization system.

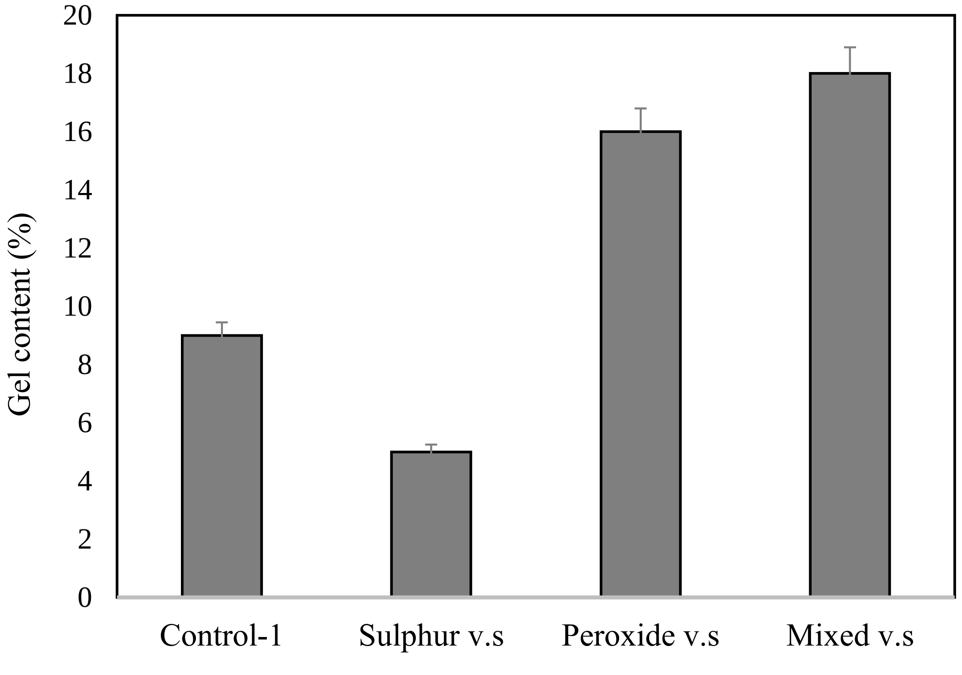


Figure 4.10**:** Gel content of 50/50 NR/LDPE blends prepared with different vulcanization systems

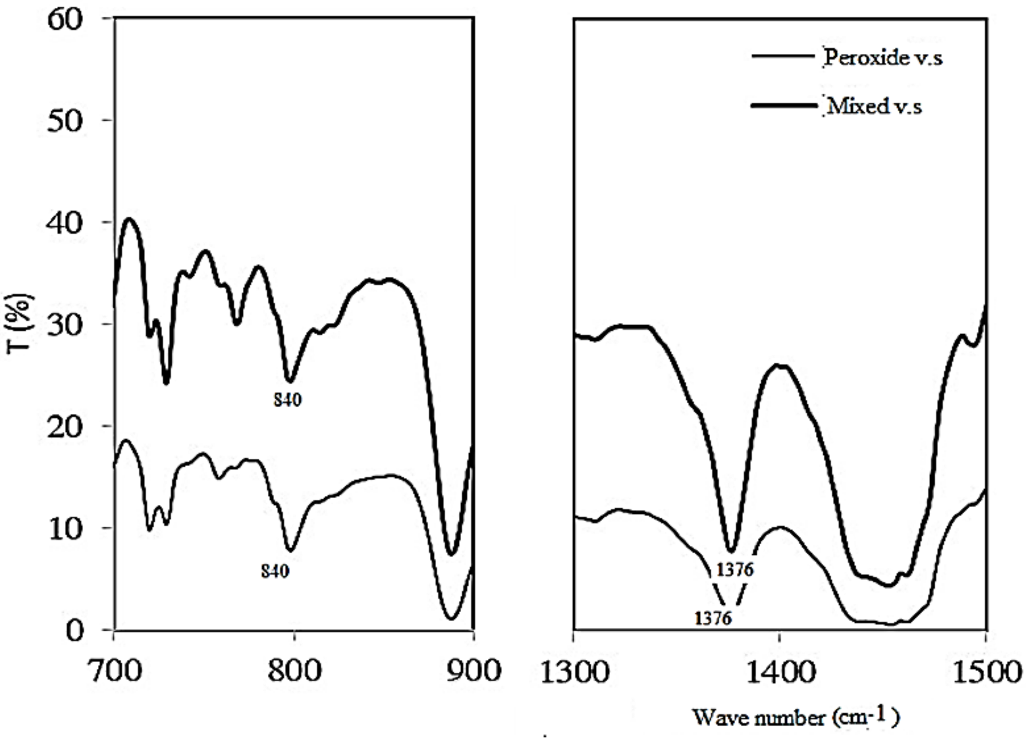


Figure 4.11: FTIR Spectra of gels of 50/50 NR/LDPE blends prepared with the peroxide and the mixed vulcanization systems

### 4.1.4 Water absorption

According to Figure 4.12, blends prepared with the peroxide and the mixed vulcanization systems show low water absorption indicating higher water resistance. Further, blend prepared with the sulphur vulcanization system shows the highest water absorption. As sulphur is an inorganic ingredient and hence it does not react with organic polymer. On the other hand, peroxide is an organic ingredient and hence it has good compatibility and interface adhesion with NR and LDPE. It has been reported that blends become stiffer and less penetrable by the water molecules as the crosslink density of the rubber phase is increased. Therefore, the declining trend of percentage of water absorbance with increasing vulcanization agents level provides a clear indication of the increase in the crosslink density in the rubber phase of the blends with increasing vulcanization agent concentration. Similar observation has reported elsewhere for NR/PP blends and their composites (Ismail et al., 2001). In addition Rani et al. (1999) has reported that BR/LDPE blend prepared with sulphur vulcanization system showed high water absorption than peroxide vulcanization system due to inorganic nature of sulphur.

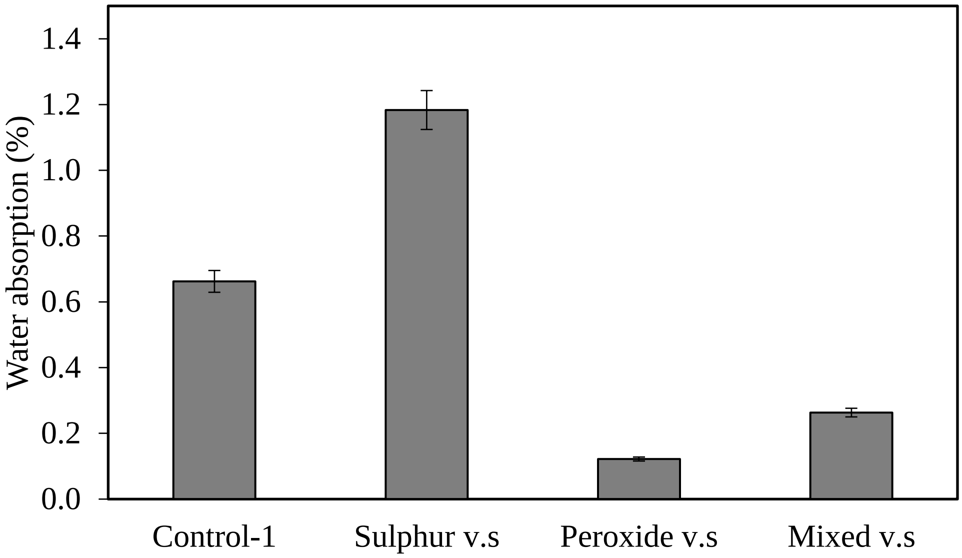


Figure 4.12: Water absorption of 50/50 NR/LDPE blends prepared with different vulcanization systems

### 4.1.5. Morphology

Figure 4.13, (c) and (d) show smoother and fine fracture surface compared to (a) and (b). Further 4.13 (a) and (b) show coarse phase morphology. Figure (a) shows a clear separation of NR and LDPE phases, probably due to poor interfacial adhesion between the phases due to the absence of any crosslinks. This phase separation indicates incompatibility between NR and LDPE, which results in poor mechanical properties. The morphological analysis shows that interfacial adhesion between NR and LDPE phases is at the highest level when a mixture of sulphur and peroxide is added as the vulcanization system. Further, the 50:50 NR/LDPE blend prepared with the mixed vulcanization system shows a higher gel content, which means there is good interaction between the NR and LDPE phases. This blend is the least heterogeneous according to its phase morphology shown in Figure 4.13 (d). Results in overall indicate that the 50/50 NR/LDPE blend prepared with the mixed vulcanization system would be suitable to manufacture heat and solvent resistant products.

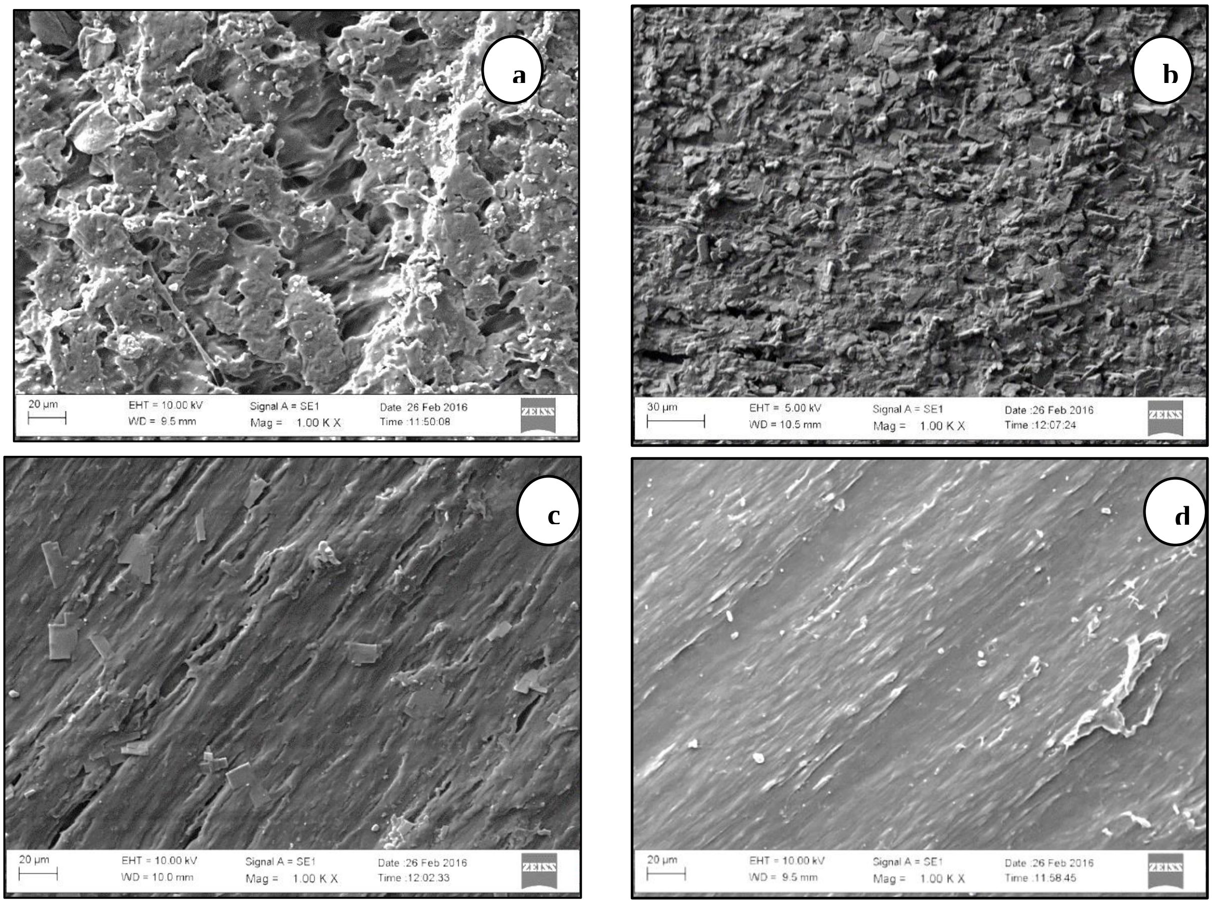


Figure 4.13: Scanning electron micrographs of tensile fracture surfaces of 50:50 NR/LDPE blends

(a) Control-1 (b) vulcanized with sulphur

(c) vulcanized with DCP (d) vulcanized with the mixed vulcanization system.

## 4.2 Effect of Blend Ratio on Physical Properties of NR/LDPE Unfilled Blends

### 4.2.1 Physico-mechanical properties

Stress-strain curves of unfilled NR/LDPE blends prepared according to different blend ratios are shown in Figure 4.14. The stress-strain curve for pure LDPE is also given for comparison. Stress-strain curves for blends having LDPE loading of 10 pphp shows the nature of a highly elastic and soft material and lie well below those of other blends. As LDPE loading increases, nature of the blends changes from soft to hard. Tensile strength and elongation at break obtained from stress-strain curves are shown in Figure 4.15 and Figure 4.16, respectively.

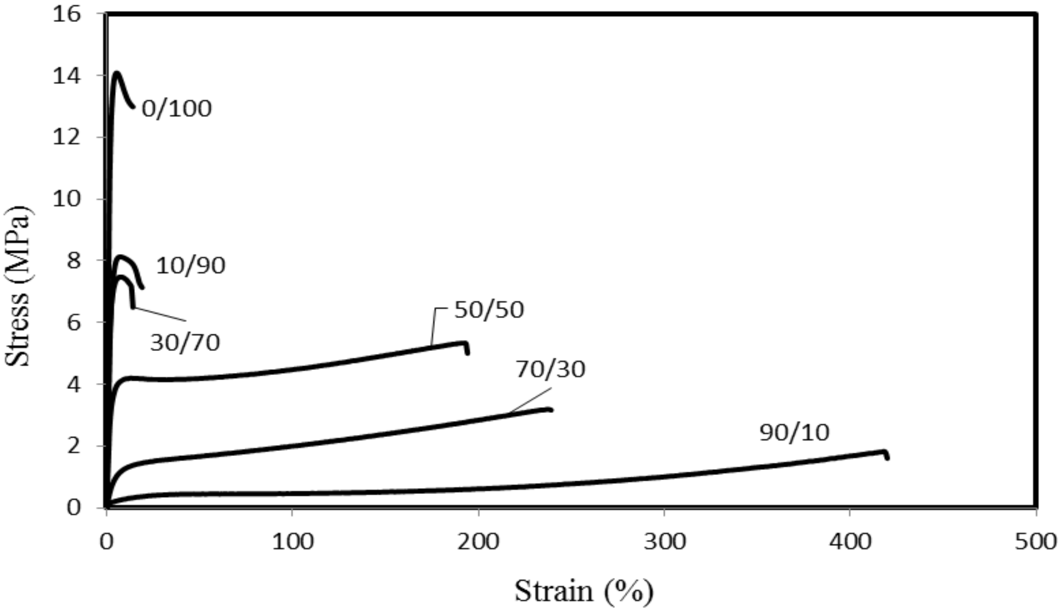


Figure 4.14: Stress-strain curves of NR/LDPE blends at different blend ratios

It can be seen that the tensile strength increases with the increase of LDPE loading. Pure LDPE presents the highest tensile strength than the blends. LDPE is hard and semi crystalline, and hence it exhibits a high tensile strength. Figure 4.16 indicates a decrease in elongation at break with increase in LDPE loading. Blends with dispersed rubber phase in thermoplastic continuous phase generally exhibit increased stiffness and strength, and decreased flexibility. Low level of homogeneity of blends may also result in rapid decrease in elongation at break of blends (Sombatsompop et al., 2001). Further, it was reported that, elongation at break of NR/LLDPE blends at every composition were greater than those of NR containing compound prepared without LLDPE. When tensile properties of the blends are concerned, they decreased with increase in LLDPE loading (Gajanayake et al., 2012). According to the statistical analysis (one way ANOVA ) at 95% confidence interval, there is an effect of blend ratio on properties of NR/LDPE unfilled blends (p= 0.000). It was concluded that the blends with LLDPE loading from 10 pphp up to 40 pphp show higher tensile properties than the NR compound (Gajanayake et al., 2012).

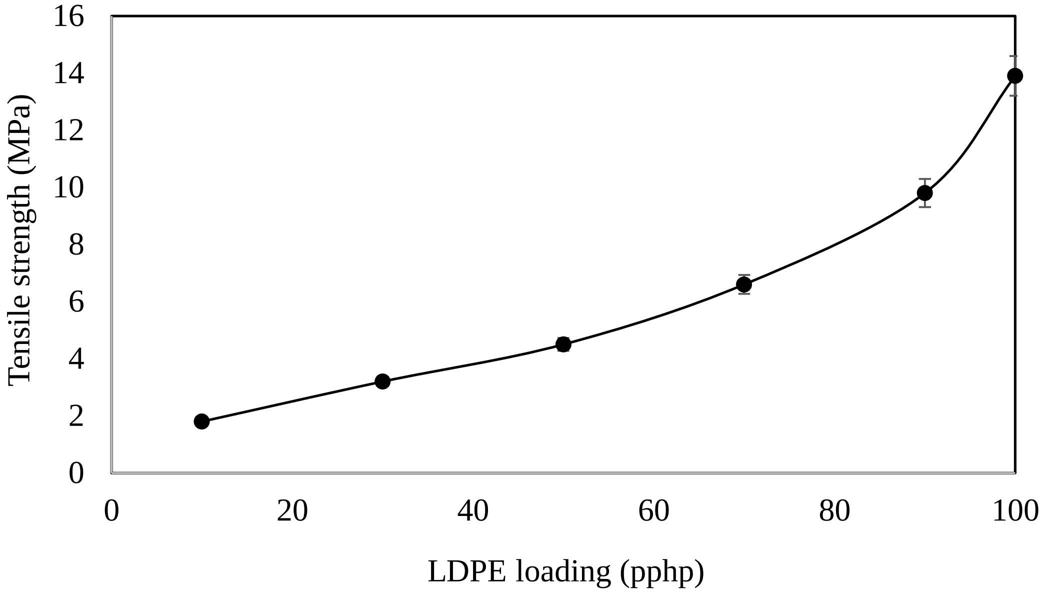


Figure 4.15**:** Tensile strength of NR/LDPE blends at different blend ratios

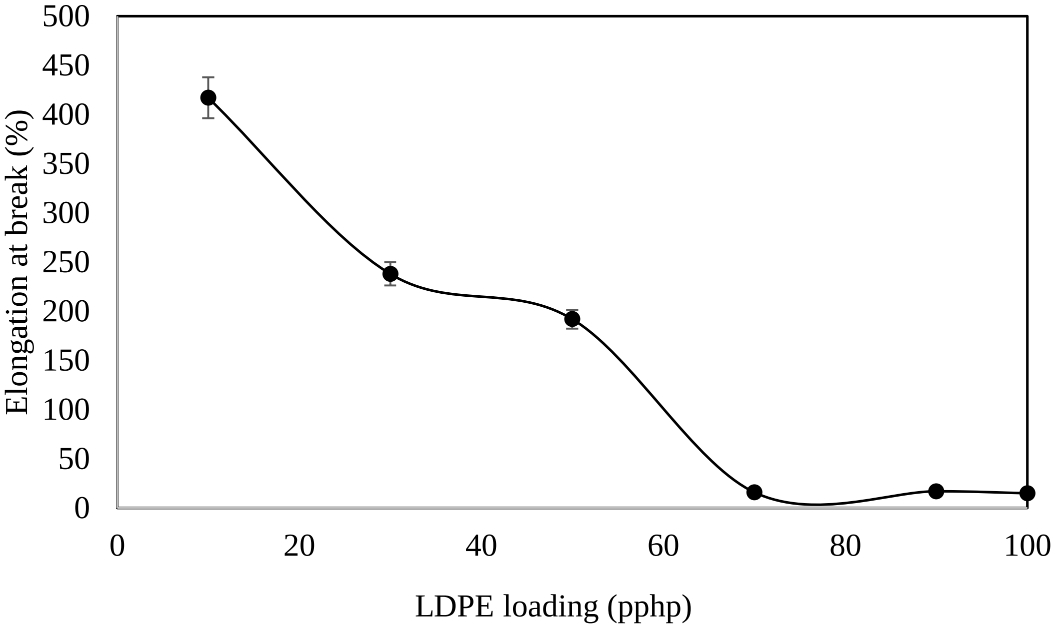


Figure 4.16**:** Elongation at break of NR/LDPE blends at different blend ratios

Variation of tear strength of the blends, which is illustrated in Figure 4.17, is similar to tensile strength. Further, tear strength increases significantly from 30 pphp to 50 pphp of LDPE loading. This may be attributed to the phase change and further to increased interfacial adhesions developed in NR/LDPE blends. Stress-strain curves in Figure 4.14 proved the phase change from 30 pphp to 50 pphp of LDPE loading. Further, tear strength difference between blend prepared with is 27 kN/mm. Consequently, it would additionally prove that phase change from 30pphp to 50pphp LDPE loadings.

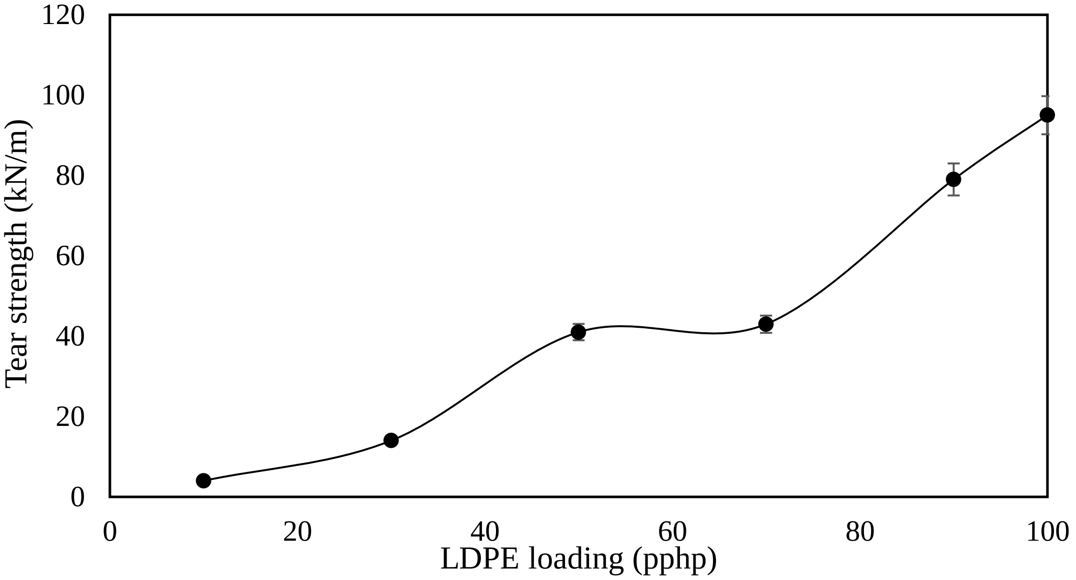


Figure 4.17**:** Tear strength of NR/LDPE blends at different blend ratios

Variation of hardness of the blends is shown in Figure 4.18. Hardness below 50 pphp of LDPE loading is less than that of the other blends. Similar to the variation of tear strength, hardness drastically increases from 10 pphp to 50 pphp of LDPE loading. These physical properties conform that a phase change from soft to hard will occur after 30pphp LDPE loading. Further, Figure 4.18 indicates a increase in hardness with the increase of LDPE loading. Due to the high degree of crystallinity, high LDPE loaded blends are significantly harder than low LDPE loaded blends. The hardness of the material is predominantly governed by the continuous phase of the blend. Therefore, it could be inferred that addition of more than LDPE has not resulted in a phase inversion of the blend. Gajanayake et al. (2012) have reported a similar variation for NR/LLDPE blends.

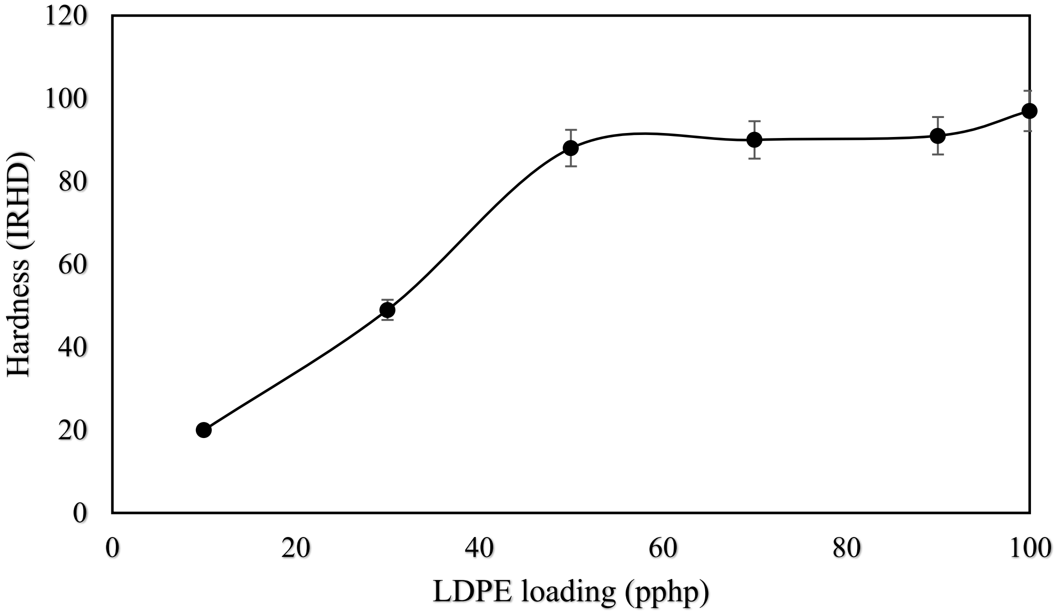


Figure 4.18: Hardness of NR/LDPE blends at different blend ratios

### 4.2.2 Glass transition temperature

DSC thermograms for NR/LDPE blends are shown in Figure 4.19. Glass transition temperature of NR phase in NR/LDPE blends is lower than room temperature. A lower Tg is desirable, because it reduces the lower service temperature of the final blend (Willis et al., 1984). It can be seen from Figure 4.19 that Tg of the blends slightly increase, with LDPE loading. The slight but significant variation suggests a considerable effect on the NR phase by the LDPE phase. This may be due to development of interfacial adhesion between the two phases (Radheshkumar et al., 2002).

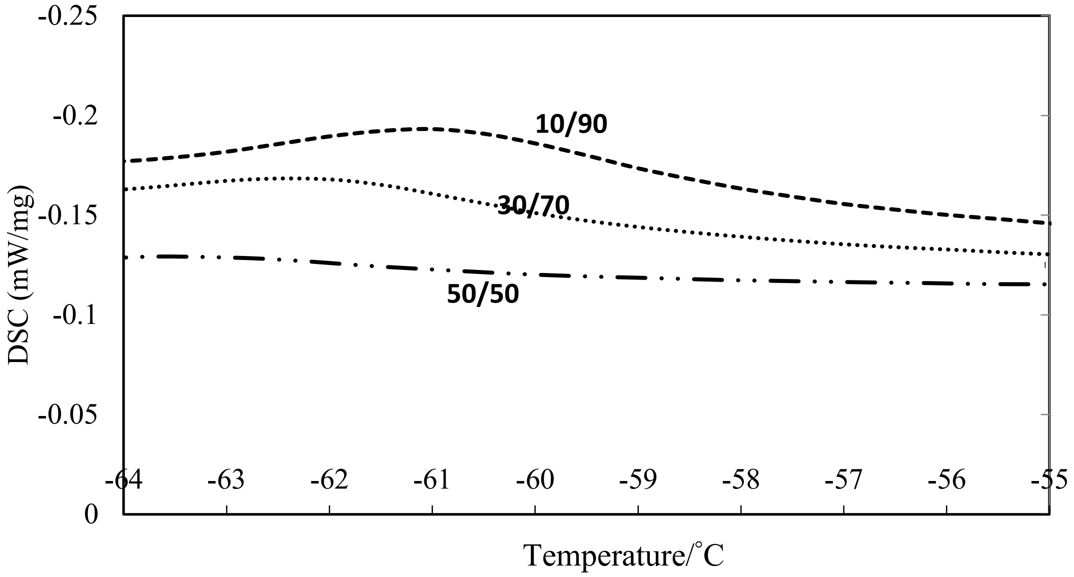


Figure 4.19: DSC thermograms of NR/LDPE blends at different blend ratios

### 4.3 Effect of Titanate Coupling Agent on Properties of NR/LDPE/ Composites

NR/LDPE composite was prepared with and without conventional type titanate based coupling agent and properties were evaluated. 20 pphp of $CaCO_3$ and 0.5 pphp of titanate CA were used to study the performance of NR/LDPE blends

#### 4.3.1 Physico-mechanical properties

Stress-strain curves for NR/LDPE composites at different blend ratio without titanate CA showed the conduct of semi-crystalline thermoplastic material from 30 pphp to 90 pphp of LDPE loading. The blend of NR/LDPE having 10 pphp of LDPE loading displayed the performance of a highly elastic and soft material. Stress-strain curves for NR/LDPE blends with titanate CA are also showed similar behaviors which are shown in Figure 4.20. Stress-strain curves for NR/LDPE composites having LDPE loading from 50 pphp to 90 pphp and pure LDPE show behavior of a semi-crystalline thermoplastic material. NR/LDPE composites having 10 pphp and 30 pphp shows a behavior of a rubber. This change in bahaviour suggests that a phase change of the composites would occur from 30 pphp to 50 pphp of LDPE loading.

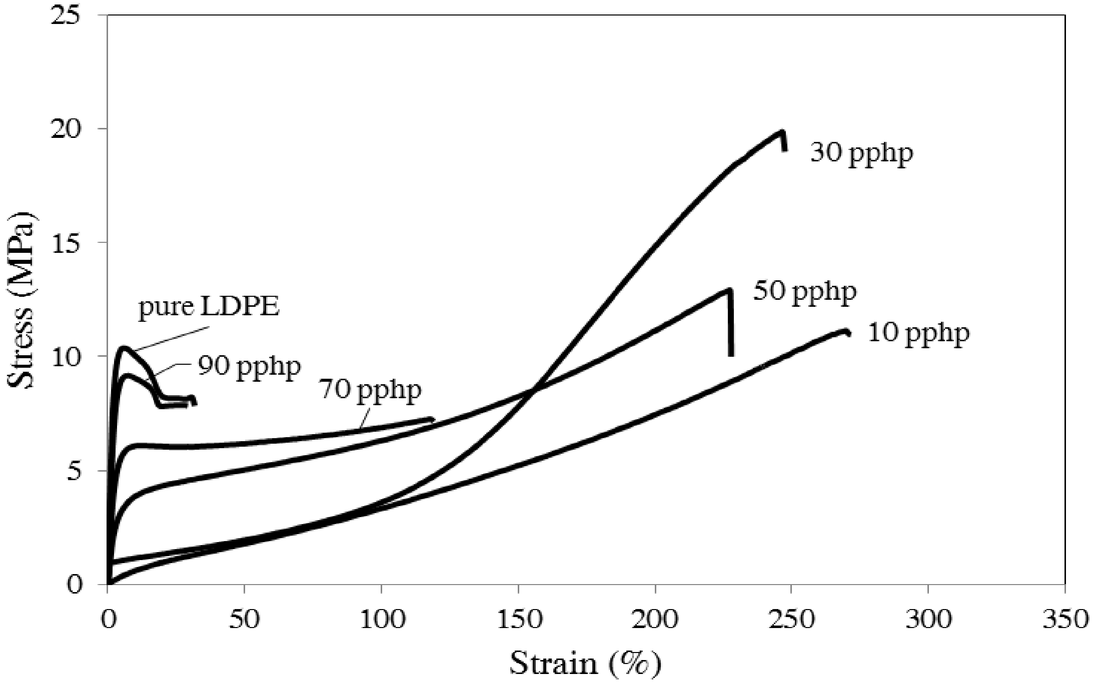


Figure 4.20: Stress-strain curves of NR/LDPE composites with titanate CA at different blend ratios

Tensile properties shown in stress-strain curves for NR/LDPE composites with and without titanate CA are shown in Figure 4.21 and Figure 4.22. Tensile strength of NR/LDPE composites without titanate CA display an initial rise up to 50 pphp of LDPE loading, and then reaches a plateau. Tensile strength of the NR/LDPE composites with CA rises up to 30 pphp of LDPE loading and then reduces. The growth in tensile strength is comparatively more distinct with the composites containing $CaCO_3$ with titanate CA. The causing reinforcement is a function of the amount of $CaCO_3$ dispersion within the polymer matrix, and the possibility of interaction of titanate CA with the polymers. Strong connections among filler particles and macromolecular chains of the polymeric matrix through a CA will lead to profound variations at the interfacial phase (Doutnoune et al., 2008). Tensile strength of NR/LDPE composites having 30 pphp LDPE loading is 6.9 MPa and the same with titanate CA is 18.8 MPa. 172 % increase of tensile strength suggests that the added 20 pphp of $CaCO_3$ provide the highest reinforcement at that LDPE loading. Titanate CA at the loading of 0.5 pphp develops adhesion between NR, LDPE and $CaCO_3$ and increases dispersion of $CaCO_3$ so that agglomerations causing compactness can be eliminated. The gradual reduction in tensile strength after 30 pphp LDPE loading is linked with reduced dispersion of $CaCO_3$. As LDPE loading rises, dispersion of $CaCO_3$ becomes reduced efficient due to higher compactness and hindering role of the titanate CA. Accordingly, higher LDPE loading tend to decrease activity of titanate CA. As per the statistical study (one way ANOVA ) at 95% confidence interval there is an influence of titanate CA on properties of NR/LDPE composites (p= 0.000).The surface activity is an significant feature, representing the extent of polymer-filler interaction. With good polymer-filler interaction, there would be growths in modulus as well as mechanical possessions.

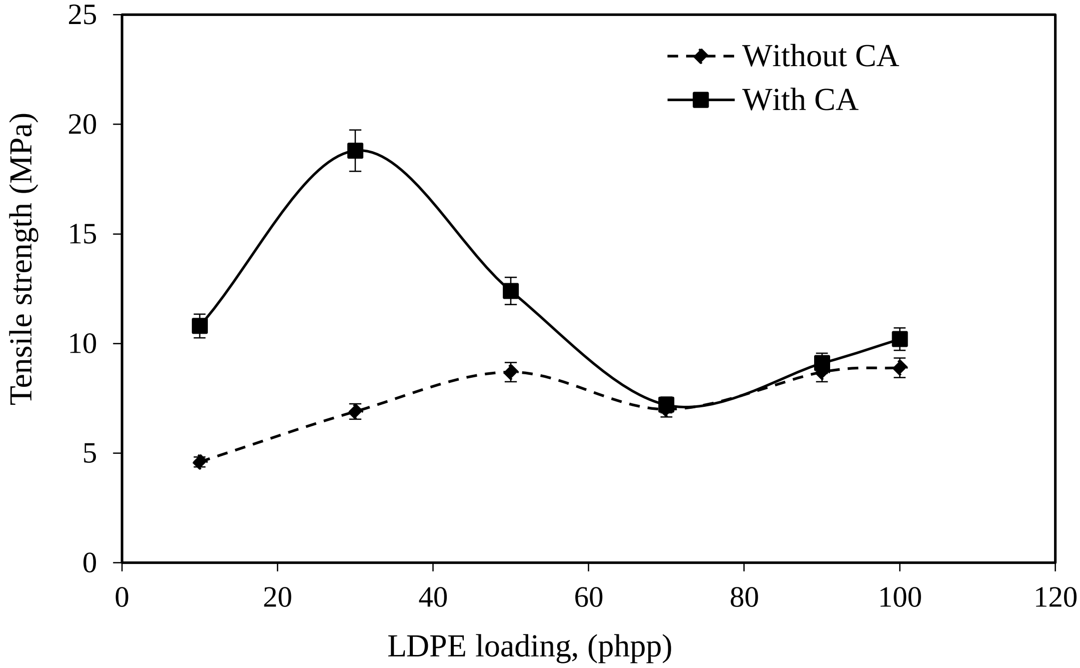


Figure 4.21: Tensile strength of NR/LDPE composites, with and without titanate CA

Figure 4.22 displays that elongation at break reductions regularly with the growth of LDPE loading for NR/LDPE composites with and without titanate CA. This reduction in elongation is because of the replacement of more elastic NR by semi-crystalline LDPE. Nevertheless, NR/LDPE mixtures with titanate CA show advanced elongations at every LDPE loading. Additional, this growth is significant at lower LDPE loadings. This suggests that poor bond between NR and LDPE phases and/or reduced dispersion of $CaCO_3$ occurred with NR and LDPE in the lack of titanate CA. Dispersion of inorganic fillers and their connection to an organic substrate is hard due to most thermoplastics and rubbers are non-polar materials. Titanate CAs are well-known as adhesion promoters for non-polar materials (Monte, 2005). The coupling of titanate to inorganic/organic substrate in monolayers lets for removal of air voids, enhanced hydrophobicity, and a fully continuous phase for stress/strain transfer (Monte, 2005). Figure 2.15 (Chapter 2) displays how filler is dispersed in a polymer matrix with and without titanate CA.

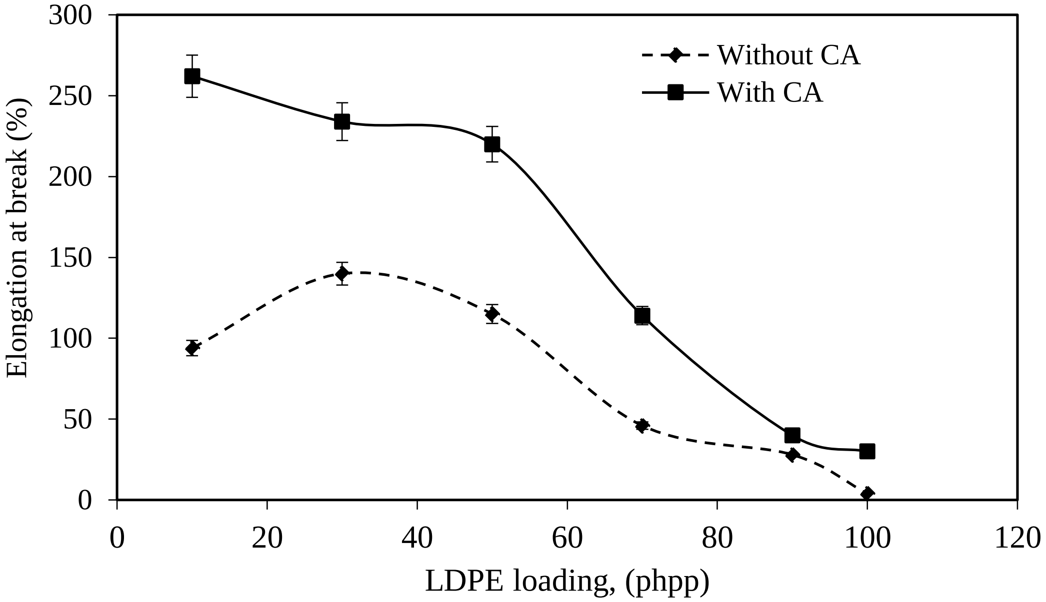


Figure 4.22: Elongation at break of NR/LDPE composites, with and without titante CA

Tear strength of NR/LDPE blends with and without CA are showed in Figure 4.23. Tear strength rises expressively with LDPE loading for both series of blends. This is attributed to interchange of NR with semi- crystalline LDPE and additional to the phase change suggested. Higher tear strengths of blends with CA at each LDPE loading is because of the enhancement of interfacial bonds between NR, LDPE and $CaCO_3$ promoted with the activity of titanate CA.

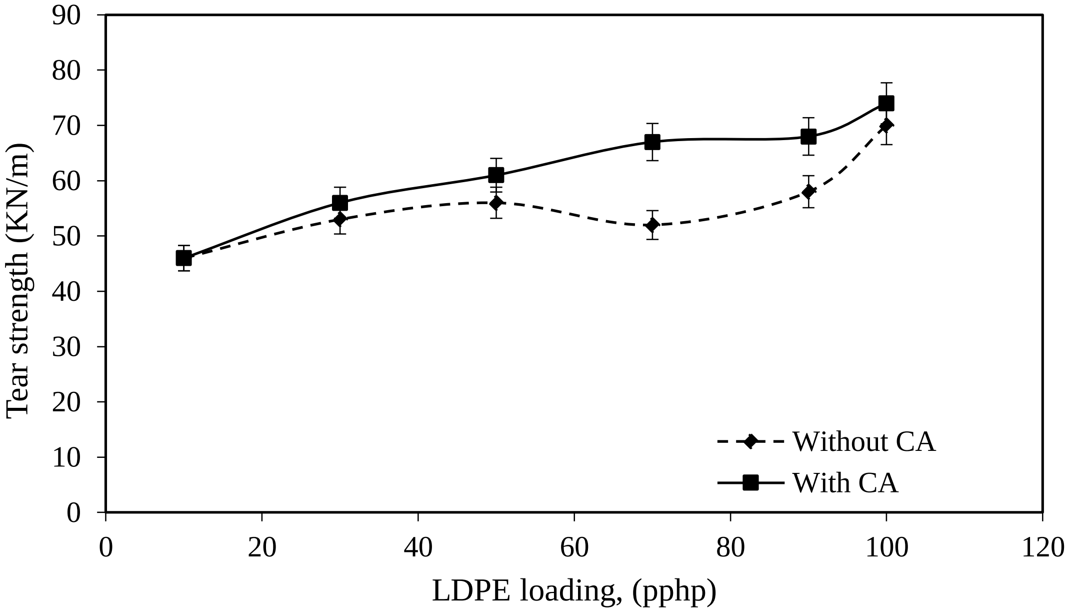


Figure 4.23: Tear strength of NR/LDPE composites, with and without titanate CA

Variation of hardness of NR/LDPE composites with and without titanate CA is shown in Figure 4.24. Hardness up to 50pphp of LDPE loading shows a gradual increase with replacement of soft NR by hard and semi-crystalline LDPE. At higher LDPE loadings, hardness is not changed and is similar to pure LDPE. This unchanged high hardness of NR/LDPE composites having LDPE loading above 50 pphp confirms that LDPE is the matrix phase in these NR/LDPE blends. This confirms again that a phase change has happened from 30 pphp to 50 pphp of LDPE loading. Improved hardness of the NR/LDPE compounds with CA is due to good linkage of $CaCO_3$ with NR and LDPE and better dispersion of $CaCO_3$ in NR and LDPE. Density of NR/LDPE composites reductions slowly with increase in LDPE loading due to interchange of high density NR from LDPE. Density of NR/LDPE composites lie in between 1.02 and 1.06 g/cm$^3$. In addition, $CaCO_3$ is an inorganic filler, which performs as inert filler (non-reinforcing filler) because of the non-reactive functional groups on the surface. Thus $CaCO_3$ is better dispersed and hence, its non-reinforcing effect is more significant.

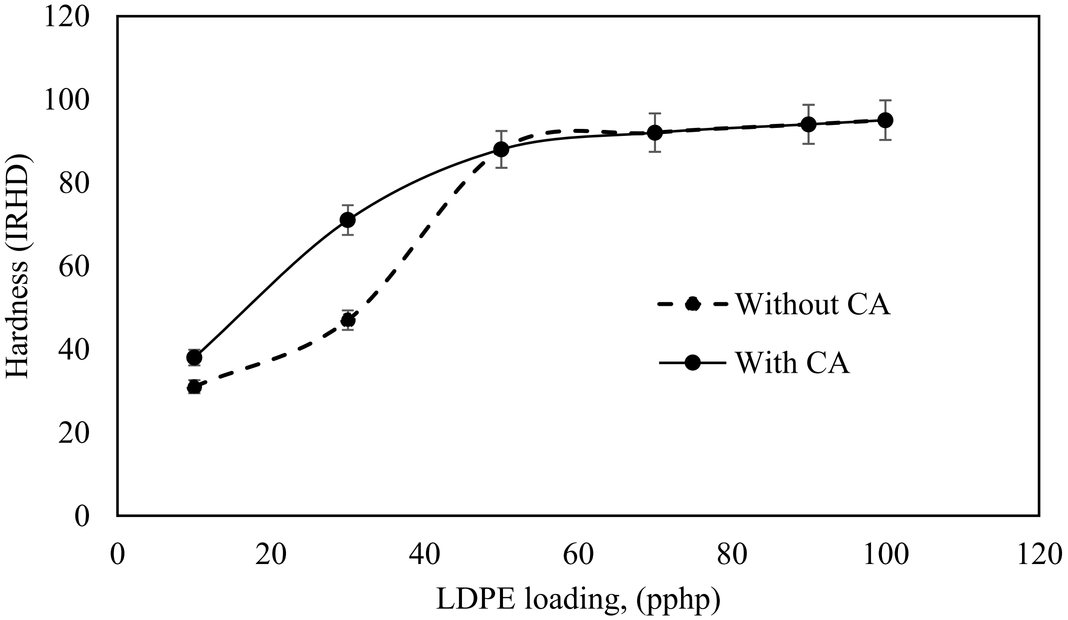


Figure 4.24: Hardness of NR/LDPE composites, with and without titanate CA

### 4.3.2 Formation of network

The possible reaction mechanisms of the formation of a network with covalent bonds between $CaCO_3$ and LDPE through titanate CA is shown in figure 4.25. Crosslinking could also lead to a stabilization of the morphology improving the long-term properties compared to non-cross-linked composites. Moreover, crosslinked composites also give possibility of utilizing mixtures of polymer eventually leading to useful materials (Chodak., 1995). $CaCO_3$ attached NR will then form a strong interface with LDPE improving mechanical properties as observed in

Figure. 4.21, Figure.4.22, Figure 4.23 and Figure 4.24. Crosslinking of NR and DCP could also lead to stabilization of the morphology improving long-term properties compared to non-cross-linked composites (Chodak, 1995). The enhanced properties could be cleared from the stress–strain curve for NR/LDPE composite having 30pphp of LDPE loading with titanate CA, which is shown in Figure 4.26. According to Figure 4.26, 70pphp loading of NR has good reaction with 20pphp $CaCO_3$ and then with LDPE due to formation of covalent bonds between $CaCO_3$ and titanate CA. These morphological results are well matched with the tensile strength results given in Figure 4.21.

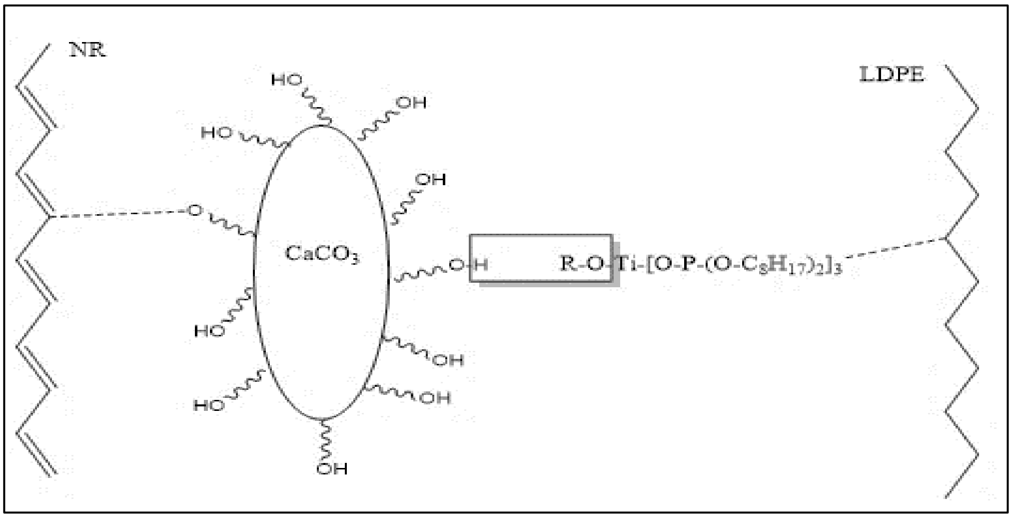


Figure 4.25: Formation of a network with covalent and/or hydrogen bonding between NR and LDPE through $CaCO_3$ and titanate CA

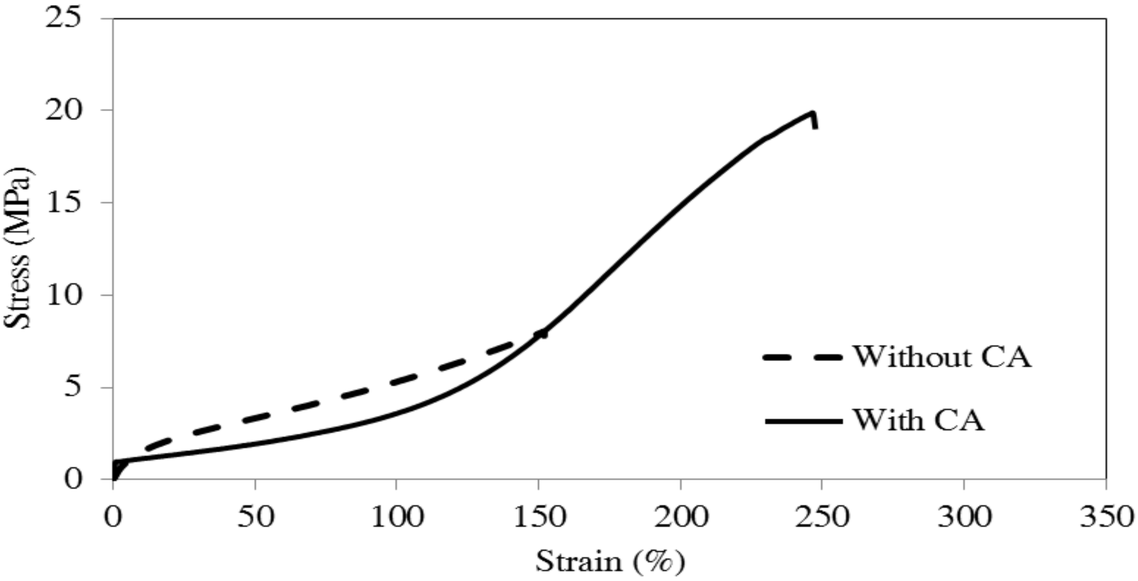


Figure 4.26: Stress-strain curves for 70/30 NR/LDPE composites with and without titanate CA

### 4.3.3 Morphology of composites

As indicated by Figure 4.27, surface morphologies of tensile fracture surfaces of NR/LDPE composites with and without titanate CA and surface images have been taken by optical light-microscopy. The black area represents LDPE as it transmits light and white area represents NR as it reflects light. All images illustrated a two types of morphology. Figure 4.27 (a) and (c) show satisfactory phase morphology with well adhesion features of NR and LDPE. Figure 4.27 (b) and (d) show coarse phase morphology. The composite heterogeneity or the proof of domains is reported for NR/LDPE/Silica composites also (Teoh et al., 2014). Further, Figure 4.27 (b) evidently shows that the NR agglomerates resulted due to poor mixing and dispersion features. These results clarify that good interfacial adhesions between NR and LDPE phases were formed when $CaCO_3$ was added with titanate CA. This variation in phase morphology is in accordance with formation of network proposed in Figure 4.25. In absence of titanate CA, $CaCO_3$ does not make proper interactions with LDPE, although it is attached with NR. This phase separation indicates incompatibility of NR and LDPE that results in poor mechanical properties. Figure 4.27(c) shows failure in NR phase revealing that NR/LDPE composite having 50 phpp of LDPE loading was not properly dispersed compared to NR/LDPE composite having 30 phpp of LDPE loading.

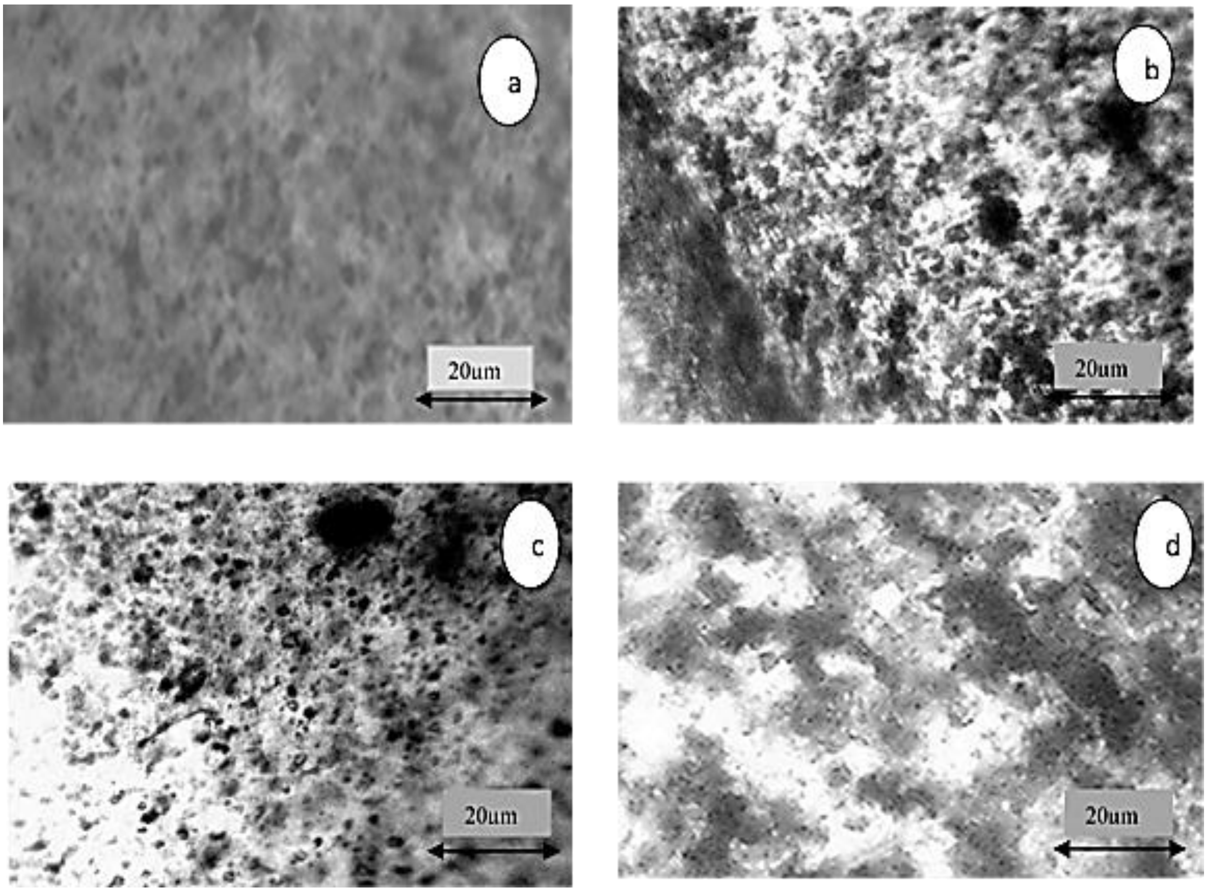


Figure 4.27: Optical microscopic images of fracture surfaces of NR/LDPE composites at magnification 400

(a) LDPE loading of 30 pphp with titanate CA

(b) LDPE loading of 30 pphp without titanate CA

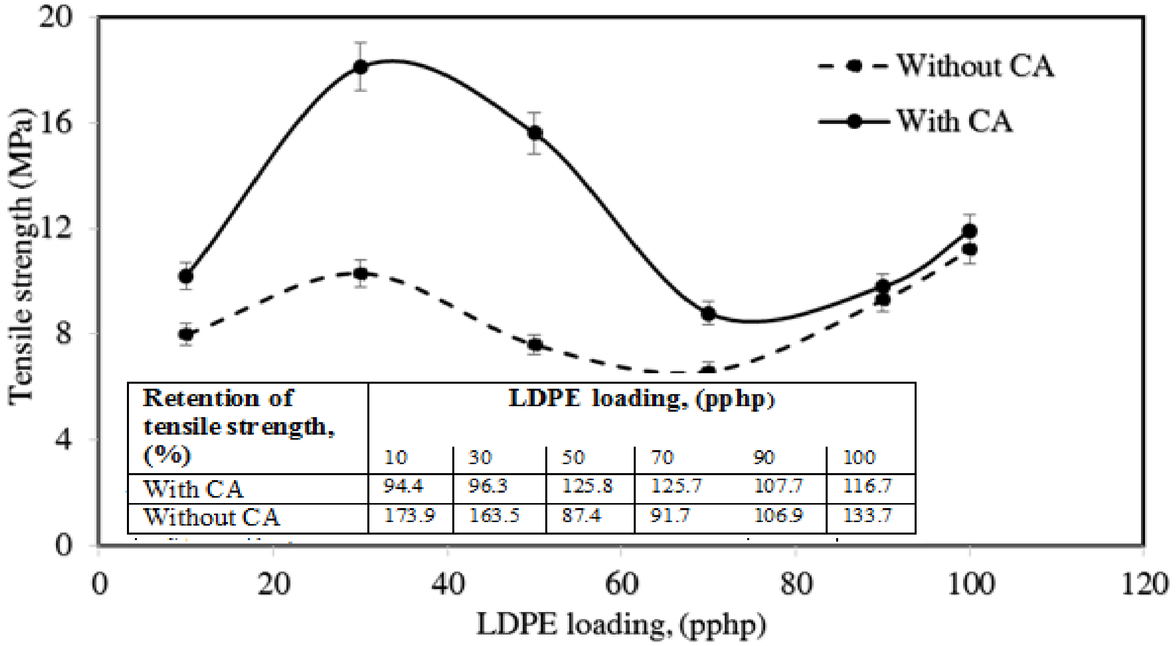
(c) LDPE loading of 50 pphp with titanate CA

(d) LDPE loading of 50 pphp without titanate CA

### 4.3.4 Ageing properties

Figure 4.28 shows tensile strength of NR/LDPE composites with and without titanate CA, after ageing. Tensile strength of the composites with titanate CA after ageing was greater than that without titanate CA at every blend composition. Moreover, 70/30 NR/LDPE composite showed the highest tensile strength after ageing revealing that 0.5 pphp loading of titanate CA would be suited to provide good thermal stability for the 70/30 NR/LDPE composite. The retention of the tensile strength was 96% (Appendix B: I). The composites having LDPE loading above 30 pphp showed increased in tensile strength after ageing revealing that new crosslinks were formed in the LDPE continuous phase during further heating. Titanate CA promotes esterification reaction with polymer and filler (Monte, 2005), and therefore, titanate CA would form strong adhesions between LDPE, NR and $CaCO_3$.

Tensile strengths of the composites without titanate CA at LDPE loading up to 30 pphp were increased after ageing confirming that the crosslinks were formed during further heating at the thermal ageing test. This reveals that the heating time compression moulding of 15 minutes (Section 3.2.2) is not sufficient to form crosslinks in the continuous NR phase by DCP. However, with the change of the continuous phase to LDPE, tensile strength of the composites at LDPE loading of 50 and 70 pphp were decreased after ageing and the retention was in a range of 87 - 92% (Figure 4.28). This explains that crosslinks which were formed during compression molding were broken instead of formation of new crosslinks under further heating.

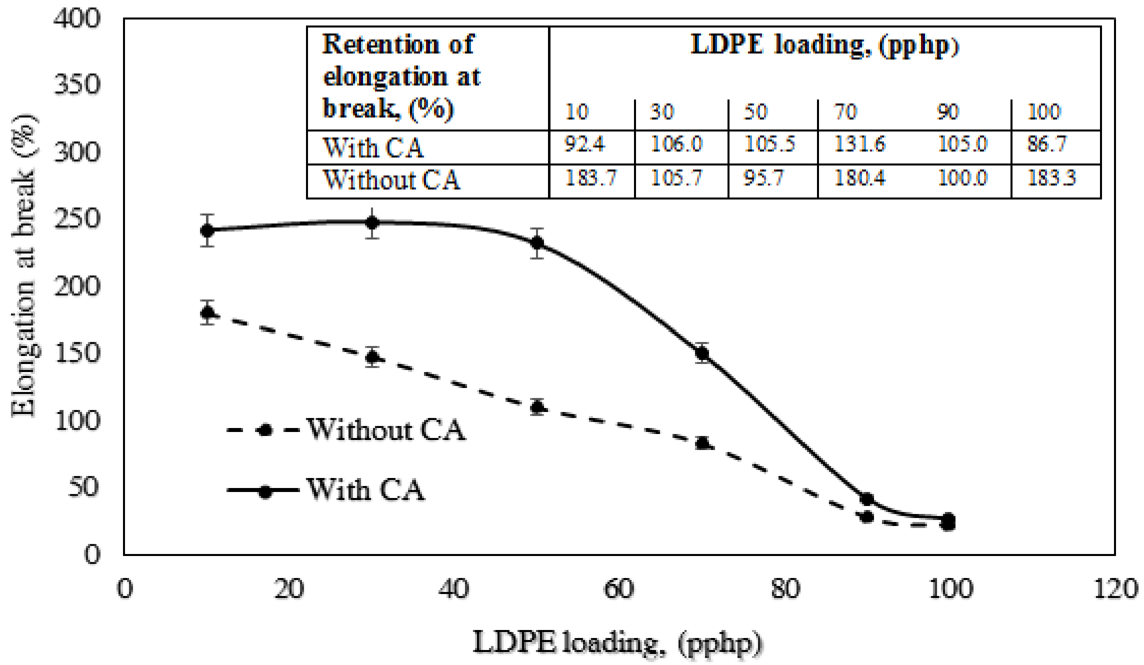


| Retention of tensile strength, (%) | LDPE loading, (pphp) | | | | | |
|---|---|---|---|---|---|---|
| | 10 | 30 | 50 | 70 | 90 | 100 |
| With CA | 94.4 | 96.3 | 125.8 | 125.7 | 107.7 | 116.7 |
| Without CA | 173.9 | 163.5 | 87.4 | 91.7 | 106.9 | 133.7 |

Figure 4.28: Tensile strength of NR/LDPE blends with and without titanate CA, after ageing

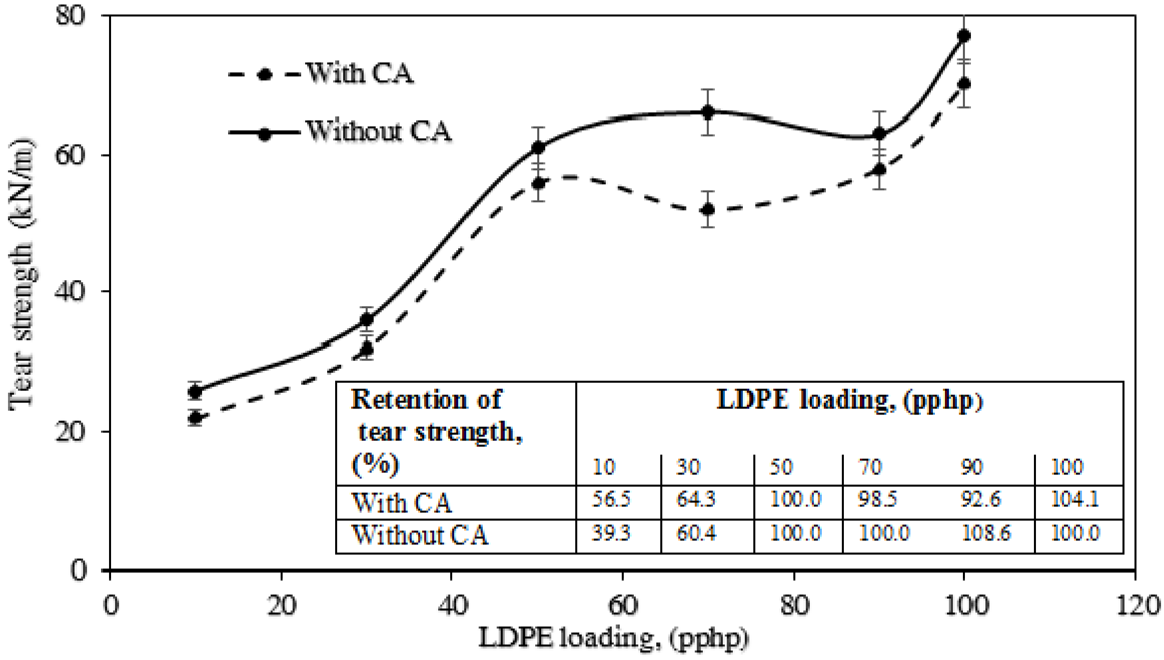
Elongation at break of all composites decreases with LDPE loading. In contrast, the composites which are prepared with titanate CA, showed better results compared to those without titanate CA (Figure 4.29). According to morphological images (Figure 4.27), 70/30 NR/LDPE composite with titanate CA showed good adhesions between NR and LDPE phases. Hence, 70/30 NR/LDPE composite with titanate CA showed the highest elongation at break. It was reported that, 50/50 LLDPE/GRT blend prepared with ethylene octene copolymer (EOC) compatibilizing agent showed a significant increase in ageing performance of tensile properties and in fine phase morphology (Rocha et al., 2014). In addition, retention of elongation at break of the composites with titanate CA increased with LDPE loading up to 70 pphp and then decreased. However, retention of elongation for the composites without titanate CA did not show a typical variation pattern with the increase in LDPE loading (Figure 4.29).

Figure 4.30 shows variation of tear strength of NR/LDPE composites with and without CA, after ageing. Tear strength has increased with the increase LDPE loadings. The composites with titanate CA compared to that without CA, showed high tear strength at LDPE loading. It was reported that the titanate treated inorganic fillers were organo-functional and therefore, exhibited enhanced dispersibility and bonding with the rubber and plastic (Kattas et al., 2000). Further, the amount and the type of CA, and also the composite ratio affect ageing properties (Kasetsart J, 2006). Hence, ageing properties of the composites studied show a cyclic pattern. Further, retention of tear strength was increased after LDPE loading of 30 pphp due to continuos phase transfer from NR to LDPE at each LDPE loadings comparable difference of the tear strength after ageing was signifinat, but, the retention of tear strength was more or less same (Figure 30).



| Retention of elongation at break, (%) | LDPE loading, (pphp) | | | | | |
|---|---|---|---|---|---|---|
| | 10 | 30 | 50 | 70 | 90 | 100 |
| With CA | 92.4 | 106.0 | 105.5 | 131.6 | 105.0 | 86.7 |
| Without CA | 183.7 | 105.7 | 95.7 | 180.4 | 100.0 | 183.3 |

Figure 4.29**:** Elongation at break of NR/LDPE blends prepared with and without titanate CA, after ageing



| Retention of tear strength, (%) | LDPE loading, (pphp) | | | | | |
|---|---|---|---|---|---|---|
| | 10 | 30 | 50 | 70 | 90 | 100 |
| With CA | 56.5 | 64.3 | 100.0 | 98.5 | 92.6 | 104.1 |
| Without CA | 39.3 | 60.4 | 100.0 | 100.0 | 108.6 | 100.0 |

Figure 4.30**:** Tear strength of NR/LDPE blends prepared with and without titanate CA, after ageing

### 4.3.5 Gel content

Composites prepared with titanate CA showed a high gel content than that prepared without titanate CA (Figure 4.31). Titanate CA has supported to increase crosslinks between NR, LDPE and $CaCO_3$. Further, Monte. (2005) has reported that titanate CAs are well established adhesion promoters. Furthermore, gel content of composites decrease with increase in LDPE loading. Hence, high amount of NR may increase compatibility between NR and $CaCO_3$ through titanate CA. In literature, 30/70 NR/LDPE blends were prepared with different fillers namely carbon black, silica, $CaCO_3$ etc. and they showed significant variation of gel content and bound rubber indicating a strong chemical interaction between the filler particles and polymer matrix. As the finding, agglomerate particles size and polymer-filler interaction were found as the factors determining the physical and chemical properties of NR/LLDPE blends (Ahmad et al., 2004). Also, crosslinks due to both sulphur and peroxide vulcanizing agents formed at higher NR loadings. In contrast crosslinking due to peroxide vulcanizing agent only formed at high LDPE loadings (Ghosh et al., 1992).

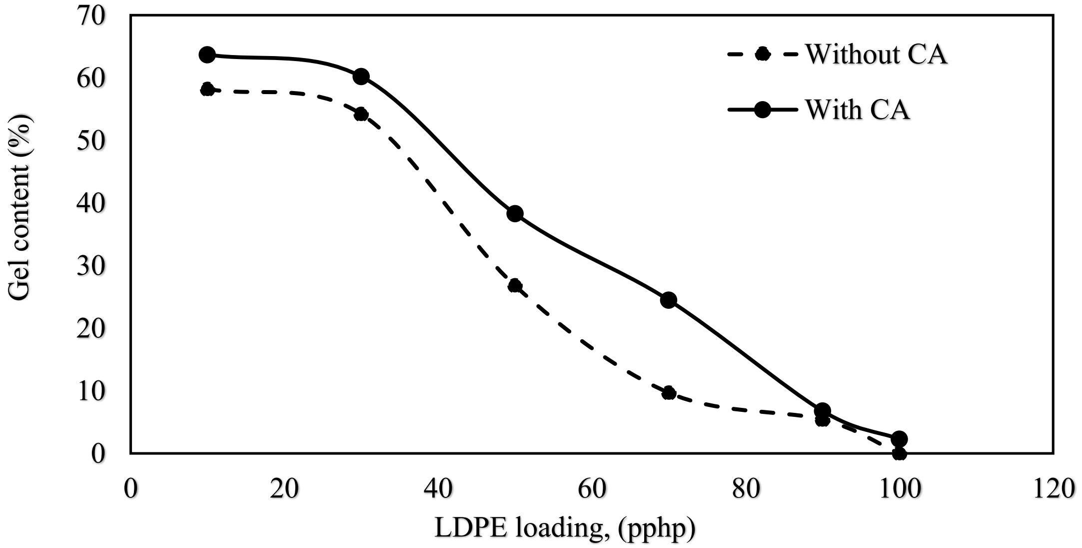


Figure 4.31: Gel content of NR/LDPE blends prepared with and without titanate CA

### 4.3.6 Water absorption

Figure 4.32 shows water absorption percentage of NR/LDPE composites with and without titanate CA. Composite prepared with titanate CA shows low water absorption than that prepared without titanate CA. Titanate CA is a orgonophilic material and also, it is nonpolar (Monte, 2005). Hence, titanate CA is not compatible with water. Further, water absorption decreases with increase in LDPE loading as LDPE is a crystalline material. Furthermore, rubber is an amorphous material and hence it has high water absorption than LDPE. It was reported that titanates also provide superior hydrolytic stability in wet environments, which should be considered in fabricating dental composites. The addition of a small amount of titanates can improve the resistance of the composites to moisture (Elshereksi et al., 2017). Hence, composites prepared with titanate CA would be suitable for waterproof applications such as roofing sheet.

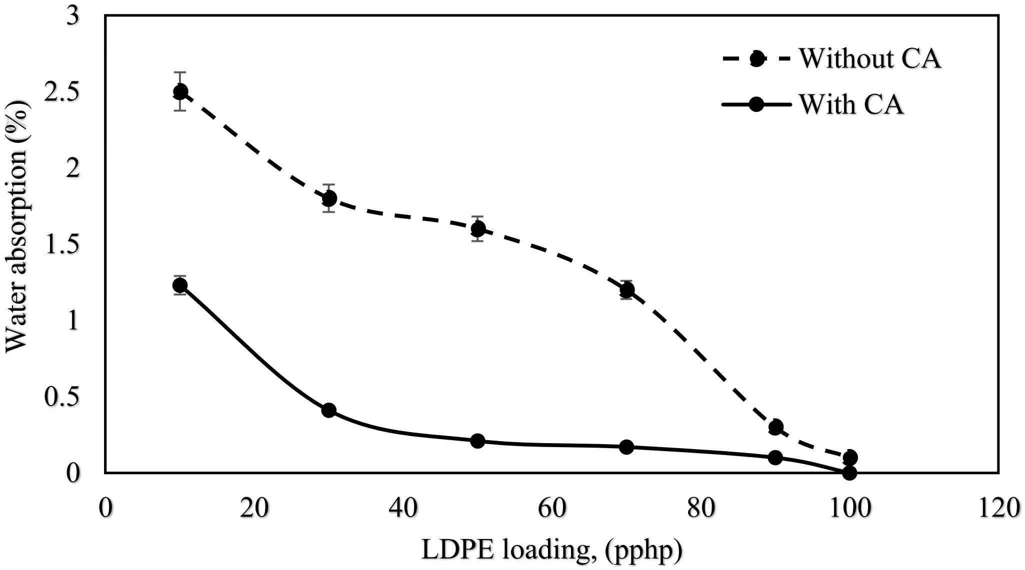


Figure 4.32**:** Water absorption of NR/LDPE blends prepared with and without titanate CA

## 4.4 The Effect of Mixing Route on Properties of NR/LDPE Composites Prepared with titanate CA

50/50 NR/LDPE composite was prepared with different mixing routes and properties were evaluated to find the suitable mixing route. 0.5 pphp of titanate CA was used to study the suitable mixing route for 50/50 NR/LDPE blend.

### 4.4.1 Physico-mechanical properties

Figure 4.33 shows the stress/strain curves of the composites prepared according to three mixing routes. All 50/50 NR/LDPE composites exhibit semi crystalline behaviour and they represent semi-crystalline nature. Therefore, all composites confirm LDPE as the continuous phase. All composites which were prepared with titanate CA show high stress and strain properties. Further, the properties would change according to the mixing sequence of titanate CA.

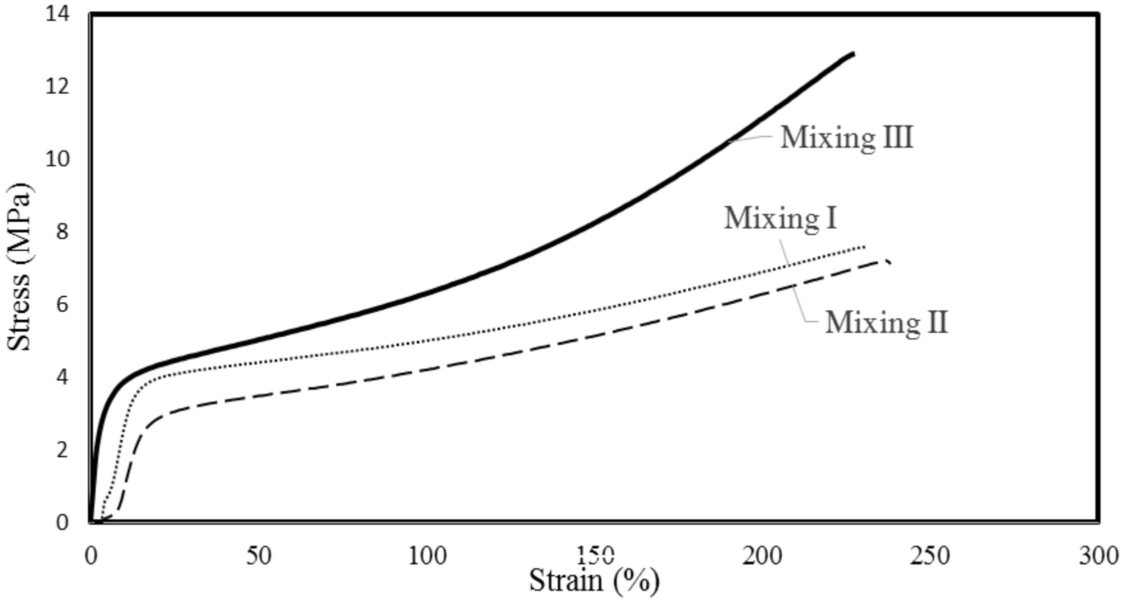


Figure 4.33: Stress/strain curves of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

Figures 4.34 and 4.35 show variation of tensile strength and elongation at break of the composites .The blend which was prepared by Mixing III route shows the highest tensile strength and elongation at break. Further, mixing III route shows the best tensile strength compared to other composites due to better dispersion of $CaCO_3$ within the polymer matrix. Literature also showed similar results (Monte., 2005). In contrast, other composites showed lower tensile strength due to agglomeration of $CaCO_3$ in the polymer matrix without better dispersion. In addition, titanate CA would develop intermolecular interactions among the NR and LDPE via $CaCO_3$. According to the statistical analysis (one way ANOVA ) at 95%

confidence interval there is an effect of mixing route on properties of NR/LDPE/$CaCO_3$ composites prepared with titanate CA (p= 0.000).

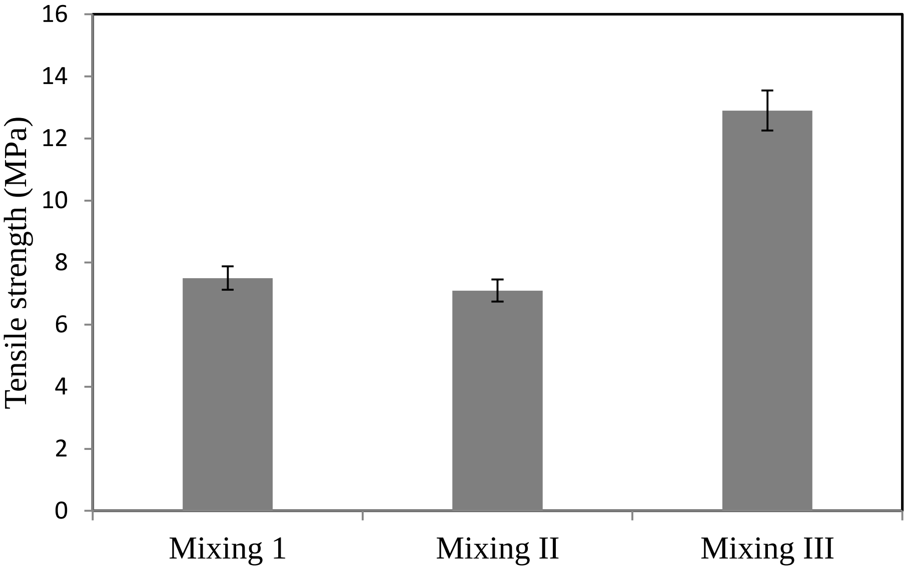


Figure 4.34: Tensile strength of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

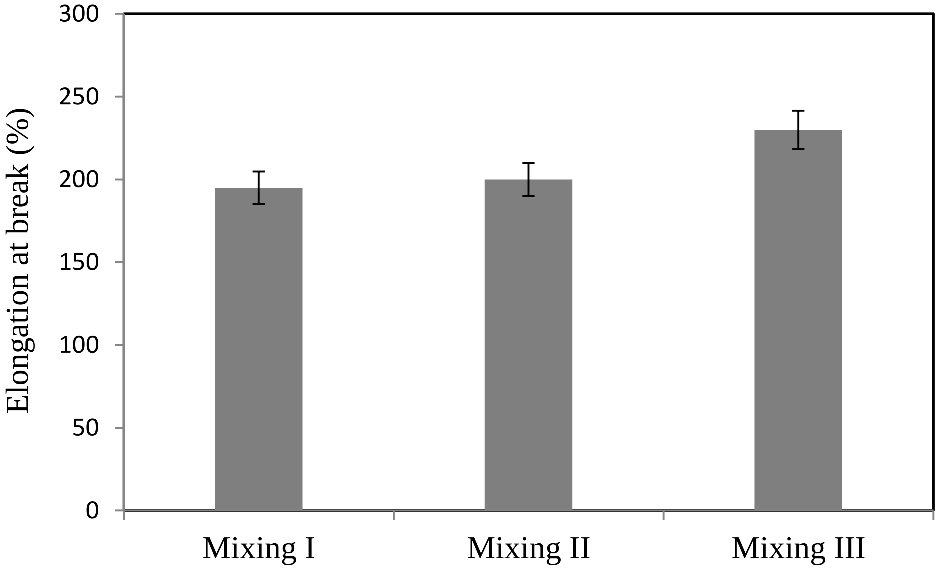


Figure 4.35**:** Elongation at break of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

Tear strength of the composite prepared according to mixing III route shows the maximum as shown in Figure 4.36. High tear strength of composite of mixing III route may be attributed to improvement of interfacial adhesion between NR and LDPE phases, which could reduce crack propagation during tearing. As expected, composite of at mixing III routes showed high tear strength compared to other counter parts. Further, Katbab et al. (2012) have reported that properties of polymer blends are controlled by many factors such as the nature of polymer, blend composition and as well as mixing route.

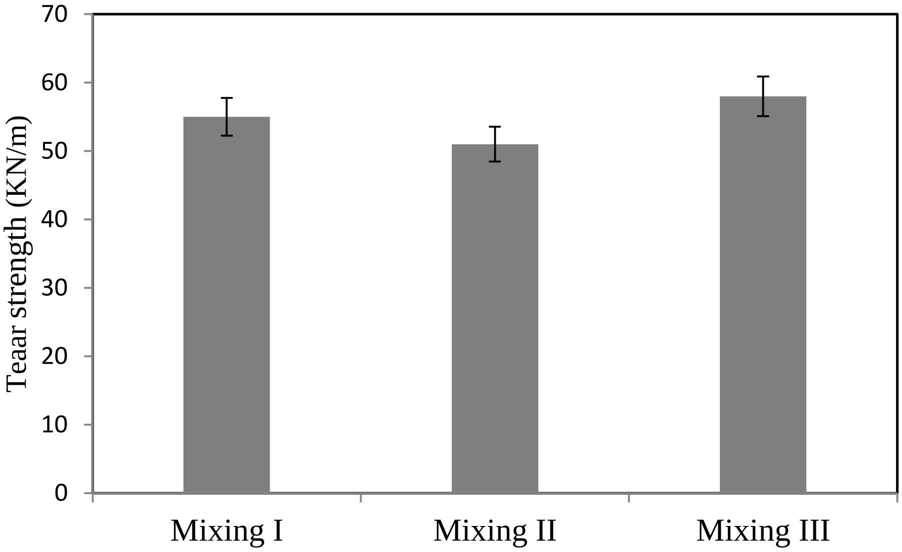


Figure.4.36: Tear strength of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

Hardness of NR/LDPE composites at different mixing routes is shown in Figure 4.37. Hardness of all composites measured within the range 72 to 85 IRHD. Hardness of mixing III route which has been added titanate CA after $CaCO_3$ showed the highest value and further, crosslink density could be increased in the composite. Previous literature also suggested, free volume inside the polymer matrix reduced when addition of CA after the filler addition (Monte, 2005).

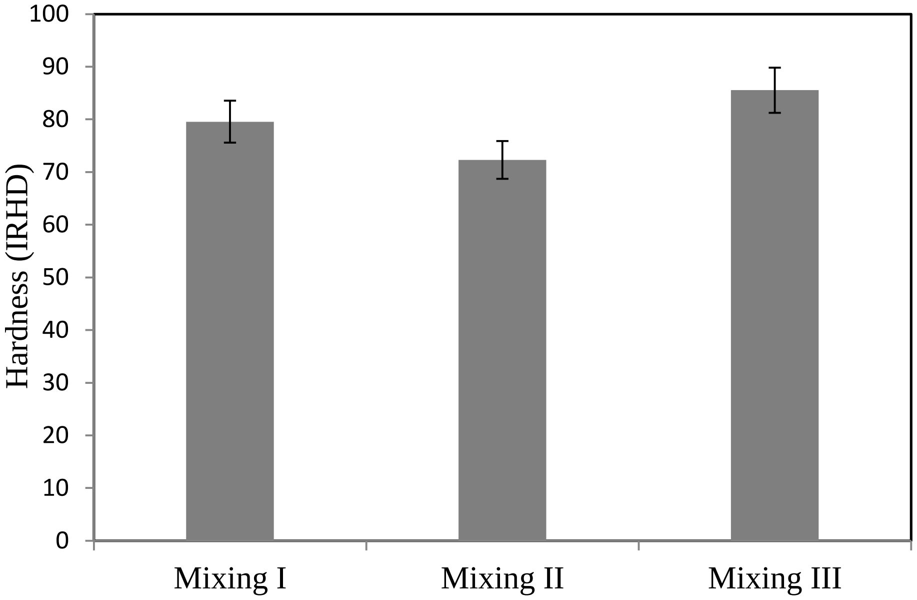


Figure 4.37: Hardness of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

### 4.4.2 Gel content

Variation of gel content of the composites is shown in Figure 4.38. Further, the gel content of all composites is greater than 20%. Hence, intermolecular interaction has increased (Elshereksi et al., 2017) due to increase of chemical interactions between NR, LDPE and $CaCO_3$ through CA. Moreover, mixing III would be a suitable route to enhance the properties of 50/50 NR/LDPE composite. Furthermore, stronger polymer – filler interactions from when titanate CA is added after the filler addition (Monte., 2005). Further, Ying et al. (2014) have reported a similar observation for NR/LDPE filled silica composites. Chemical properties in LDPE/NR/silica composites were strongly dependent on the filler incorporation route (Ying et al., 2014).

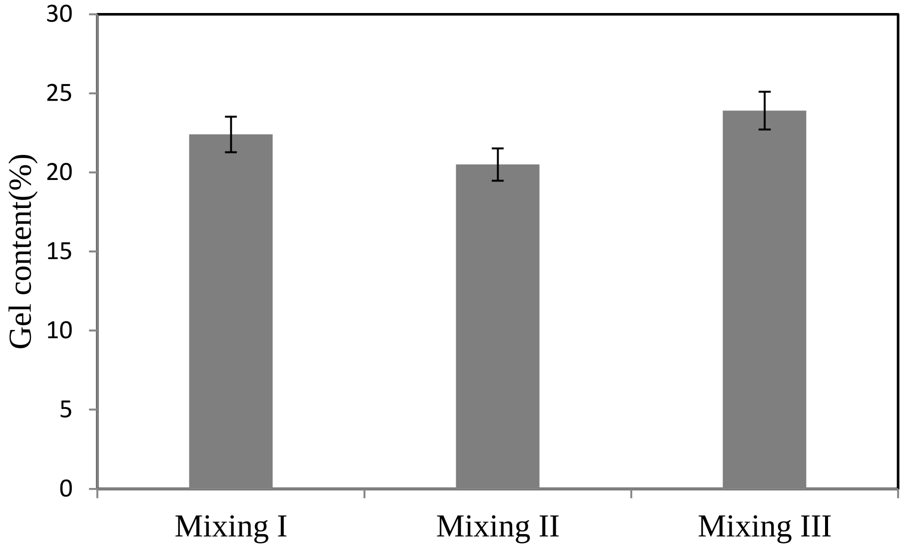


Figure 4.38: Gel content of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

### 4.4.3 Water absorption

Variation of water absorption of 50/50 NR/LDPE composites is shown in Figure 4.39. The mixing I route indicated the highest water absorption compared to other mixing routes. Further, composite of mixing III route shows the low water absorption. Hence, it is expected that strong network structure is built inside the polymer matrix due to addition of titanate CA after addition of filler.

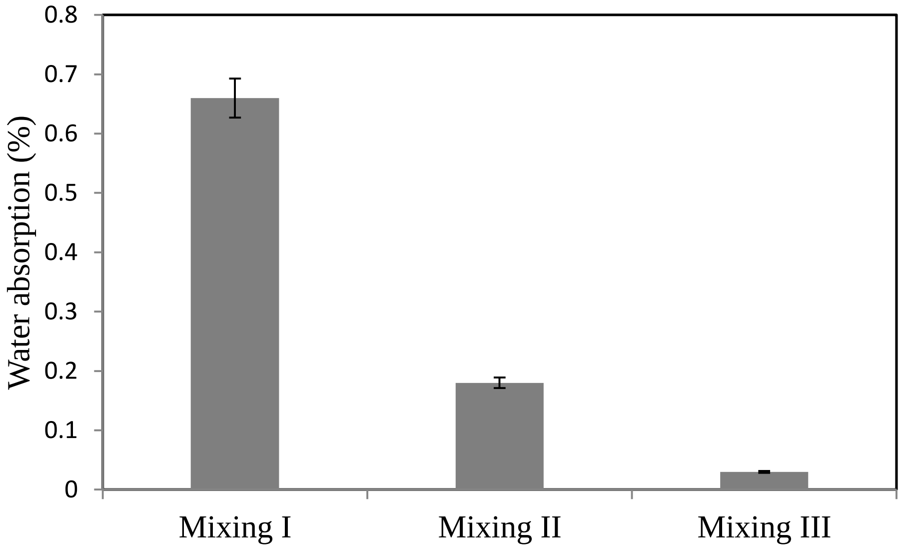


Figure 4.39: Water absorption of 50/50 NR/LDPE blends with titanate CA prepared according to different mixing routes

### 4.4.4 Morphology

According to the Figure 4.40 (b), mixing III route shows fine morphology compared to the mixing I route. The morphology image of mixing I route shows weak interface and uneven fracture surface. It could be seen that fillers are not dispersed uniformly, which may also contribute to the demonstrated poor properties of the mixing I route. In contrast, all physical properties of mixing III route is higher than other counterpart due to the fine fracture surface. Mixing III route would be a better mixing sequence to improve the homogeneity of NR/LDPE 50/50 composite. Further, silica filled NR/LDPE composites have prepared with according to different silica mixing routes (Ying et al., 2014). The effect of filler incorporation route on morphological and tensile properties of composites was studied. Morphologies of phases in LDPE/NR/Silica composites were strongly dependent on the filler incorporation route (Ying et al., 2014).

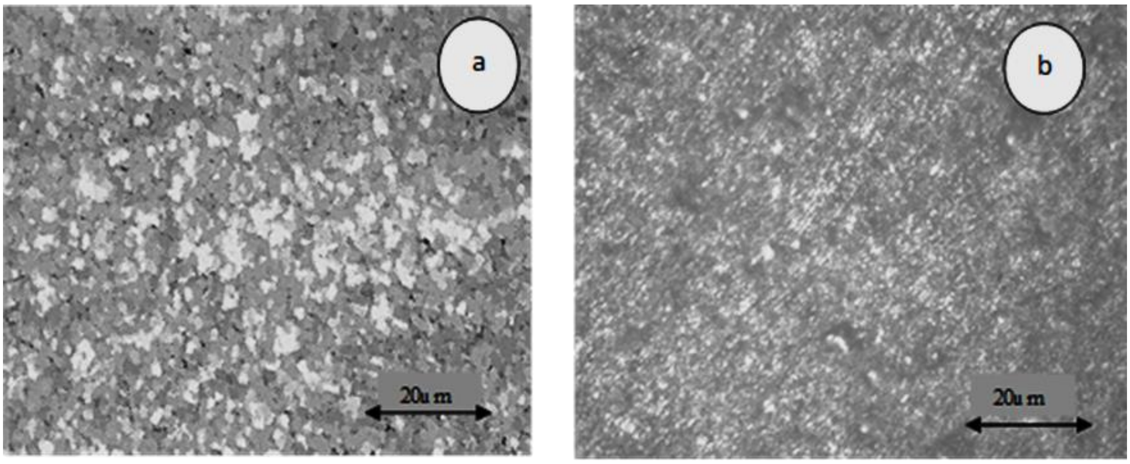


Figure 4.40: Optical microscopy images of tensile fracture surfaces of 50/50 NR/LDPE composites prepared using different mixing routes

(a) Mixing I (b) Mixing III

## 4.5 Effect of CA Loading on Properties of 70/30 NR/LDPE Composites

70/30 NR/LDPE composites were prepared by different titanate CA loadings and properties were evaluated. 20 phpp $CaCO_3$ was used to mix with 70/30 NR/LDPE blends.

### 4.5.1. Physico-mechanical properties of 70/30 NR/LDPE composites

Figure 4.41 shows the stress-strain behavior of composites with and without titanate CA. Control-2 was prepared without titanate CA. All composites exhibit rubbery behavior confirming that rubber is in the continuous phase. Further, composites with titanate CA at most of the loadings show higher stresses and strains compared to the Control-2. Furthermore, the area under the stress-strain curve is evidenced to explain elastic potential energy of polymer, which shows a greater value when titanate CA loading is at 0.5 pphp and 0.7 pphp. This shows that the two composites provide high elastic energy and good toughness.

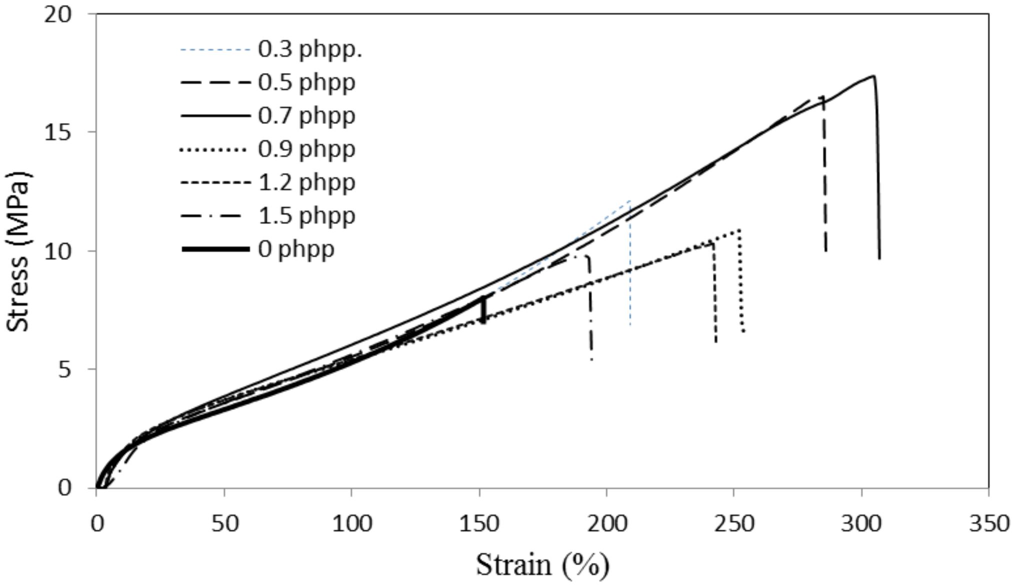


Figure 4.41: Stress-strain curves of NR/LDPE composites with titanate CA at different loadings

Figure 4.42 shows that, the tensile strength significantly increases with titanate CA loading up to 0.7 pphp and then decreases. The best tensile strength is exhibited at titanate CA loading of 0.7 pphp and is associated with the higher degree of crystallinity of LDPE in the composites (Table 4.4), and may be due to good interfacial adhesions between NR and LDPE phases. Poor interfacial adhesions develop poor stress transfer between the matrix and the dispersed phase (George et al., 1995) and will decrease tensile strength at higher CA loadings. The excess CA, which is the amount greater than necessary to form a monolayer, would not result in a plastic network at the interface (Pocius et al., 1997) and therefore it is suspected that it can form a weak boundary layer resulting in poor properties. According to the statistical analysis (one way ANOVA ) at 95% confidence interval there is an effect of titanate CA loading on properties of 70/30 NR/LDPE composites (p= 0.000).

Furthermore, viscosity of composites will be decreased at higher titanate CA loadings due to decrease of tensile strength. It was reported that the titanate treated inorganic fillers show good dispersability and bonding with plastics in composites (Monte et al., 2005), but at higher loadings of titanate CA, it reacted as a plasticizer by decreasing the viscosity of plastic composites. Elongation at break also increases with the addition of titanate CA, and further increases with the loading up to 0.7 pphp. Elongation at break decreases thereafter with further addition of titanate CA loading (Figure 4.43). According to Figure 4.42 and Figure 4.43, 0.7 pphp will be the optimum titanate CA loading to enhance the interfacial adhesions between LDPE and NR phases through $CaCO_3$.

Tear strength of a polymeric material depends mainly on the crack propagation property. Tear strength of the composites show a variation from 40 kN/m (for the Control-2) to 53 kN/m (for the composite at titanate CA loading of 0.7 pphp), with an increase of 28%. Increase in titanate CA loading beyond 0.7 pphp, shows a decrease in tear strength. Tear strength variation also confirms good adhesion between the phases at a titanate CA loading of 0.7 pphp.

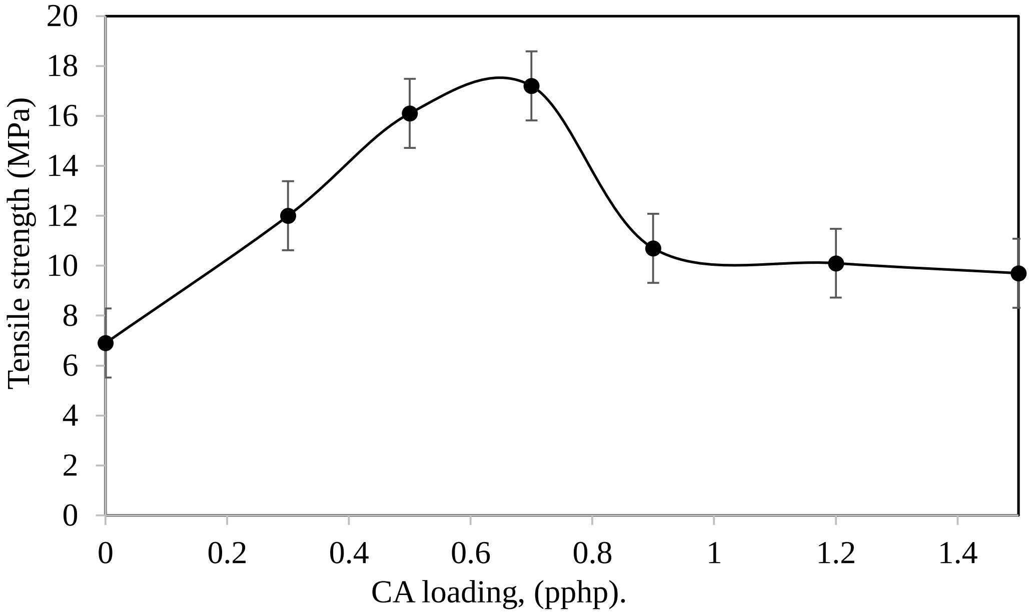


Figure 4.42: Variation of tensile strength of NR/LDPE composites with titanate CA loading

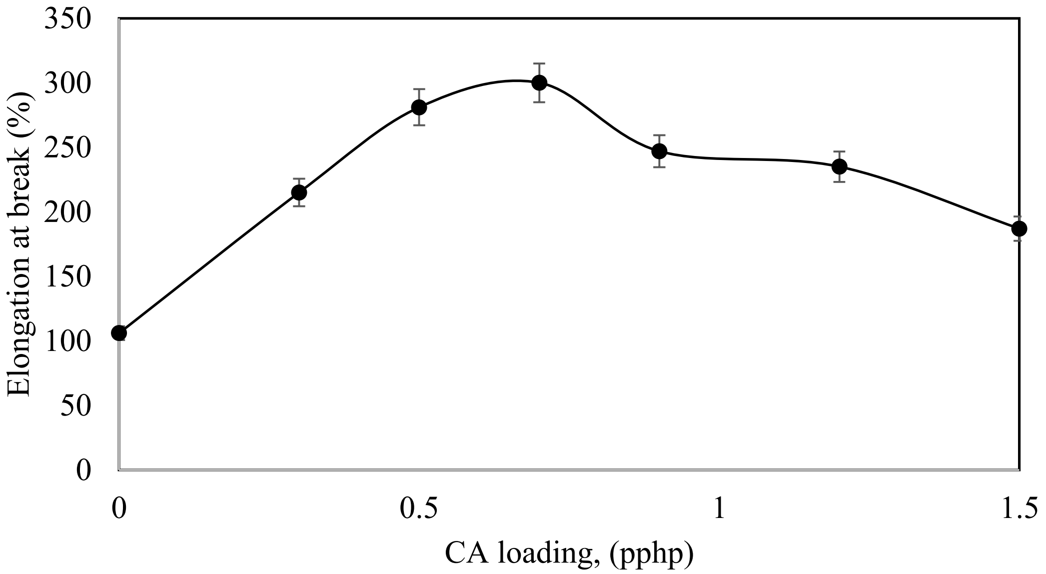


Figure 4.43**:** Variation of elongation at break of NR/LDPE composites with titanate CA loading

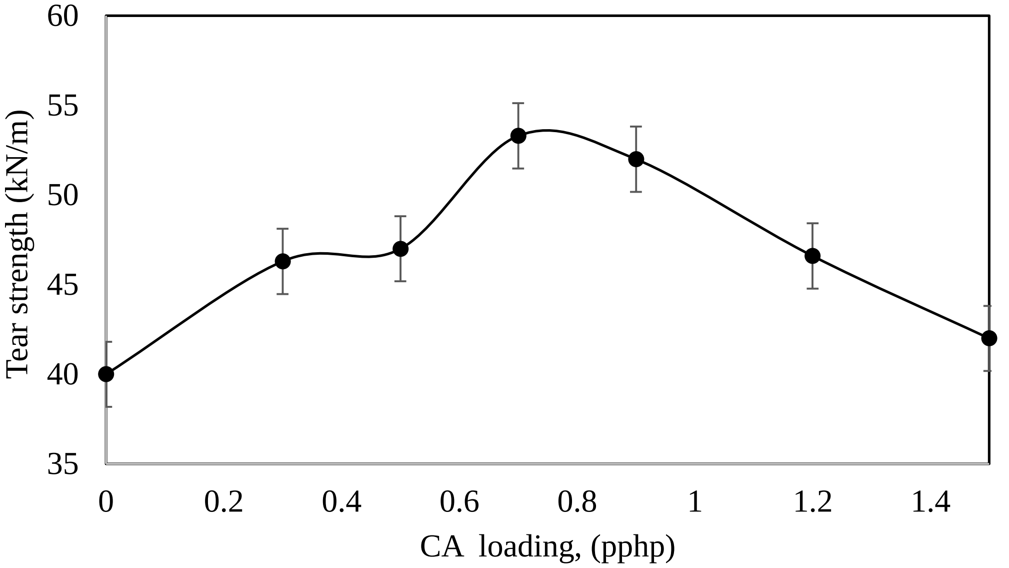


Figure 4.44: Variation of tear strength of NR/LDPE composites with titanate CA loading

Hardness of NR/LDPE composites at different titanate CA loadings is shown in Figure 4.45. Hardness of all composites is within the range 60 to 65 IRHD. This confirms the presence of rubber in the continuous phase in all composites, and is in agreement with the stress-strain behaviour shown in Figure 4.41. Hardness of all composites with titanate CA is greater than that of the Control-2, and is associated with the formation of crosslinks between the two polymer phases. Hardness increases with the addition of titanate CA loading at 0.3 pphp by

5%, and decreases thereafter with increase in titanate CA loading. This decrease may be due to enhancement in plasticizing effect of titanate CA at higher loadings. Furthermore, the longer crosslinks developed through $CaCO_3$ with increase of titanate CA loading might have provided a softness to the composite.

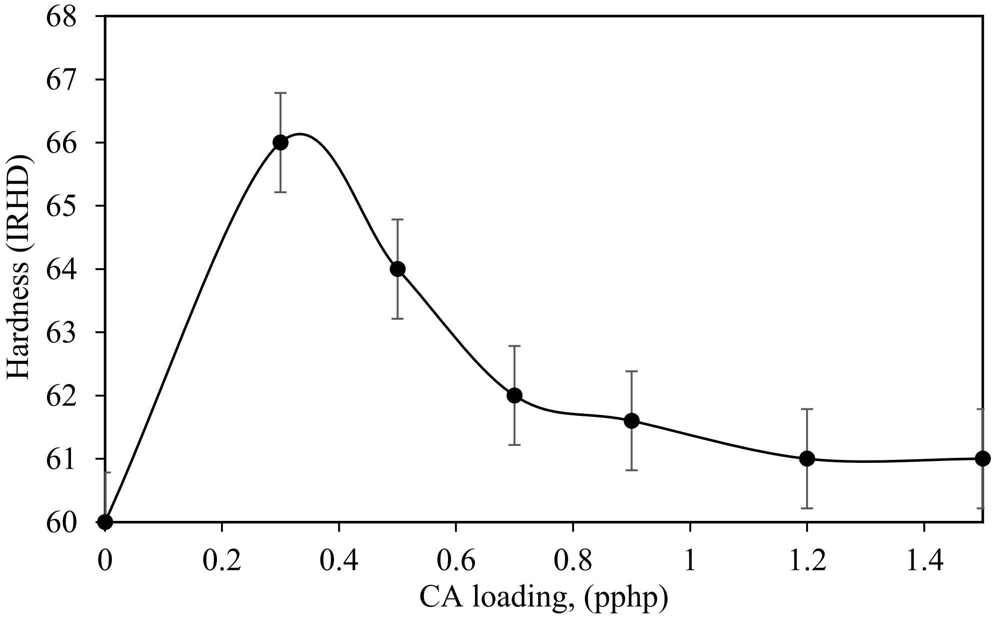


Figure 4.45: Variation of hardness of NR/LDPE composites with titanate CA loading

### 4.5.2 Chemical characteristics

Figure 4.46 shows the variation of degree of swelling with titanate CA loading. Degree of swelling decreases with titanate CA loading up to 0.7 pphp and gradually increases after that with increase in titanate CA loading. The lowest swelling at 0.7 pphp titanate CA loading is associated with the maximum level of interactions developed between NR and LDPE. Swelling property of a thermoplastic elastomer defines the solvent absorption capacity of that material. If the material exhibits a high degree of swelling, it can absorb a high amount of solvent without completely dissolving in it. Further, the coupling of the titanate allows elimination of air voids in plastic (Monte, 2005). Titanate-treated inorganic fillers are organophilic and will absorb more organic solvent (p-xylene) at higher titanate CA loadings.

Gel content is also used for determining the solvent resistance of a thermoplastic or rubber. It is known to be directly proportional to the crosslink density. Higher gel content indicates a higher crosslink density and results in a lower degree of swelling. In Figure 4.47, gel content gradually increases with titanate CA loading up to 0.7 pphp and slightly decreases thereafter with increase in titanate CA loading. The high gel content at 0.7 pphp reconfirms the formation of crosslinks or interfacial interactions in the composite. In addition, formation of gel is associated with ionic linkage of phosphate group.

Hardness of gel of the composites has been varied from 32 to 45 IRHD (Figure 4.48), and is lower than hardness of the composites. This suggests that the gel contains interacted or cross-linked rubber molecules. The composite at titanate CA loading of 0.7 pphp shows the highest hardness of gel due to presence of more interacted/cross-linked NR. DSC curves of LDPE, gels of the Control-2 composite and the composite at titanate CA loading of 0.7 pphp are given in Figure 4.50. The gel of the composite at titanate CA loading of 0.7 pphp, shows a peak of melting endotherm at 124 °C while both LDPE and gel of the Control-2 composite show peaks of melting endotherms at 109 °C, revealing presence of LDPE in gels attached to NR. Shift of peak at melting endotherm of the composite with titanate CA to a higher temperature indicates formation of chemical crosslinks between NR and LDPE. Further, gels of the composites with titanate CA show greater ash content compared to the Control-2 composite (Table 4.2) revealing presence of more $CaCO_3$ in the gels of the composites containing titanate CA. This suggests formation of crosslinks between NR and LDPE through $CaCO_3$.

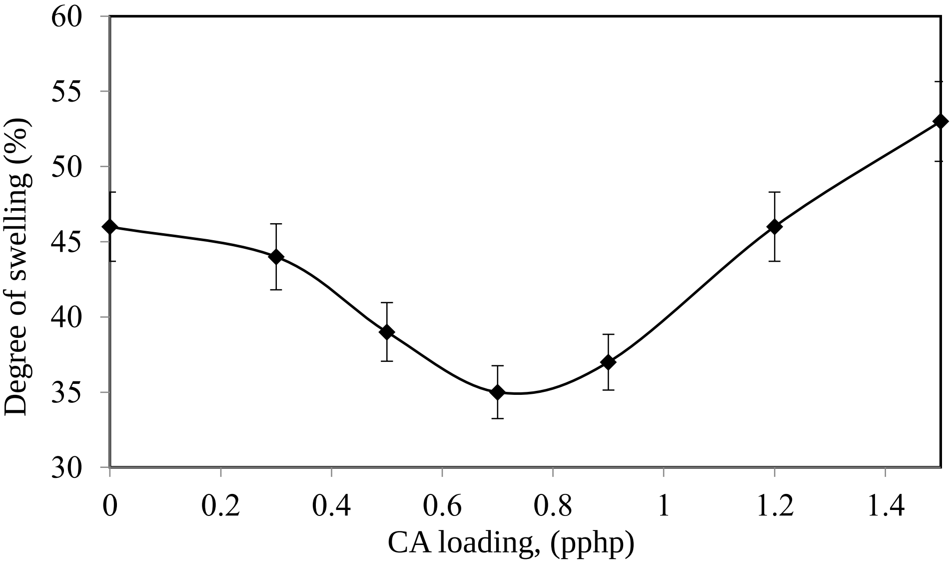


Figure 4.46: Variation of degree of swelling of NR/LDPE composites with titanate CA loading

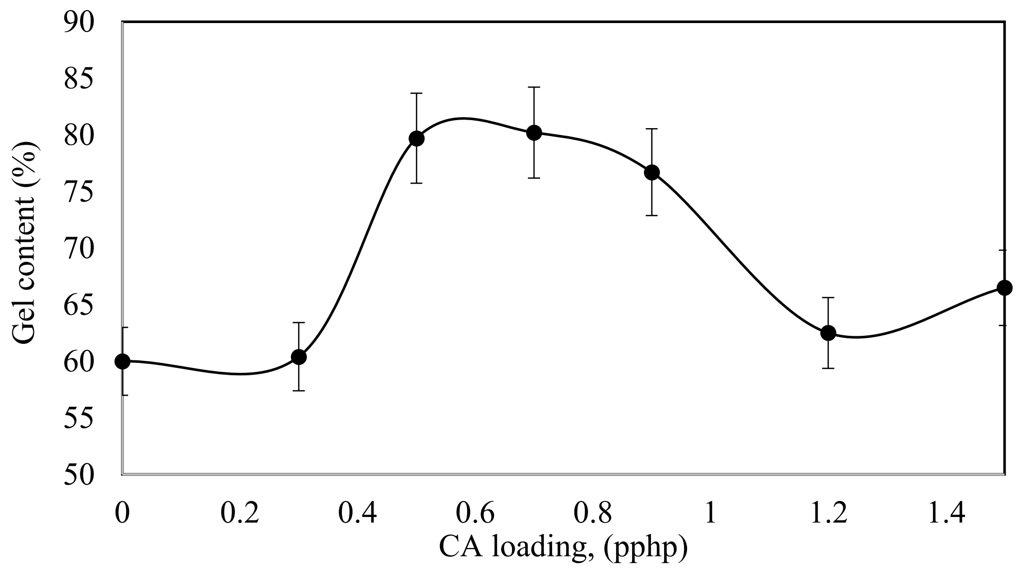


Figure 4.47: Variation of gel content of NR/LDPE composites with titanate CA loading

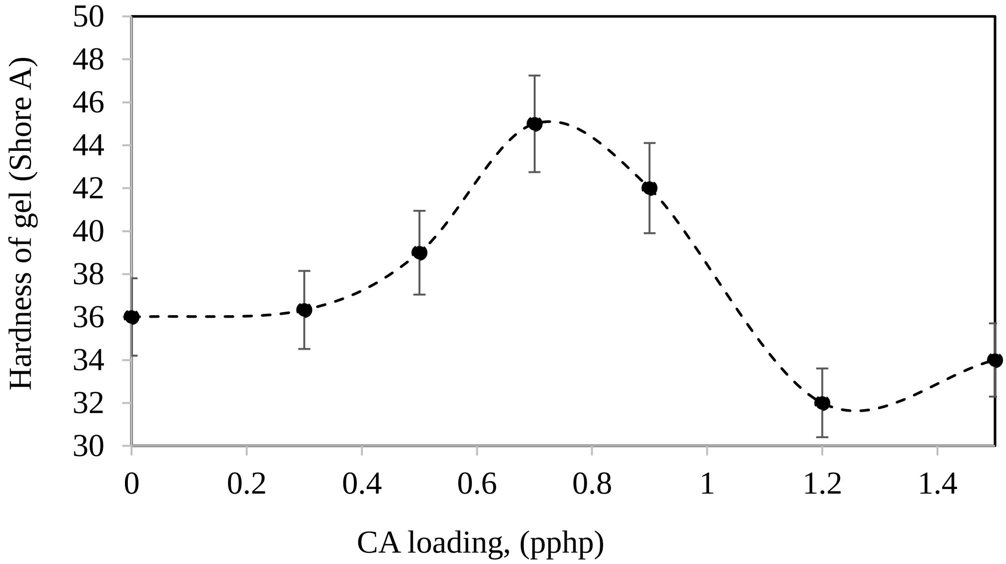


Figure 4.48: Variation of hardness of gel of NR/LDPE composites with titanate CA loading

Water absorption of the composites is shown in Figure 4.49. Water absorption decreases with titanate CA loading up to 0.7 pphp and gradually increases with titanate CA loading. Water being an inorganic substance is not compatible with organophilic titanate and hence titanate will restrict absorption of water. However, the composite at titanate CA loading of 1.5 pphp shows higher water absorption and it may be due to presence of excess CA, which makes a weak interface between $CaCO_3$ and polymer (Pocius et al., 2012). High porosity created at higher titanate CA loadings absorbs higher degree of water. When titanates are incorporated into polymer systems, they often promote adhesion, dispersion, and improve impact strength (Monte, 1987). Good interfacial adhesions and good $CaCO_3$ dispersion developed in the composite at titanate CA loading of 0.7 pphp inhibited creation of porosity and hence showed lowest water absorption.

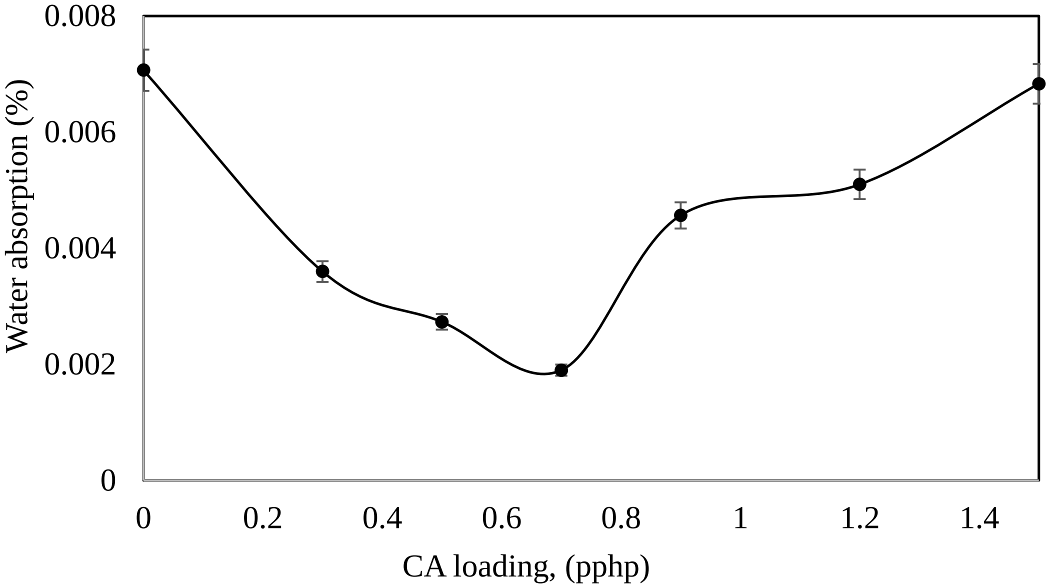


Figure 4.49: Variation of water absorption of NR/LDPE composites with titanate CA loading

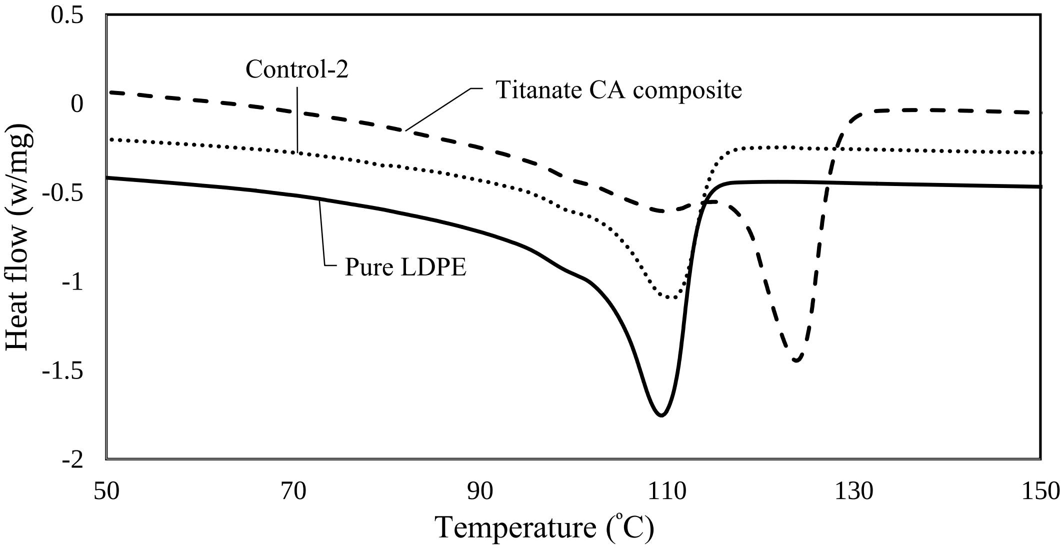


Figure 4.50: DSC curves of LDPE and gels of the Control-2 and the composite at titanate CA loading of 0.7 pphp

Table 4.2: Ash content of NR/LDPE composites

| **Titanate CA loading (pphp)** | **Ash content (%)** |
|---|---|
| Control-2 | 21.5 |
| 0.5 | 23.5 |
| 0.7 | 30.2 |

### 4.5.3 Ageing properties

Table 4.3 shows ageing properties of the Control-2 composite, and the composites at different titanate CA loadings. Most of the composites showed good retention of tensile properties after ageing and are closer to 90%. Composites at titanate CA loadings of 0.7 pphp and 0.9 pphp show the highest percentage and hence showed the higher resistance to thermal degradation, while the composite with a titanate CA loading of 1.5 pphp shows poor resistance to thermal degradation. Reactivity of titanate coupling agent is very high as it has six reactive sites. This tetravalent titanium is reacted strongly with filler and polymer and hence, titanate CA at its optimum loading will react effectively with $CaCO_3$, NR and LDPE.

Table 4.3: Ageing properties of NR/LDPE composites

| **Titanate CA loading, pphp** | **Retention of tensile strength, (%)** | **Retention of elongation at break, (%)** |
|---|---|---|
| Control-2 | 94 | 99 |
| 0.3 | 83 | 93 |
| 0.5 | 89 | 88 |
| 0.7 | 100 | 99 |
| 0.9 | 100 | 100 |
| 1.2 | 97 | 81 |
| 1.5 | 65 | 77 |

### 4.5.4 Thermal properties of NR/LDPE composites

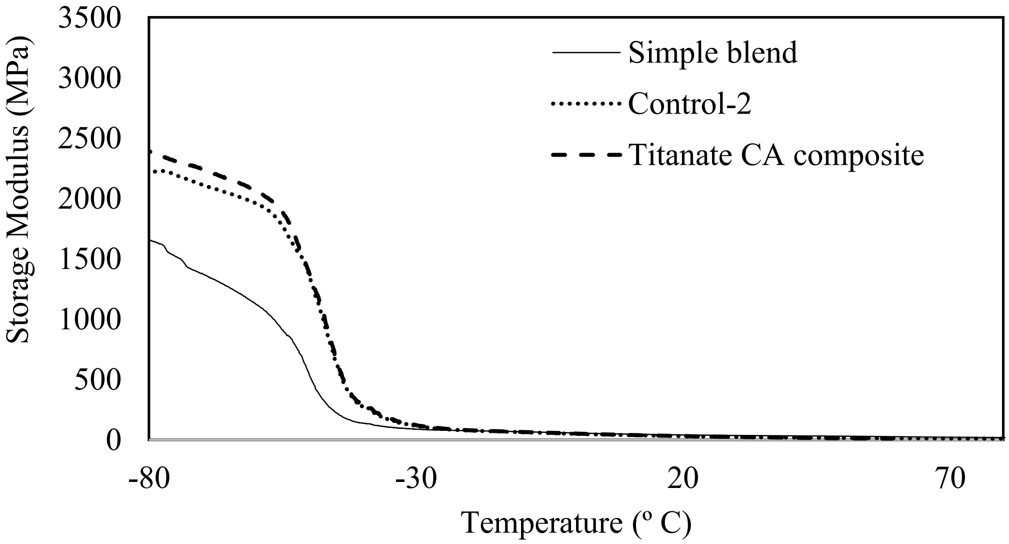
Table 4.4 shows the glass transition temperature ($T_g$), melting temperature ($T_m$) and degree of crystallinity ($X_c$) of the Control-2 composite and the other composites at different titanate CA loadings. $T_g$ decreases with the addition of titanate CA and remains unchanged with the titanate CA loading. Moreover, $T_g$ measurement revealed the plasticizing effect caused by titanate CA loading, which has imparted changes in morphological character (Figure 4.48). Plasticizer in a polymer lowers the $T_g$ of the polymer and consequently promotes a change in properties from hard and brittle to those of soft, flexible and tough (Billmeyer, 1984). $T_m$ variation is not significant up to 0.7 pphp, but thereafter at higher loadings Tm decreases. $X_c$ increases with increase in titanate CA loading up to 0.7 pphp and then decreases, suggesting an effect of titanate CA on crystallinity. $X_c$ of neat LDPE is in the range 50-60% (Seymour et al., 1984). It was reported in a previous study (Bajaj et al., 1989) that the degree of crystallinty was highest at 0.7%, out of the four concentrations of titanates, 0.3, 0.5, 0.7 and 1% in PP/mica composites, and it was the optimum loading to create effective interfacial interactions. It was reported in another study (Govorčin et al., 2014) that interfacial adhesion and degree of crystallinity would be increased due to proper filler dispersion in the talc filled thermoplastic polyurethane/polypropylene composite.

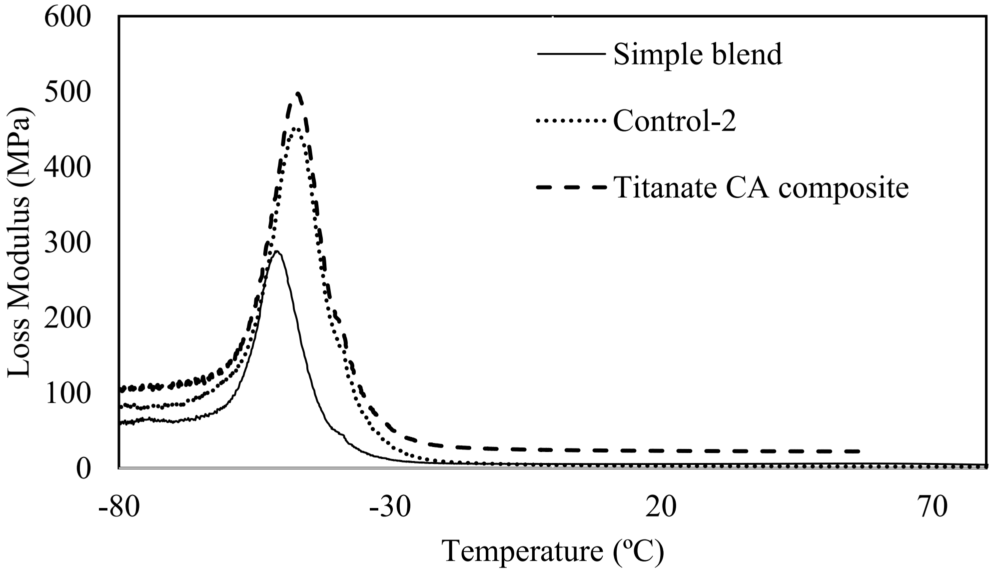
Table 4.4: Thermal properties of NR/LDPE composites

| **Titanate CA loading, phpp** | **$T_g$(°C)** | **$T_m$(°C)** | **$X_C$ (%)** |
|---|---|---|---|
| Control-2 | -56.4 | 109.3 | 20.4 |
| 0.3 | -62.1 | 109.8 | 35.5 |
| 0.5 | -62.6 | 110.3 | 59.4 |
| 0.7 | -62.6 | 110.2 | 59.8 |
| 0.9 | -62.1 | 107.5 | 51.1 |
| 1.2 | -62.3 | 107.8 | 52.8 |
| 1.5 | -61.7 | 107.0 | 40.3 |

### 4.5.5 Dynamic Mechanical Analysis

Figure 4.51 shows storage modulus, loss modulus and tan δ versus temperature plots of the unfilled composite, the Control-2 and the composite at titanate CA loading of 0.7 pphp. Storage modulus is a measure of the maximum energy stored in the material during one cycle of oscillation and it provides valuable insight into the stiffness of the composites, representing elastic nature of material. As temperature increases, the components become more mobile and lose their close packing arrangement and hence the storage modulus decreases at the glass transition region. In the rubbery region, change in storage modulus is insignificant (Pipattananukul et al., 2014). Due to the development of interfacial adhesion, the composite at titanate CA loading of 0.7 pphp shows the highest storage modulus. Loss modulus is a measure of energy dissipated as heat due to friction and internal motion, representing viscous behavior. Greater heat dissipation was found with the Control and the composite compared to the unfilled composite due to presence of $CaCO_3$. $CaCO_3$ may act as a barrier to mobility of LDPE chains. Tan δ is the ratio of loss modulus to storage modulus and is called damping factor. The temperature at tan δ peak is taken as $T_g$ of a material and it indicates the compatibility of phases in a composite. However, interfacial adhesions generated in the composite may not be significant enough to change the $T_g$ observed under DMA.





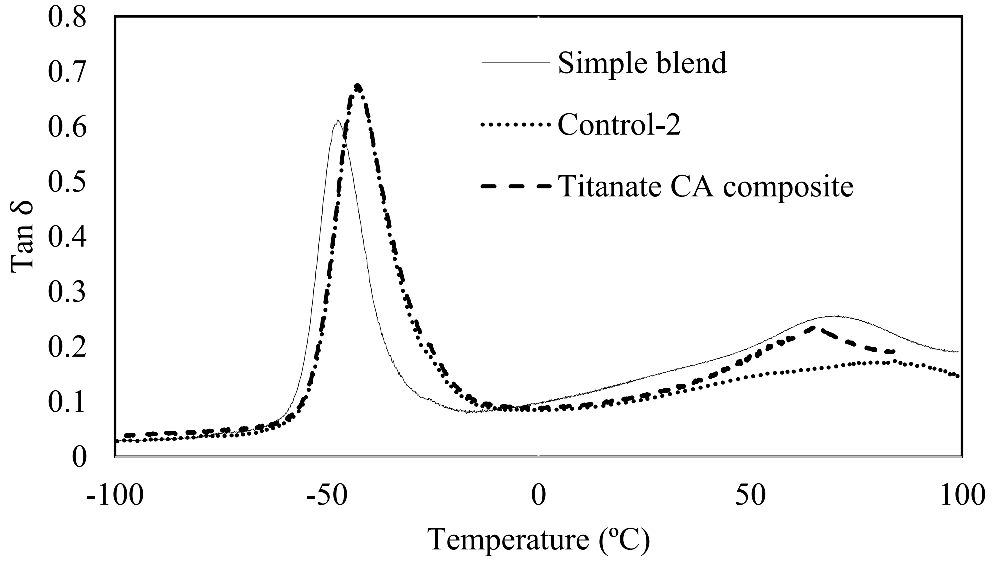


Figure 4.51: Storage modulus, loss modulus and tan δ of the 70/30/ NR/LDPE simple blend, the Control-2 and the 70/30/ NR/LDPE composite at CA loading of 0.7 pphp

### 4.5.6 Morphological analysis of 70/30/ NR/LDPE/ composites

Figure 4.52 (a) shows SEM images of fracture surfaces of the Control-2 composite, while Figure 4.52 (b) and Figure 4.52 (c) shows those of the composites at CA loadings of 0.7 and 1.2 pphp, respectively. These images clearly show that LDPE is dispersed in the NR matrix. Both the Control-2 composite and the composite at CA loading of 0.7 pphp show smooth surfaces and good interfacial adhesion between NR and LDPE phases. Figure 4.52 (c) shows a rough surface with a clear phase separation due to poor interfacial adhesion between phases. This phase separation confirms the inferior mechanical properties obtained at higher CA loadings. Figure 4.52 (b) shows a homogeneous dispersion of $CaCO_3$ in the NR/LDPE composite. This indicates the efficiency of mixing, which was attributed to good interfacial interaction, between NR/LDPE and $CaCO_3$. Interfacial bonding is also improved due to the trans-esterification reaction of CA. Further, as in Figure 4.52 (c), the NR phase is deformed and curled and hence fracture surface features a typical elastic failure (sukhanova et al., 1999). Furthermore, the composite which was prepared with CA loading of 1.2 pphp shows weak interfaces. Moreover, the morphological analysis shows that the best interfacial adhesion between NR and LDPE phases is at CA loading of 0.7 pphp.

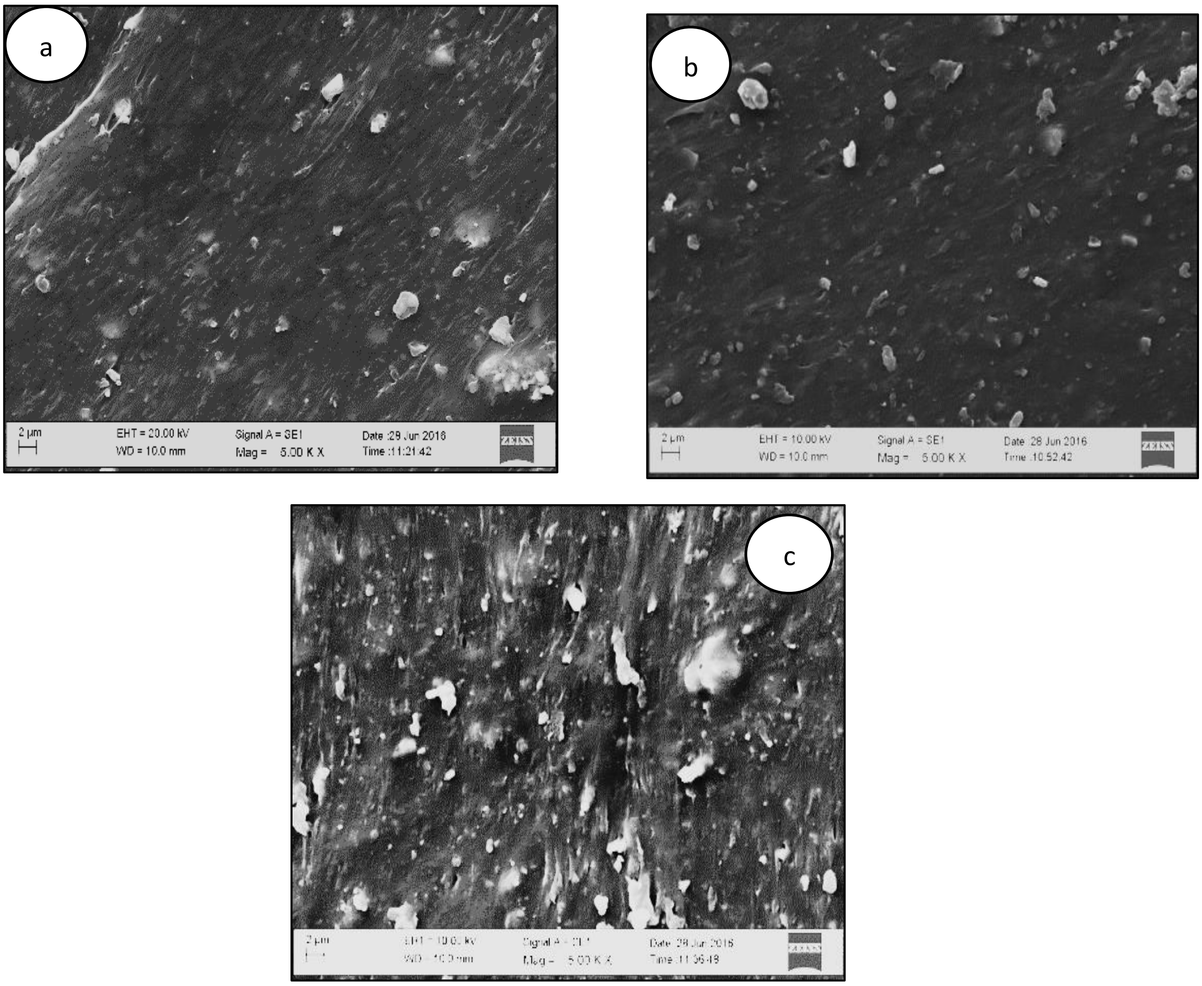


Figure 4.52: SEM images of tensile fracture surfaces of

(a) the Control-2

(b) the composite at CA loading of 0.7 pphp

(c) the composite at CA loading of 1.2 pphp

## 4.6 Effect of Peroxide (DCP) Loading on Properties of 70/30 NR/LDPE Composites

### 4.6.1. Physico- mechanical properties of NR/LDPE composites

Hardness of NR/LDPE composites at different DCP loadings is shown in Figure 4.53. Hardness of all composites is within the range 55 to 65 IRHD. Hardness increases up to DCP loading of 0.3 pphp and decreases thereafter with the increase of DCP loading. It shows an increase in hardness of 11% compared to the Control-3 (without peroxide) composite, which is the composite which contains sulfur alone as the vulcanizing agent. Other composites contain sulfur and also DCP, but at different loadings. Increase in hardness of the composite with DCP loading of 0.1 pphp, compared to the Control-3, could be due to formation of additional crosslinks in the NR phase with the addition of DCP. Remarkable increase in both gel content (Figure 4.61) and hardness of gel of the composite with DCP loading of 0.1 pphp (Figure 4.62) suggest an increase in crosslink density in the NR continuous phase when DCP is added into the composite. Further increase in DCP loading up to 0.3 pphp may have developed more crosslinks in the NR phase, and between NR and LDPE phases. It is believed that DCP initiates radical formation on the LDPE backbone by hydrogen abstraction and chain scission (Maziat et al., 2009). The radicals then may react with sulfur crosslinked NR to form NR-LDPE linkages as in Figure 4.54. Crosslink decomposition is either radical or polar in character, and generally operates at high temperatures. The decomposition will lead to a net loss in crosslink density and hence imparts reversion. Radical decomposition of polysulphidic crosslinks is governed by dissociation energies of bonds. Polysulphidic crosslinks, especifically S-S bonds of low dissociation energy, compared to C-C bonds are easily dissociated (Joseph et al., 2016). It was indicated in a previous study (Joseph et al., 2016) that peroxides can act as chemical devulcanizing agents for sulfur vulcanized rubbers as per the mechanism given in Figure 4.55. Hence, the highest hardness shown at 0.3 pphp DCP loading could be attributed to the highest crosslink density of the composite and further, the presence of excess amounts of DCP could reduce the amount of crosslinks formed.

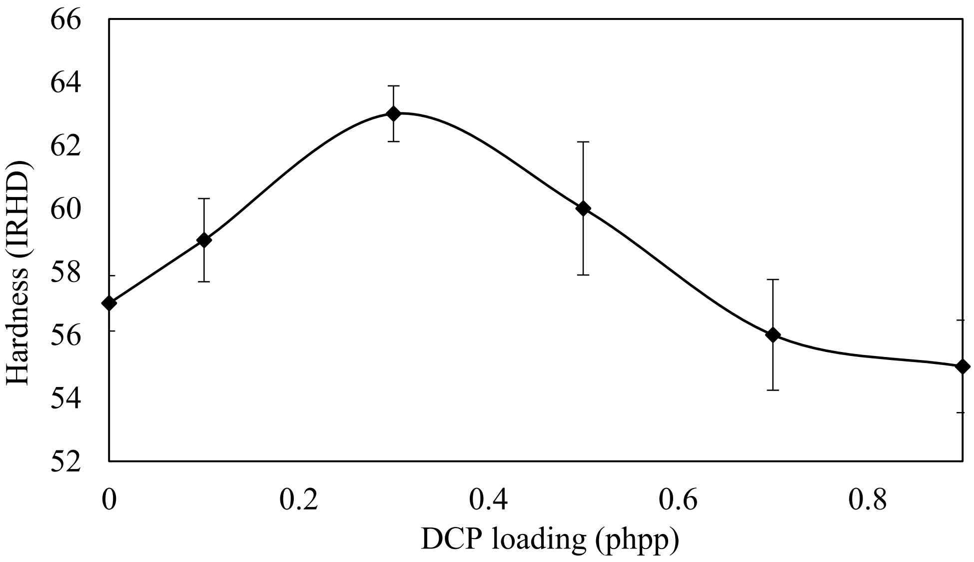


Figure 4.53: Hardness of NR/LDPE composites at different DCP loadings

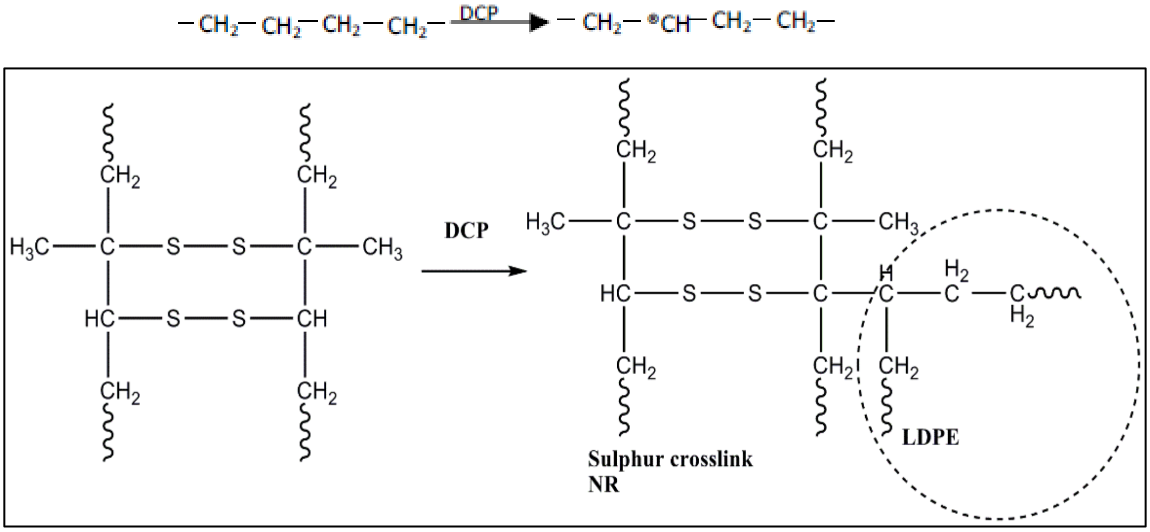


Figure 4.54: Possible reaction between NR and LDPE through DCP

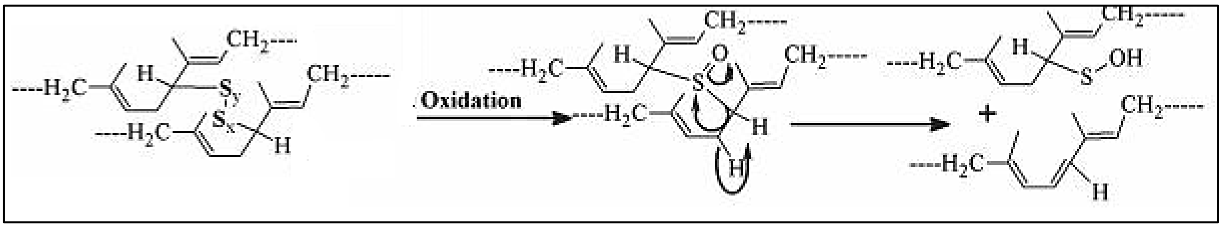


Figure 4.55: Mechanism of crosslink scission via oxidation of sulphur crosslinked rubber (Joseph et al., 2016)

Stress-strain curves for 70/30 NR/LDPE composites at all DCP loadings exhibit similar elastic behavior as shown in Figure 4.56, suggesting that the continuous phase of the composites is

NR. With the incorporation of DCP at 0.1 pphp loading, the elasticity increased and it may be associated with the increase of crosslink density in the NR phase. Sulfur crosslinked rubber shows high elasticity than DCP crosslinked rubber (Noriman et al., 2012) due to presence of flexible polysulfidic crosslinks. DCP crosslinked rubber has mainly rigid C-C crosslinks between the macromolecular chains.

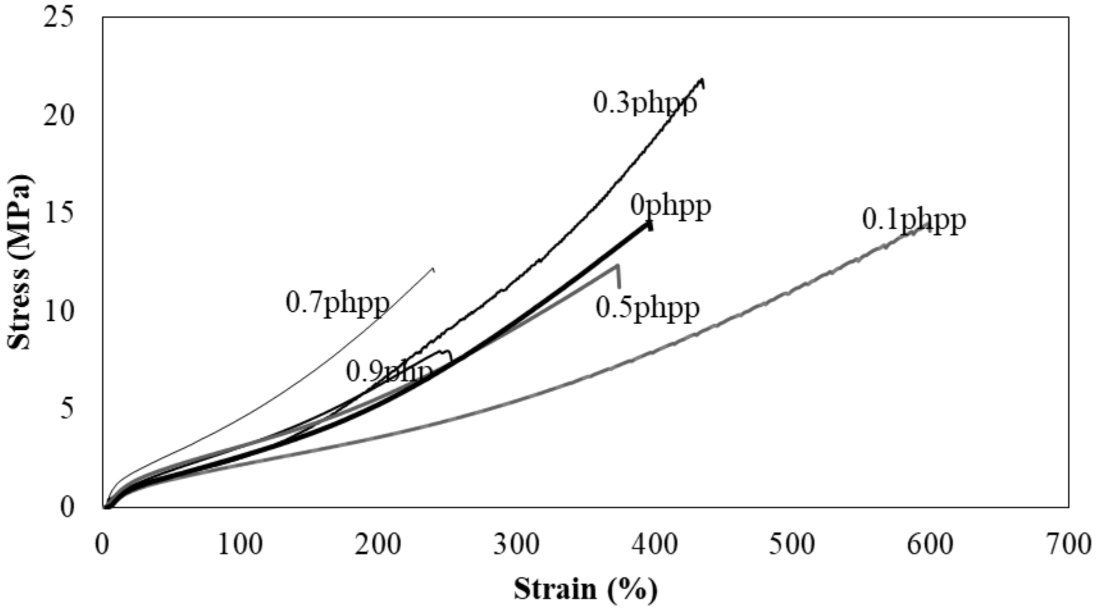


Figure 4.56: Stress-strain curves of NR/LDPE composites at different DCP loadings

Figure 4.57 shows a marked increase in tensile strength from 0 to 0.3 pphp DCP loading and a decrease thereafter. The highest tensile strength is shown at DCP loading of 0.3 pphp and may be associated with the highest crosslink density of the composite and/or with the highest degree of crystallinity of the LDPE phase at that DCP loading (see Table 4.5). Further, good adhesion between NR and LDPE phases and lower surface tension at the interface (Rector., 2006) could be expected as per the reaction mechanism shown in Figure 4.54. At higher DCP loadings, crosslink density of the NR phase may decrease while increasing the crosslink density of the LDPE phase. Highly crosslinked LDPE phase could prevent formation of adhesions between phases and could result in a failure at low elongations. A similar trend in tensile strength was reported for HDPE/GTR composites (He et al., 2015). According to the statistical analysis (one way ANOVA ) at 95% confidence interval there is an Effect of DCP loading on properties of 70/30/20 NR/LDPE /$CaCO_3$ composites (p= 0.000).

Elastic elongation is due to uncoiling, untwisting, and straightening of chains in the stress direction (Rector. 2006) and indicates an amorphous behaviour of a material. Figure 4.58 shows an increase of elongation at break with the addition of 0.1 pphp of DCP due to presence of higher degree of crosslink density, confirming that the added sulfur amount is insufficient to crosslink the NR phase in the composite. However, with the crosslinking of the NR phase, elongation at break gradually decreases with DCP loading from 0.1 pphp to 0.7 pphp. However, the variation from 0.7 pphp to 0.9 pphp DCP loading is insignificant. This suggests that the elastic behavior of the two composites is more or less similar.

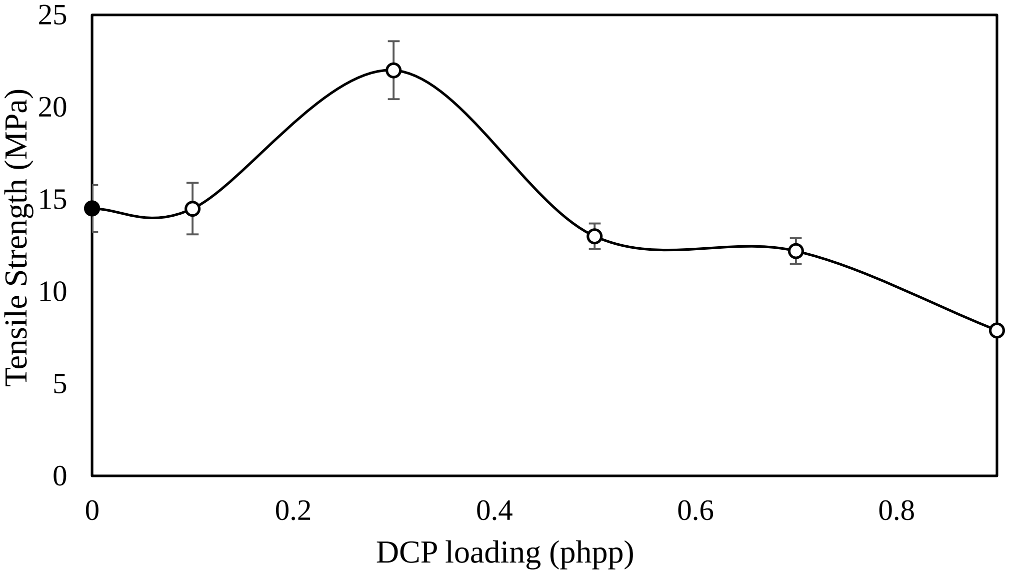


Figure 4.57**:** Tensile strength of NR/LDPE composites at different DCP loadings

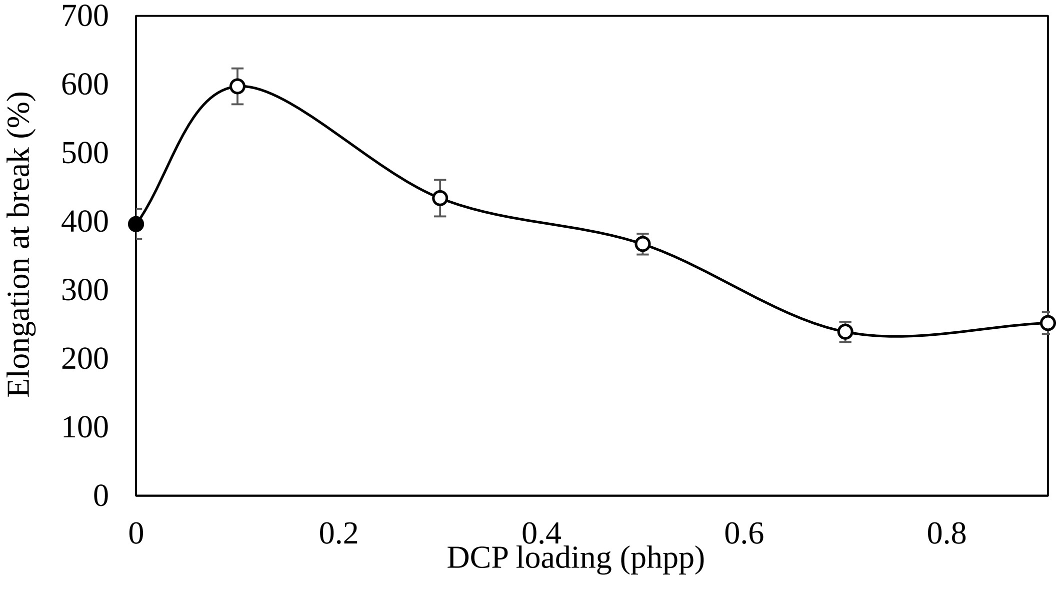


Figure 4.58: Elongation at break of NR/LDPE composites at different DCP loadings

Tear strength of the composite at DCP loading of 0.3 pphp shows the maximum as shown in Figure 4.59. High tear strength at DCP loading of 0.3 pphp may be attributed to improvement of interfacial adhesion between NR and LDPE which could reduce in crack propagation during tearing. The mechanical properties of the HDPE/GTR composites (He et al., 2015) were also reported as improved significantly at DCP loading of 0.3 pphp. As expected, composites at all DCP loadings showed high tear strength compared to the composite without peroxide. Hardness results (Figure 4.53) indicated higher crosslink density at DCP loading of 0.3 pphp.

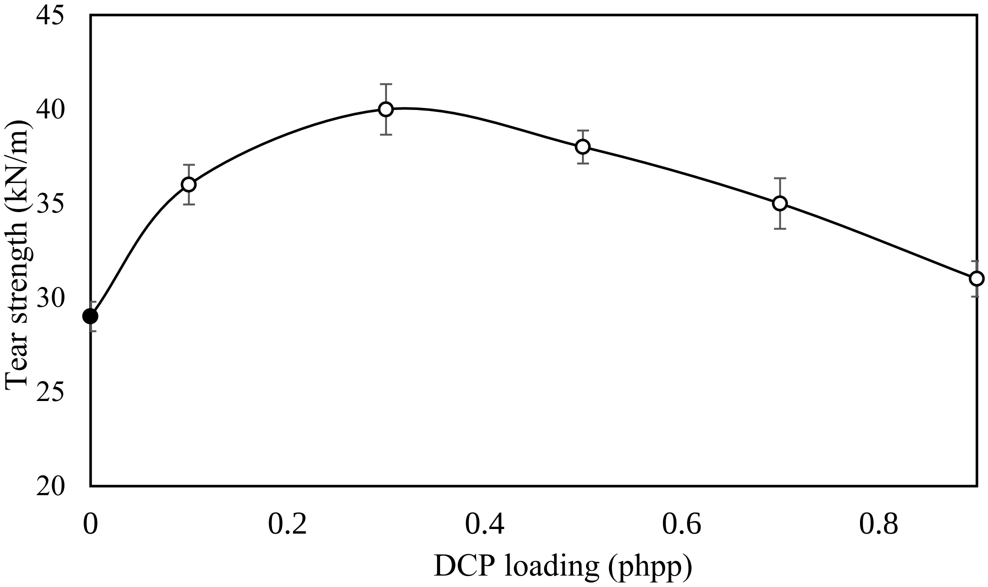


Figure 4.59: Tear strength of NR/LDPE composites at different DCP loadings

### 4.6.2 Degree of swelling and gel content

According to Figure 4.60, degree of swelling decreases with increase in DCP loading up to 0.3 pphp and increases thereafter up to 0.7 pphp. There is no significant variation shown from 0.7 to 0.9 pphp DCP loading. The crosslink density of the rubber phase is determined by the total number of chemical cross-links and trapped chain entanglements, with the latter depending on the entanglement density of the rubber during crosslinking. However, the ability of the NR phase to swell is limited by the degree of crosslinking of the NR phase and also imposed by the rigid LDPE phase, showing the influence of the morphology on degree of swelling. However, it was reported that the swelling properties of polymers are mainly related to the elasticity of the network, the extent of crosslinking, and the porosity of the polymer (Abu-Abdeen and Elamer, 2010).

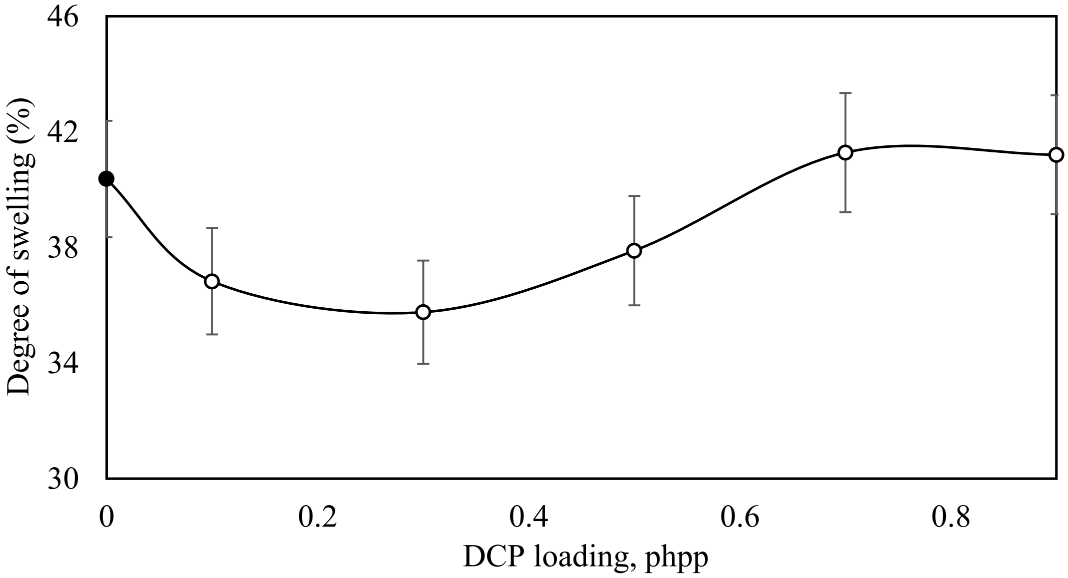


Figure 4.60: Degree of swelling of NR/LDPE composites at different DCP loadings

Gel content of the composite without peroxide and the composites with different DCP loadings are shown in Figure 4.61. Gel content of all composites with DCP exhibit higher values compared to the composite without peroxide confirming that DCP has generated more crosslinks in the NR phase of the composites. The highest gel content is shown at DCP loading of 0.3 pphp. However, all composites containing DCP did not show a significant variation in gel content. Higher degree of swelling (Figure 4.60) with constant gel content for the composites with 0.7 and 0.9 pphp DCP loading proposes some porosity in the composite. This may be due to separation of two phases due to crosslinking of the LDPE phase at a greater extent with no adhesions between phases.

Figure 4.62 shows hardness of gel of composites with different DCP loadings. Hardness of gel increases significantly with addition of DCP due to crosslinking of the NR phase and it lies below 50 proposing that the gel mainly consists of crosslinked NR phase (Muzzy. 2009). Hence, hardness of gel results is in agreement with stress-strain characteristics and hardness of the composites, and confirms that NR is the continuous phase of all the composites. Hardness of gel decreases when DCP loading is at 0.7 pphp and further decreases at 0.9 pphp and is associated with the lower crosslink density of the NR phase due to devulcanization with higher DCP loadings (Figure 4.55) and to porosity in the composites.

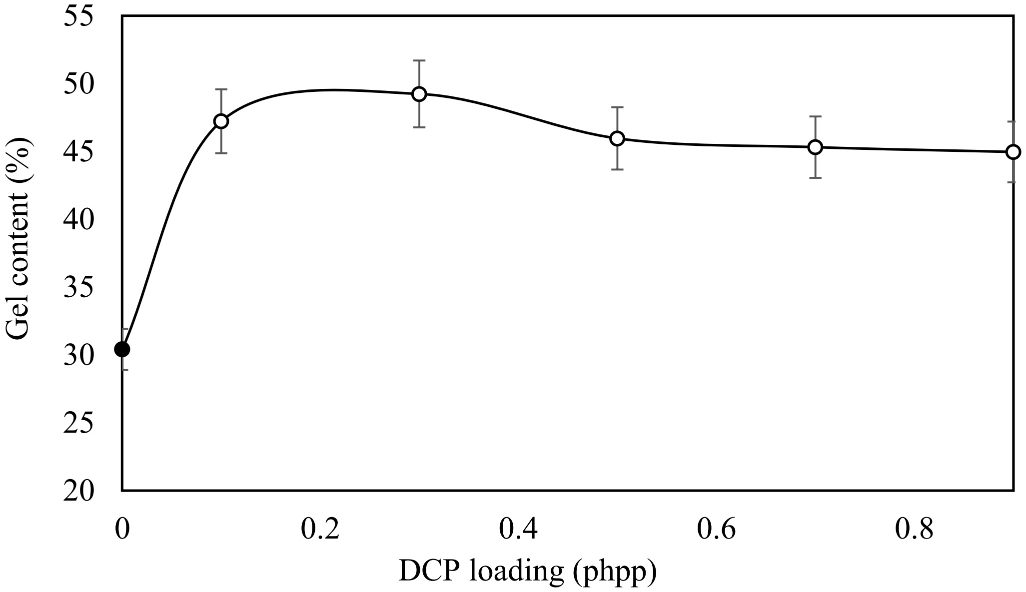


Figure 4.61: Gel content of NR/LDPE composites at different DCP loadings

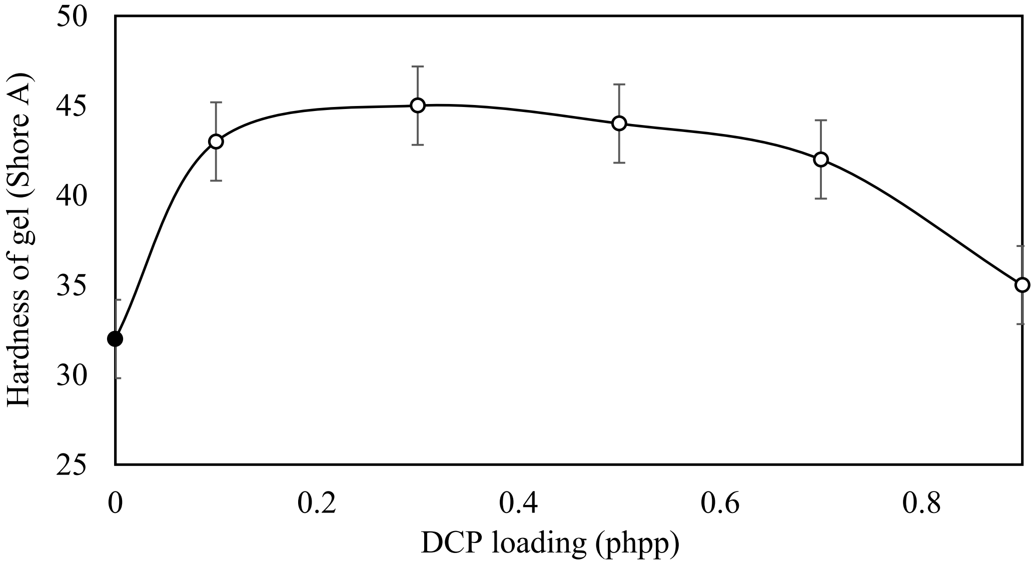


Figure 4.62: Hardness of gel content of NR/LDPE composites at different DCP loadings

### 4.6.3 FTIR spectroscopic analysis

Figure 4.63 shows FTIR spectra of raw natural rubber (NR), gel of the Control-3, and gels of the composites at different DCP loadings. S-S linkages generally show a weak stretching band in the range 500-400 cm$^{-1}$ (Rao., 1964). One sharp peak is shown at 430 cm$^{-1}$ for the gel of the Control-3 and is assigned to stretching vibration of S-S bonds (Figure 4.63(a)). This peak is not shown in the spectra of the gels of the composites with DCP, suggesting that no significant level of S-S crosslinks was present in the composites with DCP. This is associated with the S-S crosslink scission by DCP as per the mechanism shown in Figure 4.55. All spectra indicate a medium strong peak and a weak peak at 798 cm$^{-1}$ and 823 cm$^{-1}$ (Figure 4.63b), which are attributed to stretching vibrations of C-S bonds and H-C-S bonds, respectively. The gels of the composites with DCP, exhibit two peak assignments in the range 690-700 cm$^{-1}$ (Figure 4.63(b)). They are assigned to symmetric stretching vibrations of C-C bonds (Rao., 1964). As expected, only one peak assignment is shown for the gel of the Control-3, indicating that C-S bonds (assigned to 694 cm$^{-1}$) are present in the composite. According to Figure 4.63(d), a broader peak at 3440 cm$^{-1}$, which is assigned to stretching vibration of O-H bond (http://www2.ups), is exhibited in the spectrum of the gel of the composites at 0.3 pphp DCP loading. Further, the peak area at 1640 cm-$^{1}$, which is assigned to stretching vibration of C=O bond is higher in the spectra for the gel of the composite at DCP loading of 0.3 pphp. The existence of O-H is supported by possible interaction given in Figure 4.51. Thus, the formation of these bonds proves that the composite at DCP loading of 0.3 pphp achieved a better interaction between NR, LDPE and other ingredients. This also would be support to increased gel content at 0.3 pphp DCP loading.

### 4.6.4 Ageing properties

Rubber-thermoplastic composites may degrade at elevated temperatures due to oxidation process, and therefore its mechanical properties will be decreased. Table 4.5 indicates that all composites containing either sulfur vulcanizing system alone or both DCP and sulfur vulcanizing systems are highly resistant to thermal degradation. Retention of mechanical properties was greater than 100% for the Control-3 and was 94-97% for the other composites. This implies that the unreacted sulfur undergone post vulcanization when sulfur vulcanizing systems was alone present (Kumar et al., 2002).

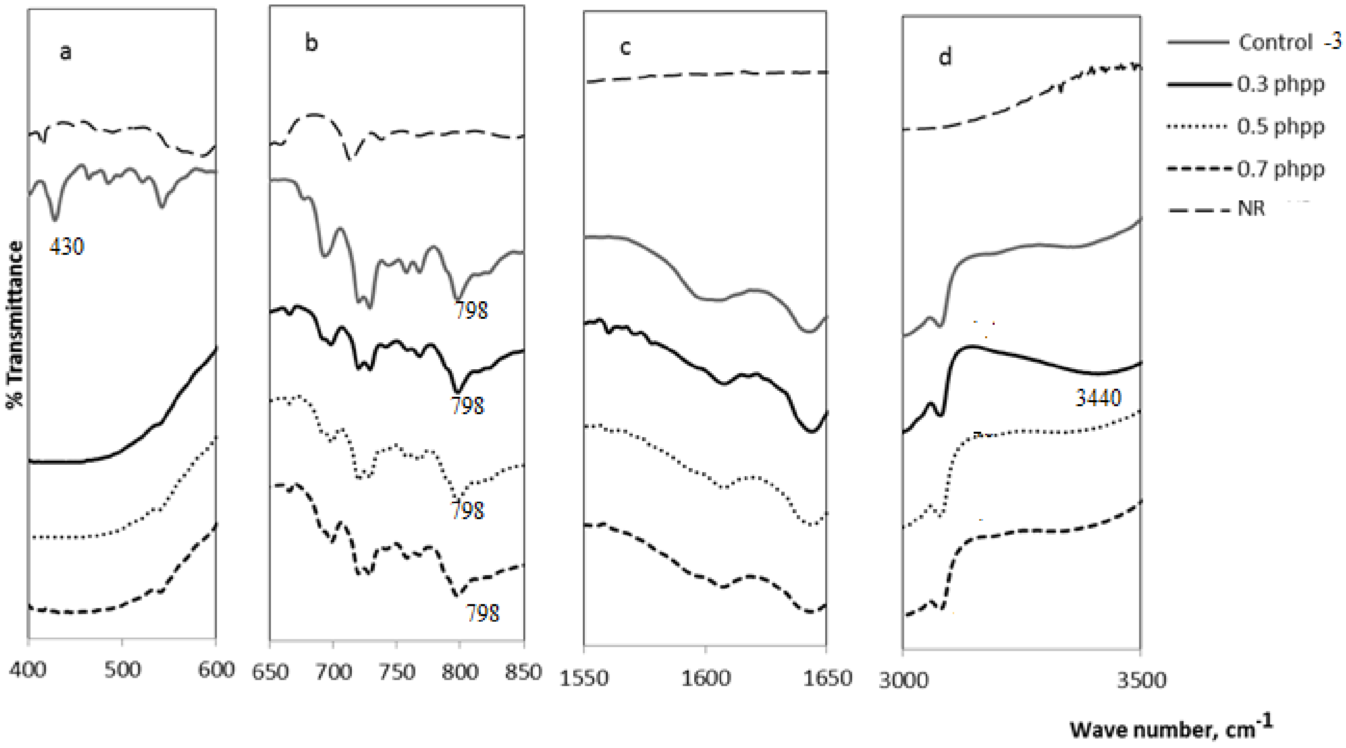


Figure 4.63: FTIR spectra of gels of the composite without peroxide and composites with DCP at different regions (a) 400 to 600 cm$^{-1}$ (b) 650 to 850 cm$^{-1}$ (c) 1550 – 1700 cm$^{-1}$ (d) 3000- 3500 cm$^{-1}$

Table 4.5: Ageing properties of NR/LDPE composites at different DCP loadings

| DCP loading, pphp | Retention of tensile strength, (%) | Retention of elongation at break, (%) |
|---|---|---|
| Control-3 | 118 | 104 |
| 0.1 | 95 | 97 |
| 0.3 | 98 | 97 |
| 0.5 | 95 | 98 |
| 0.7 | 96 | 97 |
| 0.9 | 94 | 96 |

### 4.6.5 Thermal properties

Table 4.6 shows the glass transition temperature ($T_g$), melting temperature ($T_m$) and degree of crystallinity of composites. DSC thermograms are shown in Figure B.1 (see Appendix). $T_g$ of NR increases with the addition of DCP loading of 0.1 pphp confirming that the formation of additional crosslinks in the NR phase by DCP. $T_g$ of NR further increases, but slightly, with DCP loading exhibiting more crosslinks at the NR phase. $T_m$ of LDPE also increases with the addition of DCP loading of 0.1 pphp and is associated with the higher degree of crystallinity of the LDPE phase. With the crosslinking of the LDPE phase at higher DCP loadings, $T_m$ and the degree of crystallinity decreased (Krupa and Luyt., 2002). The highest degree of crystallinty is shown at DCP loading of 0.3 pphp and tehrefore the composite at DCP loading of 0.3 pphp shows the highest tensile strength (Figure 4.56).

Table 4.6: Thermal properties of NR/LDPE composites at different DCP loadings

| **DCP loading, pphp** | **$T_g$ ( ˚C)** | **$T_m$ ( ˚C)** | **Degree of crystallinity (%)** |
|---|---|---|---|
| Control-3 | -58.6 | 109.3 | 16.6 |
| 0.1 | -56.8 | 110.0 | 19.5 |
| 0.3 | -56.5 | 110.8 | 20.8 |
| 0.5 | -56.4 | 110.5 | 18.9 |
| 0.7 | -56.3 | 109.8 | 15.2 |
| 0.9 | -55.9 | 108.3 | 15.6 |

### 4.6.6 Water absorption

Figure 4.64 shows that water absorption of the composites is less thatn 55 %. Water absorption decreases with addition of DCP loading of 0.1 pphp and further decreases until up to DCP loading of 0.3 pphp. NR and LDPE are organic polymers and hence they do not react with inorganic water molecules. The lowest water absoption at DCP loading of 0.3 pphp confirms a good adhesion between NR and LDPE phases of the composties at that DCP loading. Poor interfacial adhesions creates porosity at the interface and hence absorbes more water (Wang et al., 2005) at higher DCP loadings.

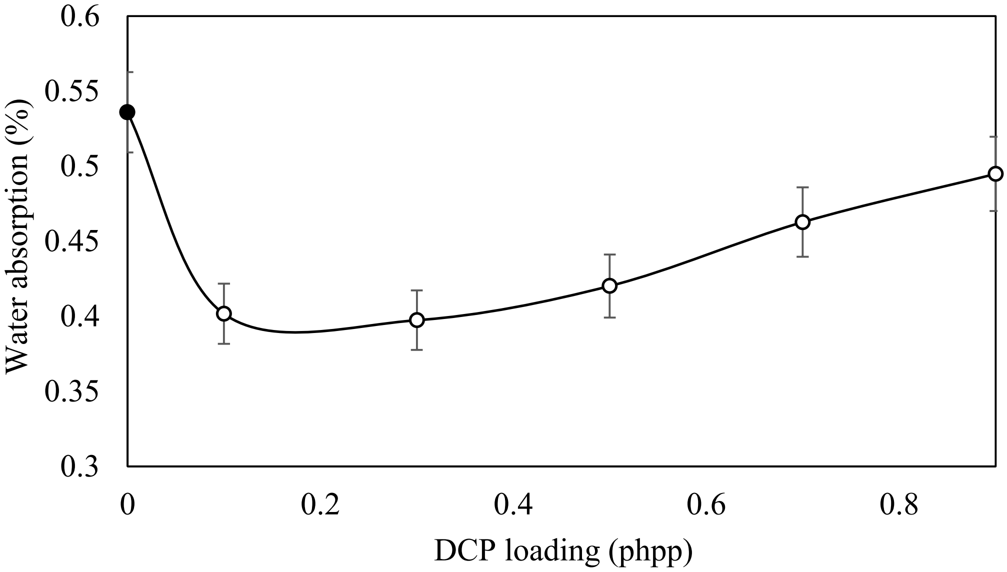


Figure 4.64: Water absorption of composites at different DCP loadings

### 4.6.7 Morphological analysis

The relation between structure and properties of rubber-thermoplastic composites are complex as it depends on many parameters (Paul et al., 1980). Figure 4.65 (a)-(c) depicts tensile fracture surfaces of the Control-3 and the composites at DCP loadings of 0.3 and 0.9 pphp. The fracture surface of the composite without peroxide is rough (Figure 4.65a), while that of the composite at DCP loading of 0.3pphp is smooth (Figure 4.65b). This smooth fracture surface indicates a good adhesion between phases. The stronger interfacial adhesions provide greater strength during tensioning, and poor crack propagation during tearing resulting in height tensile strength and tear strength of the composite. However, fracture surface of the composite at DCP loading of 0.9 pphp shows rough fracture along with porosity in the composite (Figure 4.65c). This would be the reason for the poor tensile strength, tear strength, low gel content and high water absorption of the composites at higher DCP loadings.

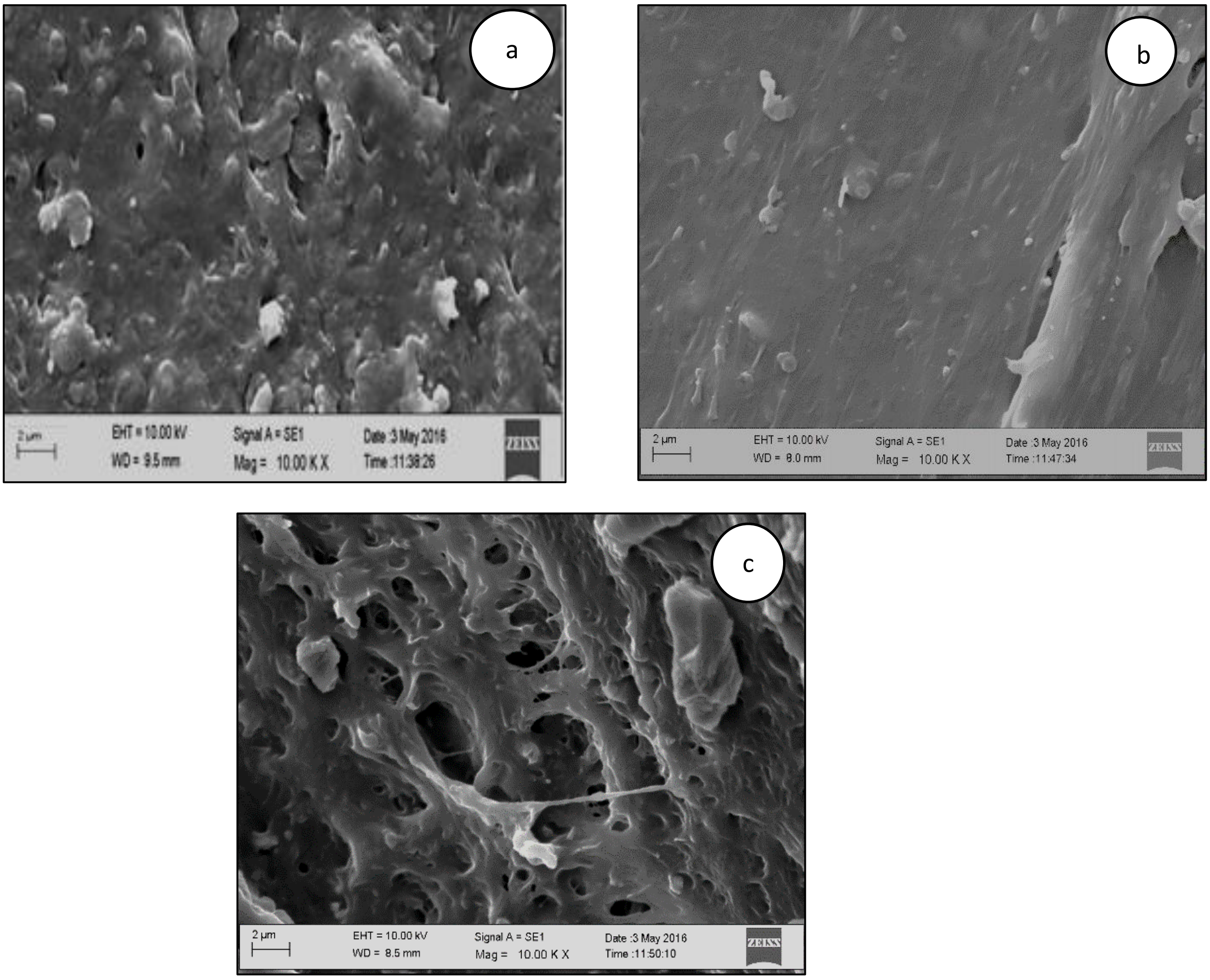


Figure 4.65: SEM images of tensile fracture surfaces of composites at different DCP loading at magnification 10k.x ( a) 0 pphp (Control-3) (b) 0.3 pphp ( c) 0.9pphp

## 4.7. Study on Using recycled LDPE (rLDPE) in Composites

rLDPE was used to prepare NR/LDPE/rLDPE composites by varying the LDPE and rLDPE ratios. Physico-mechanical and aging properties of composites were evaluated to study the optimum rLDPE loading.

### 4.7.1. Physico-mechanical properties

Table 4.7 presents the physico-mechanical properties of NR/LDPE/rLDPE composites. The tensile strength of rLDPE composites is lower than that of the NR/LDPE composite. According to a previous study, composite prepared with rHDPE/NR/ (Kenaf powder) KP reduced the tensile strength and elongation at break but increased the stabilization torque and tensile modulus. SEM images of fracture surface showed fibrillation due to the addition of rHDPE (Cao et al., 2012). Further, in the composite prepared with rLDPE, the interface would be weak

(Rector, 2006). The optimum amount to react with NR and LDPE maybe 15 pphp rLDPE, because tensile strength has been improved at that rLDPE loading. According to the statistical analysis (One-way ANOVA) at a 95% confidence interval, there is an effect of rLDPE loading on properties of 70/30/20 NR/LDPE /$CaCO_3$ composites ($p= 0.000$).

Elongation at break of the tested NR/LDPE/rLDPE composites shows a decline when compared to the control, and an increment with the addition of rLDPE up to the level of 20 pphp rLDPE. The NR/LDPE composite shows the highest elastic properties than other counterparts (Table 4.7), as it does not contain rLDPE, and has good filler dispersion. This could be due to the absence of rLDPE and good dispersion of the filler $CaCO_3$. The lowest elongation is at 30 pphp rLDPE, which is due to the high amount of rLDPE, causing resistance to elongate.

NR/LDPE composite shows the highest tear strength (Table 4.7) compared to rLDPE containing composites. If the tear strength has a high value, it indicates excellent adhesion between the phases. The lowest hardness value was obtained at the level of 20 pphp rLDPE, and the highest value from NR/LDPE composite without any rLDPE. According to Table 4.7, hardness decreased with the increment of rLDPE up to 20 pphp and increased thereafter. It was noted in the part that a high amount of post-cure treatments increases the hardness of conventional thermoplastic compounds (Mohamed, 2005).

Table 4.7**:** Physico-mechanical properties of NR/LDPE/rLDPE composites

| **LDPE: rLDPE** | **Tensile strength (MPa)** | **Elongation at break (%)** | **Tear strength (N/mm)** | **Hardness (IRHD)** |
|---|---|---|---|---|
| 30:00 | 22.3 | 359 | 57 | 67.5 |
| 25:05 | 11.7 | 235 | 35 | 59.2 |
| 20:10 | 16.3 | 295 | 44 | 61.5 |
| 15:15 | 18.0 | 321 | 45 | 54.8 |
| 10:20 | 10.0 | 297 | 33 | 55.4 |
| 00:30 | 14.5 | 212 | 39 | 62.0 |

### 4.7.2 Aging properties

Table 4.8 indicates the ageing properties of NR/LDPE/rLDPE composites. Values of NR/LDPE/rLDPE composites show good thermal resistance in all rLDPE composites. The composites, which show retention values above 100%, had not thermally degraded at the particular temperature, and they are thermally stable composites. The treatments which indicate retention values below 100% are thermally unstable composites, which had degraded under high temperatures. However, according to the results in Table 4.8, many composites show retention values above 75%. This concludes that these composites are at an acceptable level regarding aging resistance. The retentions of tear strength are close to 100%, except 20 pphp rLDPE levels.

Table 4.8: Retention properties of NR/LDPE/wLDPE composites

| **LDPE: rLDPE** | **Retention of tensile strength (%)** | **Retention of elongation at break (%)** | **Retention of tear strength (%)** |
|---|---|---|---|
| 30:00 | 78 | 100 | 74 |
| 25:05 | 166 | 114 | 68 |
| 20:10 | 82 | 102 | 63 |
| 15:15 | 75 | 139 | 58 |
| 10:20 | 105 | 82 | 97 |
| 00:30 | 106 | 168 | 72 |

## 4.8 **Proposed Reaction Mechanism for development of NR/LDPE composites**

This section describes a reaction mechanism that could occur for development of interfacial attractions in the NR/LDPE composites with titanate CA, when the mixed vulcanization system was used.

Step 1

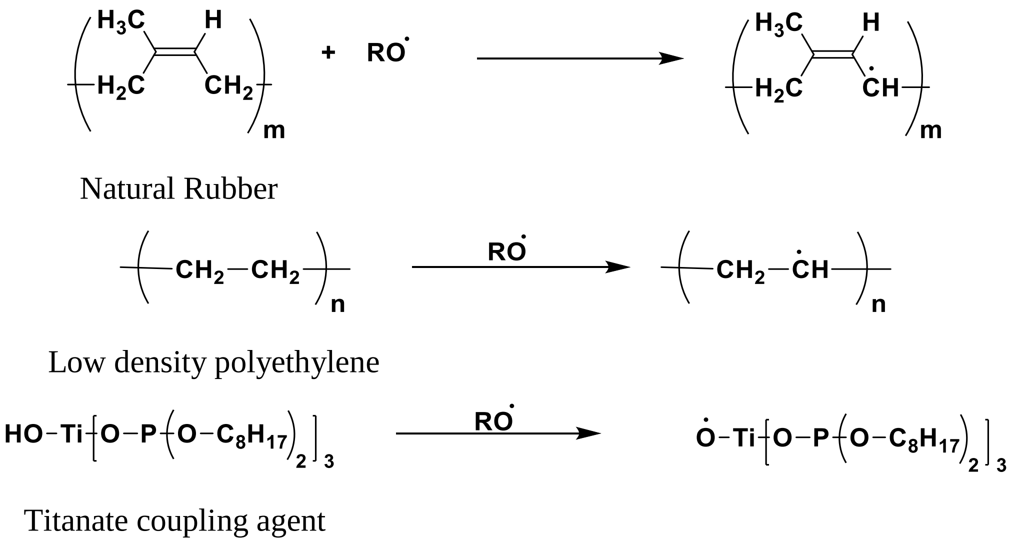
DCP in the mixed vulcanization system forms free radicals due to thermal decomposition and are called as Alkoxy radicals. (Kruželák, et al., 2017)

$$\mathrm{ROOR} \longrightarrow 2\,\mathrm{R\dot{O}}$$

Figure 4.66 Formation of Alkoxy radicals

Step 2

The alkoxy radicals generate free radicals on NR and LDPE chains and also on titanate CA due to abstraction of H atoms. These are generated from; (1) the α-methylene hydrogens of unsaturated rubbers (Kruželák et al., 2014) (2) the polymer backbone of polyethylene (Liu et al., 2014) (3) the O-H group of titanium (Monte, 2005), respectively. The corresponding reactions are presented in Figure 4.67.


Natural Rubber

Low density polyethylene

Titanate coupling agent

Figure 4.67: Formation of free radicals on NR and LDPE chains and on titanate CA

Step 3

Combination of NR and LDPE radicals would proceed in two different manners within each phase or in between the two phases ((Kruželák et al., 2014));

1. Combination of different types of radicals between the phases – Adhesion type as shown in Figure 4.68.
2. Combination of alike radicals within each phase, also called crosslinking of phase – Cohesion type as shown in Figure 4.69.

Radical combination in the blends developed in this study is evidenced by the fine morphology and the improvements in mechanical properties recorded under Section 4.1. Compared to Control-1, the 50/50 NR/LDPE blend with peroxide vulcanization system exhibited increase in tensile strength and elongation at break by 205% and 192%, respectively.

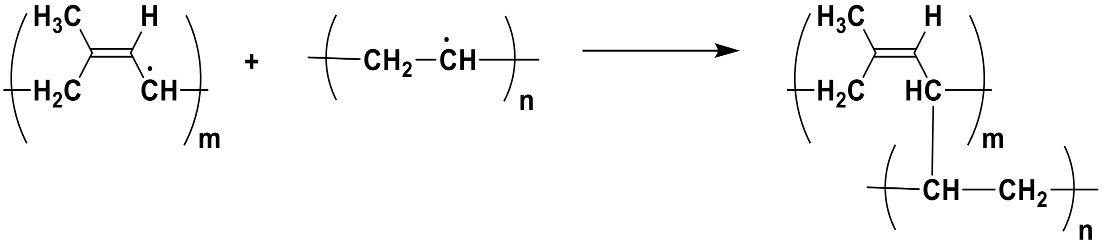


Figure 4.68: Adhesion-type radical combination

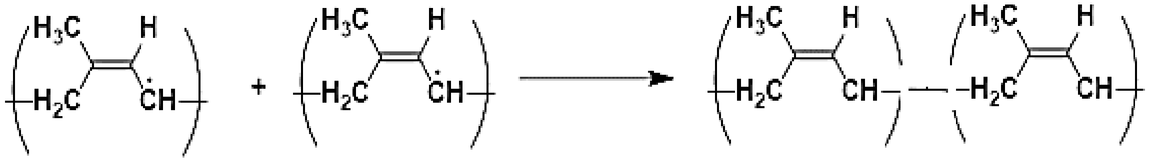


Figure 4.69: Cohesion-type radical combination

With the addition of sulphur system vulcanization with DCP as in the mixed vulcanization system, the 50/50 NR/LDPE simple blend also exhibited fine morphology along with improved mechanical properties as described in Section 4.1. Compared to Control-1, the NR/LDPE blend with mixed vulcanization system showed 174% increase in tensile strength and 252% increase in elongation at break. This is due to formation of sulphur crosslinks in the NR phase (Figure 4.70), in addition to the combination of free radicals within and in between the NR and LDPE phases.

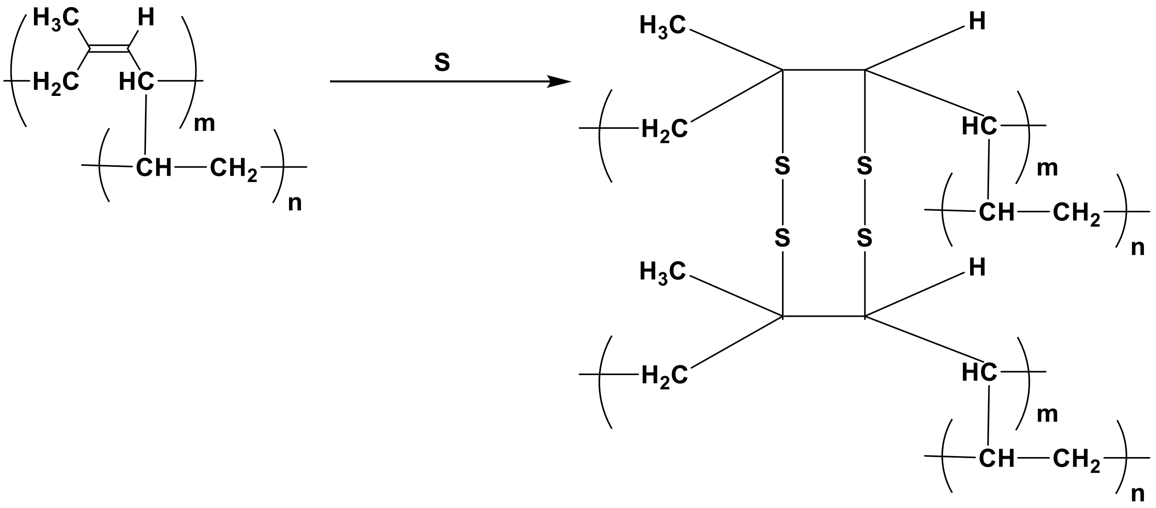


Figure 4.70: Formation of sulphur crosslinks in the NR vulcanization system along with adhesion type radical combinations between NR and LDPE phases

Addition of the mixed vulcanization system to the 50/50 NR/LDPE simple blend exhibited further enhancement in mechanical properties and is due to formation of crosslinks in the NR and LDPE phases. With the addition of titanate CA to NR/LDPE composites, in presence of 20 pphp loading of $CaCO_3$ as filler, the gel content was greatly increased while decreasing the water absorption property, revealing that the formation of more adhesion and cohesion type radical combination through titanate CA. As a result of strong linkages, tensile strength and elongation at break of 70/30 NR/LDPE composite at its optimum loadings of titanate CA at 0.7 pphp and DCP at 0.3 pphp, compared to that of the composite without titanate CA (Control-2) was increased by 220% and 310% respectively. The other physic-mechanical and chemical properties were also increased, remarkably. Linkages could be developed between NR, LDPE and titanate CA as per the reaction given in Figure 4.71. The formation of covalent bonds between titanate CA and NR and LDPE phases through $CaCO_3$ would develop according to the reaction given in Figure 4.72.

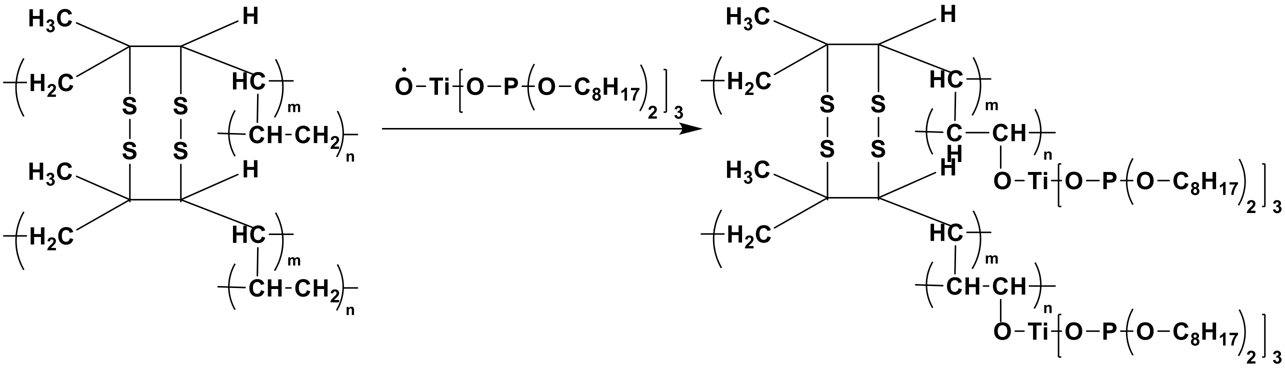


Figure 4.71: Linkages developed within NR, LDPE and titanate CA

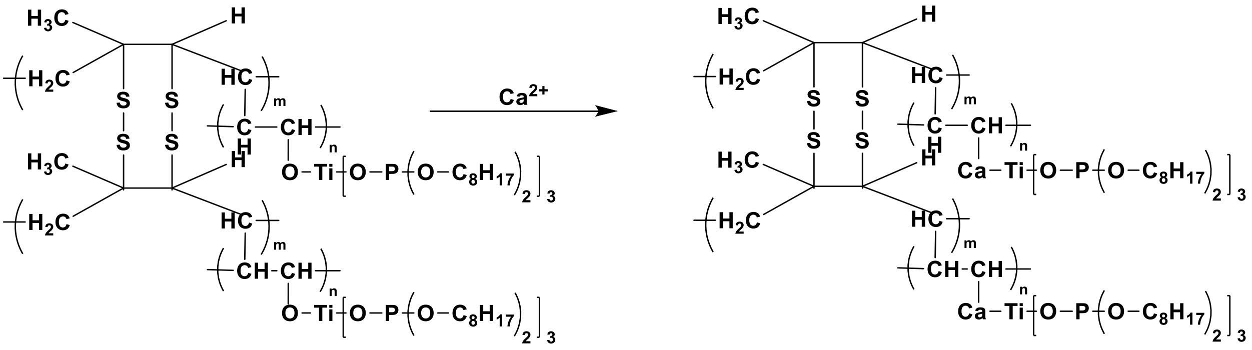


Figure 4.72: Covalent bond formation between NR, LDPE crosslinking system and titanate CA

# CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

## 5.1. Conclusions

The major conclusions drawn from the study are as follows:

- The evidence from the physico-mechanical properties, chemical properties, and surface morphology demonstrates generating a new material through melt-mixing and dynamic vulcanization of NR/LDPE blends and the formation of crosslinks in NR and LDPE phases. A 50/50 NR/LDPE blend prepared with the mixed vulcanization system showed better physical, chemical, and ageing properties with fine morphology, compared to choice with the sulphur vulcanization system and the peroxide vulcanization system.

- Incorporation of LDPE into NR enhances physico-mechanical properties of NR; thus, the blend can be used in appropriate applications, and the NR/LDPE composite at LDPE loading of 30 pphp shows the best physical and chemical performances.

- Fine phase morphology with better dispersion was observed for the 50/50 NR/LDPE composite prepared when titanate CA was added after $CaCO_{3,}$ due to formation of strong intermolecular attractions between $CaCO_3$ with NR and LDPE. Highest physico-mechanical properties were also showed, and therefore the Mixing route-III was selected as the bet mixing route to produce NR/LDPE composites.

- Results revealed that dynamic vulcanization introduced crosslinks to NR and LDPE phases which resulted in improved mechanical and physical properties. Mechanical properties of the composites enhanced with the increase of in DCP loading due to increase in crosslink density evidenced by the decrease in degree of swelling and water absorption. However, the optimum DCP concentration was found to be 0.3 pphp for the 70/30 NR/LDPE composite. Compatibility of the phases in the 70/30 NR/LDPE composite was enhanced at the optimum titanate CA loading of 0.7 pphp.

- The 70/30 NR/LDPE composites prepared with recycled-LDPE replacing LDPE showed inferior tensile properties, hardness and tear strength. Retention of mechanical properties after thermal ageing was a minimum at 58%, when the replacement was 50%. Though variation of these properties did not show a significant trend, the reduced properties could also be sufficient to use in dry rubber based applications.
- Based on the results of this study, a possible reaction mechanism was proposed for development of NR/LDPE composites using the mixed vulcanization system and a titanate CA.

## 5.2 Recommendations for Future Work

- This study focused on evaluating performance of a titanate CA, only one type of a compatibilizer. However, literature reported a wide range of compatibilizers used in NR/LDPE blends and composites with different types of fillers. Therefore, investigating of different types of potential compatibilizers will be significant to find an efficient compatibilizer/s for NR/LDPE blends/composites.

- This study was also aimed at developing NR/LDPE composites at different blend compositions. A wide range of properties obtained can be used in different manufacturing applications, although it was not studied. Therefore, studying the manufacturing applications of these blend compositions is suggested.

- Regarding the performances, this study mainly focused on selected mechanical, chemical, morphological, thermal, and ageing properties of the NR/LDPE blends and composites. However, in industrial applications, the products manufactured from NR and LDPE will be subjected to various dynamic applications. Therefore, analysing the product properties of the particular outcome of NR/LDPE composite is proposed as an extension to this work.

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# APPENDICES

## APPENDIX - A

### FTIR analysis of NR and LDPE

Table A.1: shows peak assignments and wave numbers of NR and LDPE.

Table A.1. FTIR absorption bands

| **Polymer** | **Wave number ($cm^{-1}$)** | **Peak assignment** |
|---|---|---|
| NR | 720, 798 | $CH_2$- bending vibration |
| NR | 823 (820-860) | $CH_2$- asymmetric and symmetric stretching vibration<br>=CH wagging vibration |
| LDPE | 1376 | $CH_2/CH_3$ strong stretching and bending vibrations |

# APPENDIX - B

## DSC thermograms of NR/LDPE composites at different DCP loadings

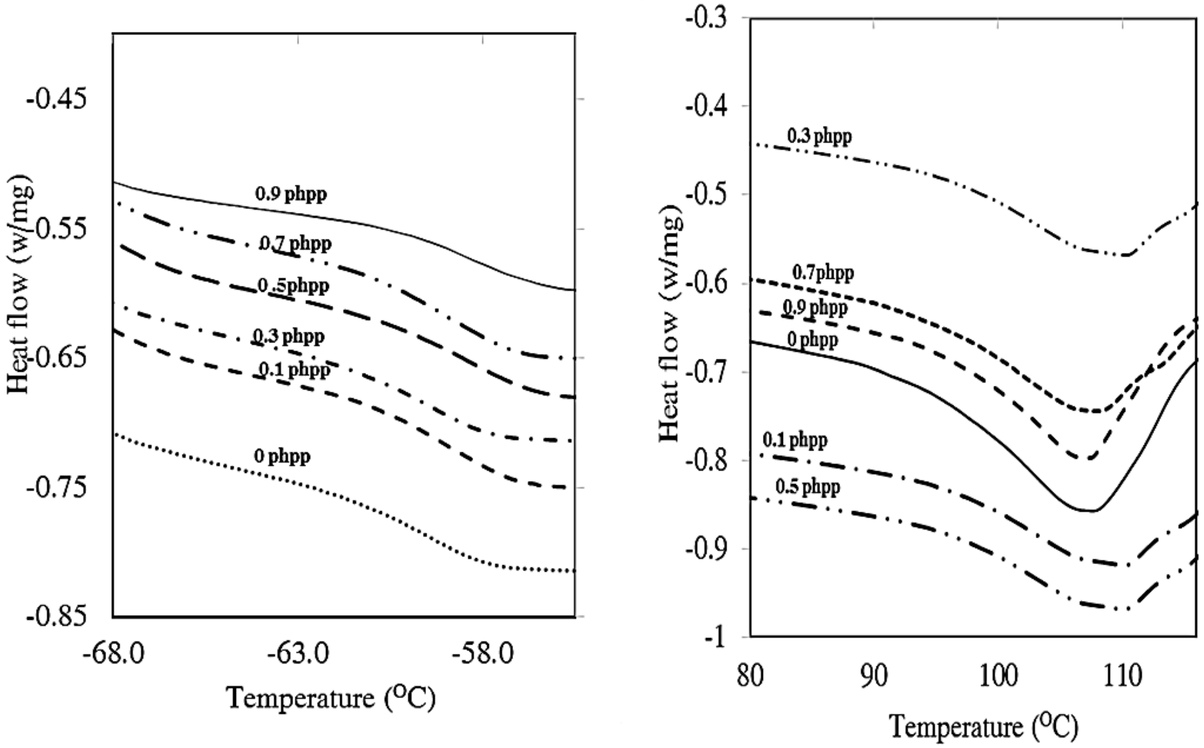

Figure B.1: DSC thermograms of NR/LDPE composites at different DCP loadings

## APPENDIX- C

### Statistical analysis of tensile stength

Tensile strength of NR/LDPE blends and composites was statistically analyzed by Minitab 17 software. The analyze report is shown as the follow.

### Effect of vulcanizing system on tensile property of 50/50 NR/LDPE composites

```
Source      DF     SS          MS         F         P
Vulca sys    3     112.6145    37.5382    505.85    0.000
Error        8     0.5937      0.0742
Total       11     113.2082

S = 0.2724   R-Sq = 99.48%   R-Sq(adj) = 99.28%


                  Individual 95% CIs For Mean Based on
                  Pooled StDev
Level       N          Mean            StDev
            3          4.200           0.100
2           3          7.920           0.026
3           3          12.260          0.026
4           3          10.707          0.534

                       5.0      7.5     10.0     12.5

Pooled StDev = 0.272


Grouping Information Using Tukey Route

Vulca
sys         N          Mean         Grouping
3           3          12.2600       A
4           3          10.7067       B
2           3           7.9200       C
1           3           4.2000       D

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Vulca sys

Individual confidence level = 98.74%
```

```
Vulca sys = 1 subtracted from:

Vulca
sys      Lower        Center      Upper
2        3.0075       3.7200      4.4325
3        7.3475       8.0600      8.7725
4        5.7942       6.5067      7.2191

                    -3.5     0.0     3.5     7.0


Vulca sys = 2 subtracted from:

Vulca
sys      Lower        Center       Upper
3       3.6275        4.3400       5.0525
4       2.0742        2.7867       3.4991

                    -3.5     0.0     3.5     7.0


Vulca sys = 3 subtracted from:

Vulca
sys      Lower         Center        Upper
4        -2.2658        -1.5533      -0.8409

                      -3.5     0.0     3.5     7.0
```

**Effect of composite ratio on tensile property of NR/LDPE simple composites**

```
Source          DF          SS           MS            F          P
LDPE loading     5        307.6000     61.5200     1604.87     0.000
Error           12          0.4600      0.0383
Total           17        308.0600

S = 0.1958   R-Sq = 99.85%   R-Sq(adj) = 99.79%

Individual 95% CIs for Mean Based on
                Pooled StDev
Level     N      Mean      StDev
 10       3      1.800     0.100
 30       3      3.200     0.200
 50       3      4.500     0.173
 70       3      6.600     0.265
```

```
 90          3      9.800    0.100
100          3     13.900    0.265

                   3.5     7.0    10.5    14.0

Pooled StDev = 0.196


Grouping Information Using Tukey Route

LDPE
loading      N        Mean        Grouping
100          3      13.900        A
 90          3       9.800        B
 70          3       6.600        C
 50          3       4.500        D
 30          3       3.200        E
 10          3       1.800        F

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of LDPE loading

Individual confidence level = 99.43%


LDPE loading =  10 subtracted from:

LDPE
loading      Lower        Center        Upper
 30          0.863         1.400        1.937
 50          2.163         2.700        3.237
 70          4.263         4.800        5.337
 90          7.463         8.000        8.537
100         11.563        12.100        12.637
                        -6.0      0.0      6.0     12.0

LDPE loading = 30 subtracted from:

LDPE
loading    Lower     Center     Upper
 50        0.763      1.300      1.837
 70        2.863      3.400      3.937
 90        6.063      6.600      7.137
```

```
100        10.163    10.700      11.237

                              -6.0      0.0      6.0      12.0


LDPE loading = 50 subtracted from:

LDPE
loading      Lower       Center       Upper
 70          1.563        2.100        2.637
 90          4.763        5.300        5.837
100          8.863        9.400        9.937

                             -6.0      0.0      6.0      12.0


LDPE loading = 70 subtracted from:

LDPE
loading       Lower         Center          Upper
 90           2.663         3.200           3.737
100           6.763         7.300           7.837

                             -6.0      0.0      6.0      12.0


LDPE loading = 90 subtracted from:

LDPE
loading       Lower         Center        Upper
100           3.563         4.100         4.637

                             -6.0      0.0      6.0      12.0
```

**Effect of CA on tensile properties of NR/LDPE/$CaCO_3$ composites**

```
Source        DF        SS             MS             F            P
CA              5      240.1597     48.0319      600.57      0.000
Error          12          0.9597      0.0800
Total          17      241.1194

S = 0.2828   R-Sq = 99.60%   R-Sq(adj) = 99.44%
```

```
                          Individual 95% CIs for Mean Based on Pooled StDev
Level      N          Mean          StDev
 10        3          10.667        0.306
 30        3          18.800        0.361
 50        3          12.400        0.400
 70        3           7.300        0.200
 90        3           9.100        0.173
100        3          10.113        0.163

                          7.0      10.5      14.0      17.5

Pooled StDev = 0.283


Grouping Information Using Tukey Route

CA       N          Mean          Grouping
 30      3          18.800         A
 50      3          12.400         B
 10      3          10.667         C
100      3          10.113         C
 90      3           9.100         D
 70      3           7.300         E

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of CA

Individual confidence level = 99.43%


CA = 10 subtracted from:

CA          Lower         Center        Upper
 30          7.358          8.133        8.909
 50          0.958          1.733        2.509
 70         -4.142         -3.367       -2.591
 90         -2.342         -1.567       -0.791
100         -1.329         -0.553        0.222
                               -7.0      0.0      7.0     14.0
```

```
CA = 30 subtracted from:

CA          Lower        Center          Upper
 50        -7.176        -6.400          -5.624
 70        -12.276       -11.500          -10.724
 90        -10.476       -9.700           -8.924
100        -9.462        -8.687          -7.911

                         -7.0      0.0      7.0     14.0


CA = 50 subtracted from:

CA     Lower          Center          Upper
 70    -5.876         -5.100          -4.324
 90    -4.076         -3.300          -2.524
100     -3.062         -2.287          -1.511
                        -7.0      0.0      7.0     14.0


CA = 70 subtracted from:

CA     Lower          Center          Upper
 90    1.024          1.800            2.576
100    2.038          2.813            3.589

                   -7.0      0.0      7.0     14.0


CA = 90 subtracted from:

CA     Lower          Center          Upper
100    0.238           1.013          1.789

                   -7.0      0.0      7.0     14.0
```

**Effect of mixing routes on tensile properties of NR/LDPE/$CaCO_3$ composites with CA**

```
Source          DF     SS            MS            F             P
Mix route        3     77.59000      25.86333      3103.60       0.000
Error            8     0.06667       0.00833
Total           11     77.65667

S = 0.09129   R-Sq = 99.91%   R-Sq(adj) = 99.88%
```

```
Individual 95% CIs for Mean Based on Pooled StDev

Level   N       Mean          StDev
1        3      6.8000        0.1000
2        3      7.5000        0.1000
3        3      7.1667        0.0577
4        3      13.0000       0.1000

                   8.0     10.0     12.0     14.0

Pooled StDev = 0.0913

Grouping Information Using Tukey Route

Mix
route   N       Mean          Grouping
4       3       13.0000          A
2       3        7.5000          B
3       3       7.1667           C
1       3       6.8000           D

Means that do not share a letter are significantly different.

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Mix route

Individual confidence level = 98.74%

Mix route = 1 subtracted from:

Mix
route       Lower        Center        Upper
2          0.4612       0.7000        0.9388
3          0.1279       0.3667        0.6054
4          5.9612       6.2000        6.4388

                     -3.5      0.0      3.5      7.0
Mix route = 2 subtracted from:

Mix
route             Lower          Center          Upper
3                 -0.5721        -0.3333         -0.0946
4                  5.2612         5.5000          5.7388

                       -3.5      0.0      3.5      7.0
```

```
Mix route = 3 subtracted from:

Mix
route          Lower          Center          Upper
4              5.5946         5.8333          6.0721

                      -3.5      0.0      3.5      7.0
```

## Effect of coupling agent loading on tensile properties of 70/30/20 NR/LDPE/$CaCO_3$ composites

```
Source                        DF      SS              MS            F            P
Coupling agent  loading       6       239.4457         39.9076      1309.47      0.000
Error                         14      0.4267          .0305
Total                         20      239.8724

S = 0.1746   R-Sq = 99.82%   R-Sq(adj) = 99.75%


                Individual 95% CIs For Mean Based on
                Pooled StDev
Level          N       Mean          StDev
1              3       6.900         0.100
2              3       12.000        0.300
3              3       16.033        0.153
4              3       17.233         0.115
5              3       10.733        0.153
6              3       10.133        0.208
7              3       9.700         0.100

                   9.0      12.0      15.0      18.0

Pooled StDev = 0.175


Grouping Information Using Tukey Route

Coupling
agent
loading        N        Mean           Grouping
4              3       17.233              A
3              3       16.033              B
2              3       12.000              C
5              3       10.733              D
6              3       10.133              E
7              3         9.700             E
```

```
1            3       6.900            F

Means that do not share a letter are significantly different.

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Coupling agent loading

Individual confidence level = 99.58%

Coupling agent  loading = 1 subtracted from:

Coupling
agent
loading        Lower        Center        Upper
2             4.613          5.100         5.587
3             8.647          9.133         9.620
4             9.847         10.333        10.820
5             3.347          3.833         4.320
6             2.747          3.233         3.720
7             2.313          2.800         3.287

                     -5.0     0.0     5.0     10.0

Coupling agent loading = 2 subtracted from:

Coupling
agent
loading        Lower        Center        Upper
   3           3.547         4.033         4.520
   4           4.747         5.233         5.720
   5          -1.753        -1.267        -0.780
   6          -2.353        -1.867        -1.380
   7          -2.787        -2.300        -1.813

                     -5.0     0.0     5.0     10.0

Coupling agent loading = 3 subtracted from:

Coupling
agent
loading        Lower        Center        Upper
  4             0.713        1.200         1.687
  5           -5.787        -5.300        -4.813
  6           -6.387        -5.900        -5.413
  7           -6.820        -6.333        -5.847
```

```
                            -5.0     0.0     5.0    10.0

Coupling agent loading = 4 subtracted from:

Coupling
agent
loading         Lower          Center         Upper
  5             -6.987         -6.500         -6.013
  6             -7.587         -7.100         -6.613
  7             -8.020         -7.533         -7.047
                      -
                            -5.0     0.0     5.0    10.0

Coupling agent loading = 5 subtracted from:

Coupling
agent
loading         Lower          Center         Upper
  6             -1.087         -0.600         -0.113
  7             -1.520         -1.033         -0.547

                            -5.0     0.0     5.0    10.0
Coupling agent loading = 6 subtracted from:

Coupling
agent
loading         Lower          Center         Upper
7               -0.920         -0.433         0.053

                            -5.0     0.0     5.0    10.0
```

**Effect of DCP loading on properties of 70/30/20 NR/LDPE /$CaCO_3$ composites**

```
Source                 DF        SS            MS            F            P
DCP loading            5      321.1911      64.2382       947.78        0.000
Error                  12       0.8133       0.0678
Total                  17     322.0044

S = 0.2603   R-Sq = 99.75%   R-Sq(adj) = 99.64%

Individual 95% CIs For Mean Based on Pooled StDev

Level    N      Mean          StDev
  1      3      14.567        0.058
  2      3      14.500        0.200
  3      3      22.000        0.265
```

```
  4      3    12.567        0.493
  5      3    12.200        0.200
  6      3     7.900        0.100

               8.0     12.0     16.0     20.0

Pooled StDev = 0.260

Grouping Information Using Tukey Route

DCP
loading  N    Mean          Grouping
  3      3    22.000           A
  1      3    14.567           B
  2      3    14.500           B
  4      3    12.567           C
  5      3    12.200           C
  6      3    7.900            D

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of DCP loading

Individual confidence level = 99.43%


DCP loading = 1 subtracted from:

DCP
loading       Lower         Center        Upper
  2           -0.781        -0.067         0.647
  3            6.719         7.433         8.147
  4           -2.714        -2.000        -1.286
  5           -3.081        -2.367        -1.653
  6           -7.381        -6.667        -5.953
                       -8.0      0.0      8.0     16.0


DCP loading = 2 subtracted from:

DCP
loading       Lower         Center        Upper
  3           6.786         7.500         8.214
  4           -2.647        -1.933        -1.219
```

```
  5            -3.014        -2.300        -1.586
  6            -7.314        -6.600        -5.886

                        -8.0      0.0      8.0     16.0


DCP loading = 3 subtracted from:

DCP
loading        Lower         Center        Upper
  4            -10.147       -9.433        -8.719
  5            -10.514       -9.800        -9.086
  6            -14.814       -14.100       -13.386

                         -8.0      0.0      8.0     16.0

DCP loading = 4 subtracted from:

DCP
loading        Lower         Center        Upper
  5            -1.081        -0.367        0.347
  6            -5.381        -4.667        -3.953

                        -8.0      0.0      8.0     16.0


DCP loading = 5 subtracted from:

DCP
loading        Lower         Center        Upper
6              -5.014        -4.300        -3.586

                        -8.0      0.0      8.0     16.0
```

**Effect of rPE loading on tensile properties of 70/30/20 NR/LDPE/$CaCO_3$ composites**

```
Source         DF     SS          MS           F       P
rPE  loading    5     306.59      61.32        14.14   0.000
Error          12     52.02       4.33
Total          17     358.61

S = 2.082   R-Sq = 85.49%   R-Sq(adj) = 79.45%

Individual 95% CIs For Mean Based on Pooled StDev
```

```
Level   N    Mean       StDev
  1     3    22.333     0.208
  2     3    11.800     1.000
  3     3    16.267     2.120
  4     3    18.667     3.055
  5     3    10.000     2.330
  6     3    14.500     2.390

               10.0    15.0    20.0    25.0

Pooled StDev = 2.082

Grouping Information Using Tukey Route

rPE
loading    N        Mean        Grouping
   1       3        22.333      A
   4       3        18.667      A B
   3       3        16.267        B C
   6       3        14.500        B C D
   2       3        11.800          C D
   5       3        10.000            D

Means that do not share a letter are significantly different.

Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of rPE loading

Individual confidence level = 99.43%


rPE loading = 1 subtracted from:

rPE
loading       Lower       Center      Upper
  2           -16.243     -10.533     -4.823
  3           -11.777     -6.067      -0.357
  4           -9.377      -3.667      2.043
  5           -18.043     -12.333     -6.623
  6           -13.543     -7.833      -2.123

                      -10      0      10      20


rPE loading = 2 subtracted from:
```

| rPE loading | Lower | Center | Upper |
|---|---|---|---|
| 3 | -1.243 | 4.467 | 10.177 |
| 4 | 1.157 | 6.867 | 12.577 |
| 5 | -7.510 | -1.800 | 3.910 |
| 6 | -3.010 | 2.700 | 8.410 |

-10 0 10 20

rPE loading = 3 subtracted from:

| rPE loading | Lower | Center | Upper |
|---|---|---|---|
| 4 | -3.310 | 2.400 | 8.110 |
| 5 | -11.977 | -6.267 | -0.557 |
| 6 | -7.477 | -1.767 | 3.943 |

-10 0 10 20

rPE loading = 4 subtracted from:

| rPE loading | Lower | Center | Upper |
|---|---|---|---|
| 5 | -14.377 | -8.667 | -2.957 |
| 6 | -9.877 | -4.167 | 1.543 |

-10 0 10 20

rPE loading = 5 subtracted from:

| rPE loading | Lower | Center | Upper |
|---|---|---|---|
| 6 | -1.210 | 4.500 | 10.210 |

-10 0 10 20

## APPENDIX- D

## List of publications

### A-D.1 Indexed journals

**Sampath W.D.M**, Egodage S. M. and Edirisinghe D.G., Effect of organotitanate coupling agent on properties of calcium carbonate filled low-density polyethylene and natural rubber composite. Accepted for publication in the Journal of the National Science Foundation of Sri Lanka (JNSF). (Manuscript ID- Ms. 223:2017)

**Sampath W.D.M**, Egodage S. M. and Edirisinghe D.G., Effect of peroxide loading on properties of natural rubber and low-density polyethylene composites. Accepted for publication in the Journal of the Physical Science. (Manuscript ID -JPS-OA-17-0154)

### A-D.2 Peer reviewed journals

**Sampath W.D.M**, Edirisinghe D.G and Egodage S.M (2016) “Property Improvements of Natural Rubber and Low Density Polyethylene Blends through Dynamic Vulcanization”. Journal of Rubber Research Institute of Sri Lanka, Vol. 96., pp 1-8.

### A-D.3 Full papers at national and international conferences

#### A-D.3.1 Full papers

**WDM Sampath**, DG Edirisinghe and SM Egodage (2019), Effect of recycle polyethylene (rPE) on properties of titanate coupling agent treated natural rubber (NR) /low-density polyethylene (LDPE) / rPE Composites. 3rd ICSTR Dubai International Conference on Science and Technology Research, Dubai, February 2019.

**WDM Sampath**, DG Edirisinghe and SM Egodage (2016), “Property Improvements of natural rubber and low density polyethylene blends through dynamic vulcanization”, Proceedings of the sixth symposium on plantation crop research, BMICH, Sri Lanka, Volume 2, pp 55-64, 2nd -4th November 2016.

**WDM Sampath**, SM Egodage and DG Edirisignhe (2015), "Improvement of physico-mechanical properties of calcium carbonate filled natural rubber and low density polyethylene blends with titanate coupling agent", *MERCon 2015*, Moratuwa Engineering Research Conference, University of Moratuwa, Sri Lanka, pg. 82, 7th -8th April 2015 DOI: 10.1109/MERCon. 2015.7112350, pp-228-233.

**Sampath W.D.M,** Egodage SM and Edirisinghe DG (2015) "Effects of titanate base coupling agent and mixing methods on properties of Natural Rubber and Low Density Polyethylene Blends". Proceedings of the International Rubber Conference 2015, Rubber Research Institute, Vietnam, 2nd -3rd November, 2015.

**Sampath W.D.M**, Egodage S. M.and Edirisinghe D.G. (2014), "Effect of blend ratio on properties of natural rubber/low density polyethylene blends", *Annual Transactions of Institute of Engineers, Sri Lanka (IESL)*, and Volume1 Part B: 247-253, 14th – 15th October, 2014.

**Sampath W.D.M**, Egodage S.M and Edirisinghe DG (2013). "Evaluation of Dynamic Vulcanization of Natural Rubber and Low Density Polyethylene Blend", Proceedings of the RubberCon 2013, Bangkok, 16th -18th December 2013, Thailand.

### A-D.3.2 Abstracts

**WDM Sampath**, SM Egodage and DG Edirisignhe (2015), "Effect of a titanate coupling agent on chemical and ageing properties of calcium carbonate filled natural rubber and low density polyethylene composites", *2nd Biennial International Symposium on Polymer Science and Technology 2015*, Department of Chemistry, University of Sri Jayawardenapura, Sri Lanka, pg. 10 , 3rd- 4th November 2015.

Received Award for the best theme abstract.