FLAMMABILITY PROPERTIES OF COMPATIBILILIZED DIKANUT SHELL POWDER FILLED NATURAL RUBBER/POLY (VINYL CHLORIDE) COMPOSITES

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CERTIFICATION

This is to certify that this research work entitled "Flammability Properties of Compatibilized Dikanut Shell Powder filled Natural Rubber/Poly (Vinyl chloride) composites" was carried out by ODIDI, OKPO DONALD (2013487834378) in partial fulfillment for the award of the Degree of Master of Science (M. Sc) in the Polymer Science and Engineering, Department of Polymer and Textile Engineering, Federal University of Technology, Owerri under my supervision.

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DEDICATION

This work is dedicated to the evergreen memory of my late Father, Chief S.M.O Odidi, who departed this world on the 23rd, September, 1991.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOTATIONS

SG - Styrene-co-glycidyl methacrylate

PA - Polyamide

GMA - GlcidylMethacrylate

MBS - Methymethacrylate-butadine Styrene

PEG - Polyethylene Glycol

AFM - Atomic Force Micrograph

PTMSP - Poly (1 trimethylsily-1-propyne)

EVA - Poly (ethyl-1-vinyl acetate)

DCP - DicumylPeroxide

WSR - Water-swellableRubber

SAP - Super-absorbent Polymer

TBBs - N-ter-butyl-2benzothiazyl sulphenamide

HMDA - Hexamethylene diamine

PB - Polymer blend

VARTM - VARTM-Vacuum Assisted Resin Transfer Moulding

VARIM - Vacuum Assisted Resin Infusion Moulding

SCRIMP^{TM} - Seemann Composites Resin Infusion Moulding Process

VBRTM - Vacuum Bag Resin Transfer Moulding

VARI - Vacuum Assisted Resin Infusion

ISAF - Intermediate Super Abrasion Furnace

HSR - High Styrene Rubber

LDW - Limestone Dust Waste

PCC - Precipitated Calcium Carbonate

NPCC - Nano Precipitated Calcium Carbonate

PVC - Polyvinylchloride

TMQ - TrimethylQuinine

CBS - Cyclobenzylsulphenamide

Zn-SNR - Zinc Salt of Natural Rubber

ESBS - Styrene-(epoxidized butadiene)-styrene

PE-g-MA - Maleic anhydride grafted polyethylene

GO - Graphene Oxide

DRC - Democratic Republic of Congo

APP - Atactic Polypropylene

ABS - Acrylonitrile butadiene styrene

MAPP - Maleic anhydride-g-polypropylene

LLDPE - Linear Low Density Polyethylene

HDPE - High Density Polyethylene

NR - Natural Rubber

PVA - Poly (vinyl alcohol)

DNS - Dikanut Shell

ENR - Epoxidized Natural Rubber

Tg - Glass Transition Temperature

EPDM - Ethylene Propylenediene monomer

CSM - Chlorosulphonated polyethylene

SEM - Scanning Electron Microscopy

PC - Polycarbonate

SBR - Styrene-butadiene Rubber

PET - Polyethylene Terephtate

MAPI - Maleic Anhydride-g-polyisoprene

DSC - Differential Scanning Calorimetry

PPO - Poly (Phenylene oxide)

TETA - Triethylene-tetramine

SAN - Styrene-acrolynotrile

ZnO - Zinc Oxide

PP - Polystyrene

IPN - Interpenetrating polymeric network

FTIR - Fourier Transform Infra-red

TMTD - Tetra Methyl ThiuramDisulphide

MBT - Mecapto Benzoyl Thiazol

ABSTRACT

The major objective of the study is to evaluate the flame retardant properties of NR/PVC/DNS powder filled with KBr, $Mg(Cl)_2$ and $Mg(Oh)_2$as flame retardant bio-composites obtained by using MAPI (maleic anhydride-g-polyisosprene) and TETA (triethylene tetramine).Blends of natural rubber (NR) and polyvinyl chloride (PVC) filled with dikanut shell powder (DNS) and carbon black (CB) were prepared by reactive compatibilization in a two-roll mill. A combination of maleic anhydride-g-polyisosprene (MAPI) and triethylene tetramine (TETA) was used as compatibilizers. Halogenated flame retardants ($Mg(Cl)_2$ and KBr) and metal oxide flame retardant, $Mg(OH)_2$ were used as flame retardants. Blend compositions of NR/PVC100/30 were filled with varying filler ratios of CB/DNS30/0, 30/5, 15/10, 10/15, 5/20, 0/25, 0/30 pphr. Blends were filled with flame retardants in the ratios of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 pphr. The effects of filler loading, compatibilizer loading, mesh size (particle size) and flame retardants on vulcanizate properties of filled blends such as ignition time, auto-combusting time and flame propagation rate were investigated. The results show that dikanut shell powder significantly improved the flammability properties of the blends. The flame propagation rate was greatly reduced by increasing both DNS and CB filler loading. It was observed that the composites became more resistant to ignition and propagation of flame with increasing filler content. The rate of burning of the composites also decreased with reducing filler particle size. The rate of flame propagation also showed a decrease with increasing flame retardant levels. Increases in the compatibilizer levels made the composites more resistant to burning and decomposition, thereby increasing the flame resistance. The NR/PVC/CB composite blends showed superior flame resistance characteristic than the NR/PVC/DNS composite blends. Flame retardancy of the composites showed improvements of about 200% and above in some cases. The NR/PVC/DNS can be used for high volume polymer products such as shoe soles, foot mats and car exhaust hangers at low DNS filler loading of 10pphr.

Key words : flame retardant, dikanut shell, ignition time, natural rubber

CHAPTER ONE

INTRODUCTION

1.1 Background study

Advances in the production of high-performance polymer-based compositions will in the future more likely result from the utilization of new mixtures of polymers and mixtures of polymers with reinforcing components, rather than from new polymer compositions (Brown et al 2000). Over the past fifty years the quest for better engineering and specialty polymers has led to increased research and development of polymer blends. The blending of two or more polymers results in a material with far more superior qualities than can be found in any of the constituent polymers (Fried 2007, Billmeyer 2005, Tillerkeratine and Scott, 2006). Again, the biggest advantage is that materials can be “tailor-made” to suit the peculiar demands of any industrial set-up, viz aerospace, construction, marine, medical technology, biotechnology, agricultural, automobile, research etc. The desirable properties obtained from blending are tear and abrasion resistance, modulus, resistance to degradation and improved flame resistance, among many others (Alfred and Choi; 2013, Findik et al 2004).

Natural Rubber (NR) is a high polymer like many other natural products (e.g. silk, cellulose, wool and proteins), synthetic rubbers and plastics. The distinguishing feature of these materials is the great length of the molecule which is made up of a chain of repeating monomeric residues. Rubbers have molecular chains which are flexible and are able to return to their original shape after deformation especially when cross-linked (Akpa2008).

NR is a hydrocarbon with the empirical formula (C_5H_8), where n is about 10,000. The C_5H_8monomer is isoprene. Each monomer unit has a specific geometric configuration. In NR the configuration is designated -cis giving the chemical name cis-poly isoprene called Hevea Braziliensis. The trans-configuration is found in gutta percha (Balata) (Billmeyer et al, 2005).

In the raw state NR (2-methyl but-2-ene) is a tough material which deforms in part by viscous flow and in part elastically. It crystallizes readily at temperatures of 0^oc and below and becomes soft and sticky when warm (Akpa2008). Its practical uses in the raw state are limited.

NR has a unique combination of low hysteresis and therefore high resilience at low strains and high strength due to crystallization at high strains enabling it to be used in unfilled or lightly filled compounds (Stephen et al., 2006). This ability to crystallize when stretched results from its uniform molecular structure. Strain induced crystallization is also responsible for NR’s resistance to fatigue by crack-growth mechanism, an important property in dynamic applications of rubber. Among the general purpose elastomers available, NR maintains a leading position as the most suitable for applications requiring a combination of high resilience, high strength and fatigue resistance (Sirqueir and Soares 2003, Sirisinha et al., 2004).

The veryuniform high-cis polyisoprene molecule readily crystallizes when NR is stretched beyond a certain point, producing a form of reinforcement (Akpa2008). Thus NR does not require reinforcing fillers for high tensile strength and therefore can be compounded with or without moderate amount of carbon black and mineral fillers giving highly resilient and durable products.

Strain induced crystallization is also responsible for NR’s resistance to failure and crack-growth mechanism even at low strains (Fried 2007, Billmeyer 2005).

NR has excellent physico-mechanical properties which are used in many industrial applications. However, the great drawback of NR is its low resistance to oils, organic solvents and aging on exposure to oxygen, ozone and heat. Its weakness in these media is due to its non-polar nature and the reactive double bonds in its structure. Some Researchers have reported that blending of NR with other polymers could improve oil, ozone and chemical resistance (Kwanruethai, 2008). It was found that blending with thermoplastics such as polyvinylchloride (PVC), polyethylene terepthalate(PET) etc. could improve oil, chemicals, flameretardants and solvents resistance (Asha et al 2002, Billmeyer 2005). PVC is a low cost polymer with excellent properties such as solvent resistance and electrical insulation. Thus, blends of NR and PVC are expected to show improved thermal, oil, solvent and chemical resistance compared to NR alone.

The blending of two or more polymers however, usually leads to immiscibility and the desired properties are not usually achieved without a third component, i.e. a compatibilizer, which will provide adequate interaction between the phases (Chen and White, 1993). Thus, because of the hydrophobic nature of NR blending with PVC should be phase-separated owing to differences in polarity.

While, NR is non-polar, PVC is highly polar, although both of them show strain-induced crystallization. Structural abnormality results from thermal initiation which reduces the stability of the C-Cl bonding resulting to therminal unsaturation (Alfred and Choi, 2013).

NR is often reinforced by the incorporation of fillers to improve its mechanical properties. In the industry, the fillers that are commonly used are carbon black, china clay and calcium carbonate. Carbon black is derived from petro-chemicals, but the unstable price of crude oil and environmental issues and green chemistry have led to research for fillers,derived from agricultural products. Such agricultural by-products include maize cobs, rice, husks, cocoa pod husks, sugar cane chaff, melon husks, plantain peels, wheat chaff etc. have a very high cost benefit ratio due to their low cost and are very much abundant and are not useful for food for man, only for animals. The use of cocoa pods, rubber seed shells, groundnutshells, rice husks and plantain peels has been reported by (Okieimen and Imanah 2004, 2006). The results showed a potential and good prospect for the use of agricultural residuesas fillers in natural rubber compounds.

Dikanut is a tropical nut grown in Africa. It has two main varieties: Irvingia Gabonensis, which has edible fruit pulp and Irvingia Wombolu, which is bitter and inedible. The kernel is used for making soups and is a delicacy in Nigeria. Nigeria produces about 150,000 tonnes of dikanut fruits annually (Okieimen and Imanah, 2004). Other producers include Senegal, Sudan, Uganda, the Democratic Republic of Congo (DRC) or Congo Brazzavile, Ghana, Angola, Republic of Benin, Togo, Cameroun etc.

Blends of polyvinyl chloride and natural polymers represent a new class of materials that have attracted much attention, especially in industrial and bio-applications. Polyvinyl chloride is a hydrophobic and water insoluble polymer. For this reason, it is expected that water solubility and bio-compatibility of natural rubber can be improved by blending with poly (vinyl chloride) and DNS. Hence, the blend of natural rubber and poly (vinyl chloride)and DNS is a good biomaterial of great industrial application. Surface and bulk hydrophilicity of blended polymers affects mainly their biological behaviour. Bulk hydrophilicity could be measured by surface tension and water contact angle (Bahrami 1967). DNS acts as a filler in the NR/PVC/DNS biocomposites.

In the rubber industry, fillers that are commonly in use are carbon black, china clay and calcium carbonate. Carbon black is derived from petro-chemical sources. The unstable price of crude oil and the non-renewable nature of carbon black have led to the search for fillers that are derived from other sources (Ski, 1970). This is in addition to other associated problems such as dark colour often associated with agglomeration as a result of insufficient dispersion, caused by the tendency of fillers to also form hydrogen bonds with each other during processing. Moreover, the polar hydroxyl groups on the surface of the lignocellulosic materials have difficulty in forming a well-bonded interface with a non-polar matrix, as the hydrogen bonds tend to prevent the wetting of the filler surfaces (Nelson, 1974).

Due to the hydrophilic nature of dika shell powder (a cellulosic material), blending with NR should be phase separated owing to different polarities. In this regard, maleic anhydride-g-poly (cis-l, 4-isoprene) is considered to be a potential compatibilizer for this blend system. Overview of literature sources indicates that many polymeric systems are effective in-situ reactive compatibilizers for polymer blends (Ismail and Mega, 2001, Onyeagoro, 2013, Ming-Yih and Feng, 1999). Ming-Yih and Feng 1999, reported that a combination of styrene-maleic anhydride random copolymer (SMA-8WT% MA) and tetraglycidyl ether of diphenyl diamino methane (TGDDM-an epoxy resin) is able to compatibilize polyethylene terephthalate(PET)-polystrene(PS) blends. Onyeagoro, 2013 used maleic anhydride-graft-polyisoprene and epoxy resin as reactive compatibilzers in natural rubber/carboxylated nitrile rubber blends and reported an improvement in cure characteristics and mechanical properties in the blends. The authors revealed finer phase domain size of the dispersed phasecontamination, as well as its high cost. These have necessitated continuous search for suitable alternatives. Studies on the use of agricultural by-products to replace carbon black used in rubber reinforcement have attracted significant attention in recent years, particularly for low-cost/high volume applications. Nigeria is endowed with large agricultural resources, which are still largely under-utilized. Most agricultural by-products in Nigeria are discarded as waste.

Ohaeri, 2013 and Ukeme, 2014 studied the use of maleic anlydrode graft (MAPI), hexamethylene diamine (HMDA) and triethylene tetramine (TETA)as compatiblizers for NR/PVA/DNS and NR/PET/DNS biocomposites, the results of their studies show excellent physical and mechanical properties. Dika (*IrvingiaGabonensis*), known locally as “ogbono” is a genus of African trees. It is valued for its fatty and protein rich nuts. It has high content of mucilage which enables it to be used as thickening agent in foods. Nigeria produces about 150,000 tonnes of dika annually (Okieimen and Imanah, 2004). Other dika producers in Africa are Senegal, Sudan, Uganda, Democratic Republic of Congo (DRC) and Angola (Ayo et al, 2011). Unfortunately, due to relatively low entropy of mixing, most polymer matrices and fillers are immiscible, resulting in the formation of a sharp interface between the two phases, coarse phase morphology, and poor mechanical properties.

The main disadvantage encountered during the incorporation of natural lignocellulosic materials into polymers is the lack of good interfacial adhesion between the two components, especially in the case of rubbers, due to the incompatibility of hydrophilic natural fibres that are to be used as reinforcement with hydrophobic natural rubber matrix, hence the need for compatibilizers.

It has been reported by Ming-Yih and Feng, 1999 in a study on polymer blends of PET-PS compatibilized by styrene-maleic anhydride (SMA) and epoxy dual compatibilizers that the reaction between PET and the anhydride is insignificant without the presence of a catalyst. A similar problem is expected when maleic anhydride-grafted polyisoprene (MAPI) is used as a compatibilizer in NR-PVCblends and only secondary physical interaction is expected. Therefore, hydrogen and chloride bonds are expected from the interaction of chloride groups in PVC and the hydroxyl groups of dika nutshell (C-DNS) (a cellulosic filler). ThePVCchloride terminal group is able to react with the hydroxyl group of DNS to effectively compatibilize many poly (vinyl alcohol chloride) related blends filled with cellulosic fillers. Thus, the presence of PVC in the NR-PVC-MAPI-DNS blend during processing has the potential to produce NR-co-PVC-co-MAPI copolymer at the interface as an effective compatibilizer which improves the interfacial adhesion of the two polymers and the flameretardant properties of the filled blend.

Onyeagoro, 2012 investigated the influence of carbonized dika (Irvingia Gabonensis) nutshell powder on the vulcanizate properties of NR/SAR/SAN/NBR blend. The researcher found out that the volume swell of the blends in three chosen solvents decreased with increase in carbonized dikanut shell (C-DNS) content in the blends, but increased with increased SAR content.

The performance of rubber blends is largely governed by various factors such as the nature of rubber or the elastromer (Stephen et al, 2006), Sirqueira et al, 2003; Sirisinha et al, 2004), blend compositions (Naskar et al, 1994), the phase morphology of the rubber blends (Sirisinha et al, 2004, Oluranti et al, 2010, Tol et al, 2004, Chu et al, 1999, Utracki 2000, Moliah 2011) and the interfacial cross-linking in the rubber blends (Naskar 1994, Chenc 1993, Schulze 2001). For instance, improved oil,flameretardanceand thermal aging resistance were observed when NR was blended with chlorinated polyethylene (CPE),(Sirisinha et al, 2004). Blends of NR with carboxylated styrene buladiene rubber (XSBR), (Stephen et al, 2006 and EPDM (Sirqueira et al, 2003) were reported to have better aging and ozone resistance (Sirisinha et al, 2004), demonstrated that - improved phase morphology in blends of NR and nitrile rubber (NBR) resulted in an increased oil resistance of the blends. Naskar et al, reported that blends of NR and carboxylated nitrile rubber (XNBR), had oil resistance and mechanical properties which strongly depended on the various blend ratios and the degree of interfacial crosslinking between NR and XNBR components.

Polymers swell and outrightly dissolve if they interact with solvents, and the degree of this interaction is governed by the degree of crosslinking. The degree of swelling is related to the thermodynamic properties of the system. Considerable interest has been put on the absorption, sorption and diffusion of organic solvents in polymer blends because their ability to permeate them at different rates enhances the separation of the components of their liquid mixtures through polymeric membranes, and flammabity(Frollini et al, 2003). The density of chain entanglements and chain ends, cross link density (CLD), compatibility of both polymers in the blend and the amount of filler in addition to viscosity of the penetrant liquid and the functionality of the cross links are determinants of the molecular transport of organic solvent in rubber vulcanizates. Previous studies by Dare et al, 2004 revealed that the transport of solvents through polymers is affected by polymers structure, CLD, mode and type of cross linking, presence of fillers, penetrant size and temperature, Thusan understanding of the membrane transport properties, sorption, diffusion coefficient and penetration rate with respect to toluene and solvents is necessary in order to understand some of their transport characteristics and areas of application in flame retardant uses.

The combustion of polymers follows a pattern. First, thepolymer in the presence of a flame source is pre-heated.During preheating, the polymer decomposes and releasesgaseous hydrocarbons into the atmosphere around the flamesource. These hydrocarbons at the appropriate temperaturebecomes ignited and consequently combust in oxygen torelease heat (Cullis and Hirschler, 1986). Although most ofthe heat is lost to the environment in which combustion istaking place, a fraction finds its way back to the polymerand then pre-heats, decomposes, ignites, and combusts thepolymer. Hence, the cycle continues. Disrupting this cyclewould relatively inhibit combustion. Different methods have been employed and they aim at increasing either the ignition time, or the time before which the polymer samplebegins to generate fire on its own without an external heat source (i.e., auto-combusting) (Stark, 1960; Gerard, 2010). Or reducing the flame propagation rate (i.e., rate of spread of fire) (Nelson, 1974). Interrupting the fire cycle can be achieved ineither of the three ways;(i) modifying the polymer to produce less flammable gases. (ii) inhibiting burning or quenching flame, (iii) reducing the feedback heat from the flame to the decomposing polymer (Mark, 1992). Based on these, many flame retardants have been developed, e.g.$Mg(Cl)_{2,}$ KBr,$Mg(OH)_2$ phosphorus compounds and antimony compounds.

Flame retardants incorporated into polymers can successfully extinguish fire either in the gaseous or solid phase, because flammability is a function of both solid and gas phase chemistry (Nelson, 1974). In the solid phase, theflame retardants can cause the formation of a large flame- resistant carbon compound(char or ash) over the po1ymer surface. This foamed surface is heat resistant, and can soakup the heat being fed back (Weil, 2004), consequently smothering the burning polymer. In the gaseous phase, flame retardants produce non-combustible gases which attack the fire propagating free radicals to produce relatively stable, non-combustible free radicals (Hilado, 1982).

Many chemicals have been used to improve the flame resistance of polymers. Halogenated flame retardants may either function in gaseous or solid phase (Hilado, 1982). Bromine-based retardants act in the gaseous phase to redirect or terminate chemical reactions, (Hilado, 1982). Phosphorus flame retardants include a wide variety of phosphate compounds: elemental red phosphorus, water- soluble inorganic phosphates, insoluble ammonium polyphosphate, organophosphates and phosphonates, phosphine oxides, and chloroaliphatic and bromoaromatic phosphates(Green, 1994). Vinyl and allyl phosphonates are very reactive flame retardants (Allen, 1993). Phosphorous- containing polyols have been used extensively in the polyurethane industry(Lee et al.. 1989). Phosphorous containing nitrogens or halogens have been used as flameretardants (Green, 1994). The presence of nitrogen compounds have had significant effect on flame resistance, as can be seen in the low flammability of wool, silk, and leather (Horacek and Grabner, 1993), triazine, isocyanates, urea, guanidine, and cyanuric acid derivatives are nitrogen-containing organic compounds and have been used as flame retardants (Horacek and Grabner, 1993). Silicon containing flame retardants have also been used (Iji, 1998; Zaikov and Lomakin, 1996). Boron-based compounds have also received extensive usage (Zing and Surn, 1994). Although the polymer in which these flame retardants have been added show improved flame resistance, nevertheless during combustion, most of these flame retardants release toxic gases into the atmosphere. This can be potentially harmful to the environment.

Reinforcing polymers with wood fibres have attracted increasing research activities. Besides offering improved mechanical properties, they reduce the amount of polymer resin used. This reduces the percentage of non-biodegradable low density polyethylene in the environment, Furthermore, wood fibres are readily available, and relatively easy to procure and process. Since wood fibres are basically natural, their combustion products would be CO_2 and H_2O, and this could be recycled through photosynthesis to produce bio-matter. Wood fibres therefore do not 'add' to the already available quantity of CO_2 in the atmosphere during combustion, hence they are carbon 'neutral' and eco-friendly. However, the fire performance of the composites has received limited attention in the literature (Stark, 1960). The research work investigated and compares the effects of kola Nitida(*kola nut tree*) and Alstonia Boonei (*dogonyaro*tree), plants denizenin the West Africa on the flammability properties of LDPE

1.2 PROBLEM STATEMENT

Fire causes a lot of destruction and loss of lives and property all over the world annually, resulting in the loss of billions of dollars. Polymers are chemical substances, and therefore prone to fire incidence.Fire hazards caused by polymers and blends used in appliances and fittings for man’s convenience will be greatly reducedif they are compounded with flame resistant materials.

NR is widely used in the manufacture of appliances and fitting used in our homes and industries where the risk of fire incidence is high. It therefore becomes imperative to incorporate flame retardants in these compounds in order to reduce fire hazards in the event of fire outbreak.

NR and PVC are immiscible. To improve their miscibility, compatibilizers are required. This lowers the surface tension and increases molecular interaction of the blend components.

Carbon black is considered the most effective and efficient reinforcing filler in the rubber industry. However, it is of the petroleum origin and as such non-renewable and very costly. The search for suitable alternatives from a re-newable source that are biodegradable and cheap has therefore become imperative. Dika nutshells are agricultural by-products which are presently discarded as waste in Nigeria thereby causing environmental pollution. Yet, they can be harnessed as fillers in NR/thermoplastic blends as suitable alternative to the expensive, non-renewable carbon black thereby reducing theoverhead cost of rubber articles.

1.3 OBJECTIVES OF THE STUDY

The overall objective of this study is to evaluate the flame retardant properties of NR/PVC/DNS powder, filled with KBr, $Mg(Cl)_2$ and $Mg(OH)_2$ as flame retardants bio-composites obtained using MAPI and TETA, dual-compatibilizer system.

The specific objectives of the study are to:

i. Produce NR/PVC/DNS composites with vastly improved compatibilization.
ii. Determine the effects of filler content on the flame retardant characteristics of NR/PVC/DNS composites.
iii. Determine the effect of filler particle size on the flame-retardant characteristics of NR/PVC/DNS composites.
iv. Determine the effect of flame retardant content on the flame retardant characteristics of NR/ PVC/DNS composites.
v. Determine the effect of MAPI/TETA content on the flame retardant properties of NR/PVC/DNS composites.

1.4 JUSTIFICATION OF THE STUDY

In the design and fabrication of polymeric materials for use in auto-mobiles, space vehicles, air-planes, civil and other construction engineering and other applications, the risk of fire and extreme temperatures and heat cannot be over-emphasized. Fire and related accidents results in loss of lives and properties worth billions of dollars annually. Hence, it is of utmost importance to design houses, automobiles, aircrafts, offices etc. with fire retardant polymeric materials.

1.5 SCOPE OF THE STUDY

This study is limited to:

i. The determination of the flame retandant propertiesof DNS powder filled NR/PVC powder composites as a function of time.
ii. The evaluation of the effect of DNS loading on flame retardancy of DNS powder filled NR/PVC composites.
iii. The evaluation of KBr, Mg $(Cl)_2$and Mg $(OH)_2$ flame retardantson the flame retardant properties of DNSpowder filled NR/PVC composites.
iv. The determination of the effect of MAPI/HMDA/TETA compatibilizer system on the flame retardant properties of DNS powder filled NR/PVCcomposites.
v. The comparison of the results of CB filled NR/PVC composites with those of DNS filled NR/PVCcomposites.
vi. The determination of the effect of DNS filler particle size on flame retardant properties of DNS powder filled NR/PVC composites.

CHAPTER TWO

LITERATURE REVIEW

2.1 Modern Trends in Polymer Formulation

Advances in the production of high performance polymer-based composition will in the future, more likely result from the utilization of new mixtures of polymers and mixtures of polymers with reinforcing components rather than from new polymer compositions (Fried 2007). The fact that most polymers cannot mix with each other to form homogeneous mixtures at segmental scale has been the driving force for a large number of studies on multi-phase polymeric materials. It has been known for a long time that the physical properties of these phase-separated polymers such as toughness, flowability, transparency and weather resistance etc. are dictated by their morphology (Tan 1994). A polymer blend is a mixture of two or more polymers, copolymers or terpolymers.

A variety of chemical and physical methods has been extensively exploited to control the morphology and rheology of immiscible polymer mixtures (Brown and Paul, 2000). Reactive polymers are widely utilized for various practical purposes such as the modification of surface tension between different phases via which morphology and physical properties of multiphase polymeric materials can be modified and controlled through techniques called reactive compatibilization (Tan 1994, Moliah 2011). Polymer blending is therefore a convenient way to develop new polymeric materials, which combine the best properties of both/and all the candidate polymers. Such blending can be accomplished in Twin-screw extruders, (TSEs), internal mixers or a two-roll mill:However the TSEs are considered the most appropriate tool.

2.1.1 CLASSIFICATION OF BLENDS

Polymer blends may be divided into three types:

2.1.1.1 Totally Compatible Blends

In this type, of polymer blend$\Delta H_{mix} < 0$, due to the specific interactionsand homogeneityis observed at least on a nanometer scale, if not on the molecular level. A well-known example of a blend which is miscible over a wide temperature range and in all proportions is polybutadiene(PB)/Polychloroprene , (PCR), that combines the heat resistance, inflammability and toughness of PCRwith the good processibility and low cost of PB. This type of blend exhibits only one glass transition temperature (Tg), which is between the Tgs of both blend components in close relation to the blend composition (Orr et al 2001).

Miscible polymer blends are an easy-to-use approach for investigating and refining polymer combinations. Their properties are a combination of the properties of the pure components. The characteristics of components affecting the properties of miscible blends are their chemical structure and molecular weight concentration and intermolecular interactions (Schulze et al 2001).

2.1.1.2 IncompletelyCompatible Blends

The blend component involves a small part of a component dissolving in the other. This type of blend shows a fine phase morphology, with good properties and is called a compatible blend. Both phases are usually homogeneous and have a separate Tg. The Tgs of both polymers are shifted from the values for the pure blend components towards the Tg of the other blend components. Examples include polyamide (PA)/polyisobutyleneisoprene rubber (IIR) blends which combines the heat resistance and toughness of PA with the low cost of IIR. In these blends PA and the butyl partially dissolve in one another, with wide interphase and good interfacial adhesion (Brown 1992).

2.1.1.3 Totally Incompatible Immiscible Blends

Mixing immiscible polymers in the liquid state can result in various phase morphologies. These depend on the nature and the relative amounts of the polymers used and on the flow history of the sample. Immiscible polymers behave as different materials at different flow fields. The phase morphology is an important factor in the rheology of immiscible polymer blends. Most binary polymer blends are immiscible. To a large extent, the characteristics of these immiscible polymer blends are determined by the state of the interface between the components. The interaction of two melts at the interface is primarily represented by a quantity K, called the interfacial tension. The interfacial tension is the excess free energy caused by the existence of an interface arising from the unbalanced molecular forces (White, 1981). Generally, chemically different polymers are immiscible and their blending leads to materials with weak interfacial adhesion and thus poor mechanical integrity. These blends have coarse phase morphology. The interface is sharp and the adhesion between both blend phases (each exhibiting the Tg of the pure blend components) is poor, so that these blends are useless without being compatiblized (Tol et al 2004, Helfand and Togami, 2000). A compatibilizer is a material which reduces the interfacial tension between different polymers, co-polymers and terpolymers to be blended in order to ensure better and proper mixing to achieve better properties of the blends. (Brown et al., 2000) found out that new concept of compatibilization using rigid nano-materials like silica nano-particles has been proposed. Some examples of immiscible blends are polyamide (PA)/acrylonitrile-butadiene-styrene terpolymer (ABS), polyamide (PA)/ethylene propylene-dieneterpolymer (EPDM), polyamide (PA)/poly (dimethylphenylene oxide (PPO) and polypropylene (PP)/polyamide (PA). These are commercial successful blends. Others are polystyrene (PS)/ poly(butylene terephthalate) (PBT) PS-g-PBT and polystyrene (PS)/poly styrene-ran-glycidymethacrylate) (PS-GMA) in PA6/ABS, the polyamide provides good heat and chemical resistance, good tensile properties, good flow and good paintability. ABS lowers the moisture absorption, improves the dimensional stability, and provides a lower price and good low temperature impact strength (Tol et al 2004). PA6.6 (or 6)/EPDM blends are called super-tough nylons. In PA6 or 6.6/PPO blends, the polyamide provides good processability, good chemical resistance and paintability, while PPO exhibits low moisture absorption, good dimensional stability and stiffness at elevated temperature (White, 1981, Helfand and Togami, 2000).

2.1.2 Purposes for Blending Polymers

Recently, there has been increased research interest in polymer blends. The enhanced research activities in this area are related to the hope of producing advanced high performance materials based on well-known products and the need for a basic knowledge of their phase behaviour, which in turn is a function of their flexibility, morphology and flow during processing. Polymer blending has been identified as the most versatile and economical route to producing new multi-phase polymers that are able to satisfy the complex demands of performance and also have a good cost benefit ratio (Buthaina et al 2010, Oluranti et al 2010). Over the past four decades, polymer blends have grown tremendously in leaps and bounds. In fact, the design and development of these multi-phase polymer blends are strongly dependent on two major parameters, the interfacial bonding and control of morphology. The technology of polymer blends has been one of the major areas of research and development (R&D) due to the advantages of polymer blends versus developing new polymeric materials. Thus, polymers blends offer better physico-mechanical properties, electrical properties, flame retardant and optical properties for use in engineering and specialty applications (Paul and Newman, 1978; Lu and Macosko 1992, Fried 2007, Markham 1991).

2.1.3 Merits Derived from Blending Polymers

The following are some of the merits obtainable in blending polymers:

i. The ability to combine existing polymers into newcompositions with commercializable properties reduces the cost of R&D expenses compared with the development of new monomers and polymers to yield similar property profile.
ii. In a rapidly emerging technological landscape, polymer blend technology can quickly respond to developing needs much faster than the time consuming R&D involved with new monomer/polymer development.

iii. The technical response to emerging needs is now primarily directed to polymer blend technology in order to determine if such needs can be met compared with the development of wholly new polymeric compositions.
iv. Recycling industrial/municipal wastes
v. Tailor-made properties are a very common place, because, the right choice will easily yield the right blend with the requisite properties.
vi. Low production volume and hence small losses for equipment breakdown.
vii. Ability to introduce reactants and catalysts at any desired stage and location.
viii. Rapid and precise control of pressure and temperature and good heat exchange.
ix. Working with 100% of reactant content using rapidly renewed interface, which leads to higher reaction rates than those possible in batch processes.
x. Self-cleaning system, hence narrow and adjustable distribution of residence time.
xi. Good control of the production line from start to finish.

2.1.4 Blending Methods

i. Combining the two or more molten polymers together using some force, heat or pressure in a suitable equipment i.e. two – roll mill or extruder.

ii. Dissolving the polymers to be blended in a solvent and making a solid film put of the out of the solution mixture.

iii. Taking advantage of joint solubility of the blend components in the same solvent and then precipitating to form a blend.

iv. Mixing the polymers in the liquid state such polymers then be sprayed and dried to form a blend.

v.Forming a network structure by dissolving a monomer(s) into a solution of polymer(s) i.e Interpenetrating Polymer Networks (IPN)

2.1.5 Some Reactions in Blending

Whether a particular polymer blend will be homogeneous or phase-separated will depend upon many factors, such as the kinetics of the mixing process, the processing temperature and the presence of solvent or other additives (Leszek, 2009, Utracki 2000, Chui et al, 1999, Young and Kin, 1998).However, the primary consideration for determining the miscibility of two polymers is a thermodynamic issue governed by the Gibbs free-energy of mixing. The relationship between the change in Gibbs free energy due to mixing (ΔGm) and the enthalpy (ΔHm) and entropy (ΔSm) of mixing for a reversible system is given as (Robert 2009, Leszek 2009, Chen and White 1993, Bousmina et al 2002).

$$\Delta G_m = \Delta Hm - T\Delta Sm \qquad 2.1$$

If ΔGm is positive over the entire composition range at a given temperature, the two polymers in the bind will separate into phases that are pure in either component, provided the state of thermodynamic equilibrium has been reached. For complete miscibility, two conditions are necessary: ΔGm must be negative and the second derivative of ΔGm with respect to the volume fraction of component 2 (ϕ_2) must be greater than zero over the entire composition range (Robert, 2009).

$$\left(\frac{\partial^2 \Delta Gm}{\partial \phi_2^2}\right)_{T,P} > 0 \qquad 2.2$$

If ΔGm is < 0, equation 2.2 is not satisfied and hence the blend will separate at equilibrium into two mixed-composition phases. This implies that each phasei.e. the dispersed and the continuous will contain some of each polymer (Edwards et al., 2002). In general, polymer blends can exhibit a wide range of phase behaviour, including upper and lower critical solution temperatures. At temperature T_1 which is below the upper critical solution temperature (UCST) for phase separation located at T_2, the equilibrium mixture will separate into two phases whose compositions lie in opposite sides of the bimodal at T_1(Robert 2009, Leszek 2009, Edwards et al 2002). The sinusoidal separates the stable (single phase) from the metastable state, while the spinodal marks the transition from the unstable to metastable region. At T_3, which is above the UCST but below the lower critical solution temperature (LCST) located at T_4, the blend is miscible at all compositions (Leszek A., 2009, Robert 2009, Chui et al 1999, Edwards et al 2002). Above the LSCT (e.g. at T_5), two phases again coexist with compositions given by the upper bimodal.

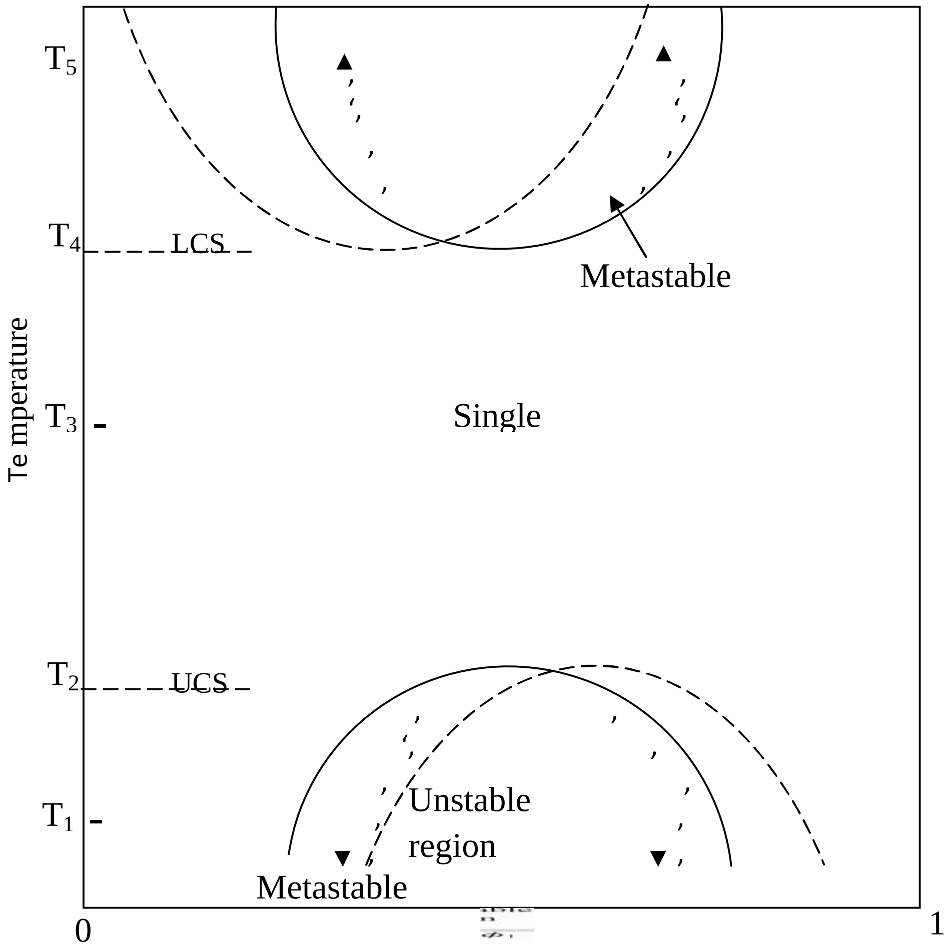


Fig. 2.1: *Idealized phase diagram of a polymer blend (Fried 2007)*

Idealized phase diagram of a polymer blend which show the various phases. The solid curve indicate a bimodal while the broken curve represents a spinodal separating the unstable and metastable regions. The upper critical (UCST) and lower critical solution (LCST) temperatures are allocated at T_2 and T_4 respectively (Fried 2007).

The bulk of experimental evidence indicates that most polymer pairs are immiscible as discussed earlier. Immiscibility is a consequence of the very small combinatorial entropy change that results when two high-molecular-weight polymers are mixed. Scot has extended the Flory-Huggins (F-H) lattice model to obtain an expression for ΔSm for a polymer blend as

$$\Delta \mathrm{Sm} = \left(\frac{RV}{Vi}\right)\left[\left(\frac{\phi_i}{x_i}\right)\mathrm{In}\phi_i + \left(\frac{\phi_2}{x_2}\right)\mathrm{In}\phi_2\right] \tag{2.3}$$

Where R is the ideal gas constant,

V is the volume of the blend,

Vi is a reference volume, (often taken as the molar volume of the smallest repeating unit), Qi is the volume fraction of polymer 1 or 2 and x, is the degree of polymerization of polymer 1 or 2 relative to the reference volume. The corresponding equation for the Gibbs free energy of mixing is then:

$$\Delta \mathrm{Gm} = \left(\frac{\mathrm{RTV}}{V_i}\right)\left[\left(\frac{\phi_i}{X_i}\right)\mathrm{In}\phi_\mathrm{i} + \left(\frac{\phi_2}{X_2}\right)\mathrm{In}\phi_2 + \phi X_{12}\phi_1\phi_2\right] \tag{2.4}$$

Where X_{12} is the Flory interaction

The thermodynamic equation for miscible system (single phase) requires the free energy of mixing to be negative (Leszek 2009).

$$\Delta \mathrm{Gm} = \Delta \mathrm{Hm} - \mathrm{T}\,\Delta \mathrm{Sm} \leq 0 \tag{2.5}$$

The thermodynamic equation for immiscible system requires therefore the free energy of mixing to be positive.

$$\Delta \mathrm{Gm} = \Delta \mathrm{Hm} - \mathrm{T}\Delta \mathrm{Sm} > 0 \tag{2.6}$$

(Fried 2007, Leszek 2009, Robert 2009).

2.2. Polymer Compositions and Composites Production

A very common composite is the bricks made of clay and straw. A composite can be defined as a material which consists of two or more chemically and/or physically different phases separated by distinction interface. The different phases are combined judiciously to achieve a system with useful structural and functional properties not in any of it components. Cellulose fibre reinforced phenolic and melamine resins, fibre glass reinforced structures such as the hull of a cabin, bathtubs, shower stalls e.t.c are examples of composites (Bhatnagar et al 2005, Green 1994). Fibre glass is a composite made from glass-fibre reinforcement of an unsaturated-polyester matrix.

Composites are used widely in applications where high strength-to-weight ratios are important (Fried 2007, Oluranti et al., 2010, Kye and Sun 1996, Orr et al 2001). Such areas are;aerospace and military, appliances and business, construction, corrosion-resistant equipment, electrical and electronics, marineand transportation. Composites exhibit desirable physical and chemical properties such as high specific stiffness and strength, dimensional stability, temperature and chemical resistance and a relatively easy processing (Green, 1994).

In most cases, composites matrices are thermosets, although there has been interest in composites made from thermoplastics and composites having carbon, ceramic or metallic matrices for high temperature and other demanding applications (Fried 2007, Bhatnagar 2005). One most important class of thermosets for composites is the epoxides. Although, epoxy resins are inexpensive and easy to process, they are brittle and have a relatively high moisture absorption, which can affect the strength of the filler-matrix interface.

The interfacial strength can be improved by the use of coupling agents (compatibilizers), which are low-molecular-weight organic-inorganic compounds that serve to promote adhesion between the filler and matrix (Barlow and Paul 1985, Roe 1993 Chen and White 1993, Young and Kin 1998, Oluranti et al 2010, Moliah et al 2011). Thermoplastics such as polysulphone offer higher impact strength than thermosets but are more susceptible to solvent attack and have higher creep compliance, which results in a loss of dimensional stability under load. Recently, some high-impact semi-crystalline thermoplastics such as poly etherether ketone (PEEK), have studied due to their good solvent resistance and impact strength (Young and Kin 1998, Fried 2007). Polyamides which can be either thermosets or thermoplastics are widely used in the aerospace industry. Thermosetting polyamides provide easier processing and higher heat-resistance, while thermoplastic polyimides offer greater toughness.

Composites are made by a variety of processes such as:Vacuum assisted resin infusion (VART) which has different acronyms (Radonjic, 1999). The various variants of VARI are:VARIM- vacuum Resin Transfer Moulding (Koefoed, 2003, Correia, 2004).VARIM – Vacuum Assisted Resin Infusion Moulding (Kentgen 1969, Kengan 1982).SCRIMP – Seeman Composites Resin Infusion Moulding Process (Boeing, 1969).VBRTM – Vacuum Bag Resin Transfer Moulding (Kang et al, 1982).VARI – Vacuum Assisted Resisted Infusion Process (Turro, 1978) etc. The base technology is utilized in all variants and involves the impregnation of a dry reinforcement by liquids.

2.3. FILLERS

Fillers are most widely used additives in polymer composition. They are used in plastics, natural and synthetic rubber and in coatings.A filleris an inert material added to a polymer composition to improve its properties and/or reduce its cost. On being mixed with resin, it forms a heterogenous mixture which can be moulded under the influence of heat or pressure or both (Blow and Hepborn 1982).

2.3 Classification of Fillers

There are three types of filler such as reinforcing fillers, active fillers, andinactive fillers. Reinforcing a polymer by high strength fibres is known as fibre reinforced plastic (FRP). FRPs have high elastic modulus, high strength to weight ratio, excellent corrosion resistance and are easy to fabricate. Low viscosity oligomers and silicate fibres produce excellent products. The matrix polymerizes or condenses into a network compound. The qualities of reinforced plastics make them useful in space craft design and in boat hulls, which are required to withstand marine salt water (Bhatnagar 2005 and Alfred Choi 2013).The main reinforcing fibres are glass, graphite, alumina, carbon, boron, beryta etc

Fully synthetic aromatic fibres sometimes have been found more useful than natural fibres. The glass fibre is largely used in FRP. Glass fibres have low coefficient of thermal, expansion,High dimensional stability, Good tensile strength, Low dielectric constant, Non-inflammability, and good chemical resistance.

The fibres are used as short chopped fibres, continuous filament or woven fabric. The polymer transfers the stress from fibre to fibre, thus forming a product of high elastic modulus and small elongation.

The strength of reinforced plastic depends on the arrangement of its fibres and elastic modulus of the polymer. The strength of the material increases by arranging the fibres in parallel. Highly oriented organic steel-like fibres give very high strength products (Moliah et al 2011).

Interaction or adhesion between the binder and the fibre goes a long way in determining the quality of the product. In the case of glass fibre it requires special treatment. The matrices used are polyester, epoxy, phenolic, silane, melamine, polyamides and vinyl derivatives (Moliah et al 2011, Tol et al 2004, Oluranti et al., 2010).

There is a great problem of shrinkage. Matrices on polymerization or condensation during fabrication bring about a decrease in volume. Opening a double bond involves an increase of 20cm^3 per molecule. This change brings about distortion in the shape of the article and causes internal stresses.

Fillers that increase the mechanical strength are called active fillers and those that do not are called inactive fillers. Examples of active fillers are carbon black, (HAF,GPB,ISAF,SRF,FFB, MTB) and silica gel, Active fillers act more strongly on synthetic elastromers and rubbers increasing the strength by 10 to 20 times. They greatly increase the strength of synthetic elastromers in rubber-like state. Below Tg, the addition of active fillers increases the value of σ_f (forced elasticity) but decreases the brittleness (Jeon et al 2002, Fried 2007, Tol et al 2004).Therefore, at low temperatures, the addition of large amounts of filler is undesirable.

Solid particles have also been found to interact with the polymer with the formation of definite compounds. The essential condition is that the polymer performs good wetting of the filler. This result in a highly oriented absorption layer on the surface of the filler resulting in increased strength of polymer material as well as improve the final/finish quality of the moulded product (Fried 2007, Young and Kin 1998). They include wood and other similar materials in different shapes and sizes. They also bring about considerable decrease in volume. Therefore, the filler to matrix ratio is very important which can be adjusted by trial and error. Inactive fillers may be organic or inorganic. Organic fillers may be further subdivided into natural and synthetic products. Examples are listed below:

A. **Organic Fillers (Bhatnagar 2005)**
   i. Cellulose-wood, $\propto -$cellulose
   ii. Organic fibres-cotton, sisal jute, kapok, lignin
   iii. Protein materials
   iv. Synthetic fibres
   v. Nylon (polyamide)
   vi. Rayon
   vii. Polyesters,
   viii. Acrylic
   ix. Fluorocarbons.

B. **Inorganic Fillers (Bhatnagar 2005, Fried 2007)**
   i. Silicates
   ii. Oxides
   iii. Carbonates
   iv. Sulphates
   v. Hydroxides
   vi. Carbon
   vii. Glass

C. Inorganic Fibres (Bhatnagar 2005, Billmeyer 2005)

i. Beryllium glass
ii. Quartz (fused glass)
iii. Carbon
iv. Aluminum silicate
v. Graphite
vi. Rockwool
vii. Aluminum oxide (Al_2O_3)
viii. Beryllium oxide (BeO)
ix. Titanium oxide (TiO_2)
x. Zirconium oxide (ZrO_2)
xi. Magnesium oxide (MgO)

D. Natural inorganic/Metals and Refractories (Bhatnagar 2005)

i. Asbestos
ii. Steel
iii. Aluminum
iv. Tungsten
v. Tantalum
vi. Molybdenum
vii. Magnesium

E. Synthetic organic (Bhatnagar 2005)

i. Fluorocarbon
ii. Polyester
iii. Acrylic
iv. Polyamide
v. Cellulose acetate
vi. Regenerated cellulose (rayon)

F. Natural organic (Bhatnagar 2005)

i. Cotton
ii. Sisal
iii. Wool
iv. Wood cellulose (paper)

A

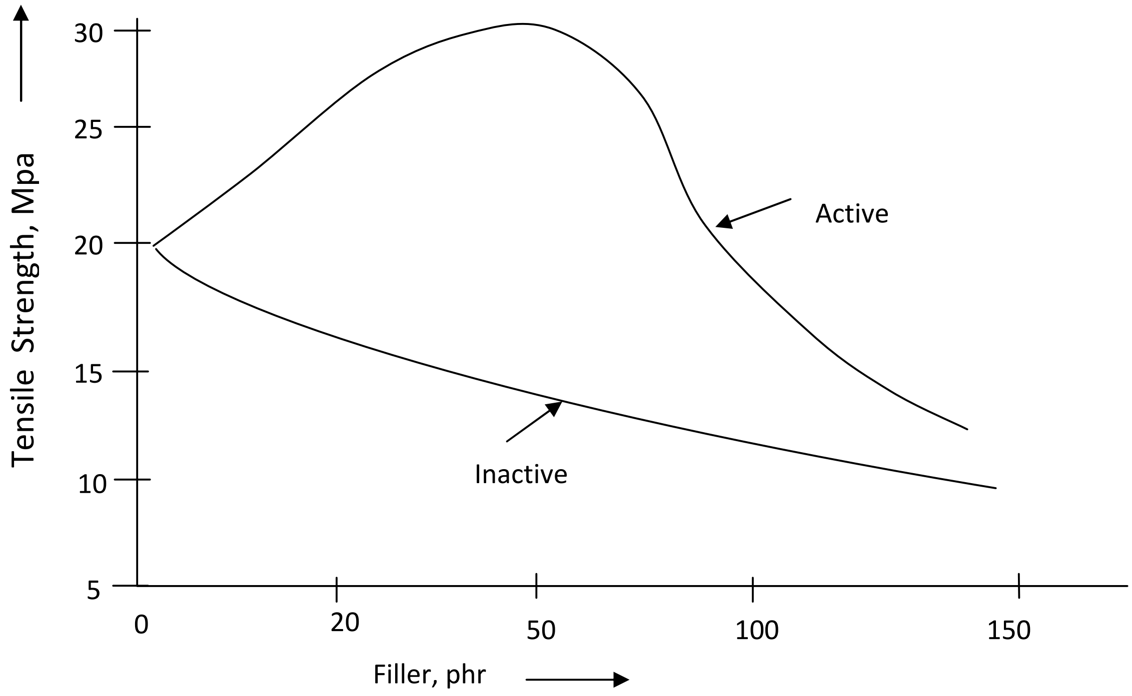


Fig 2.1: Effect of active and inactive fillers on the tensile strength of polymers.

B

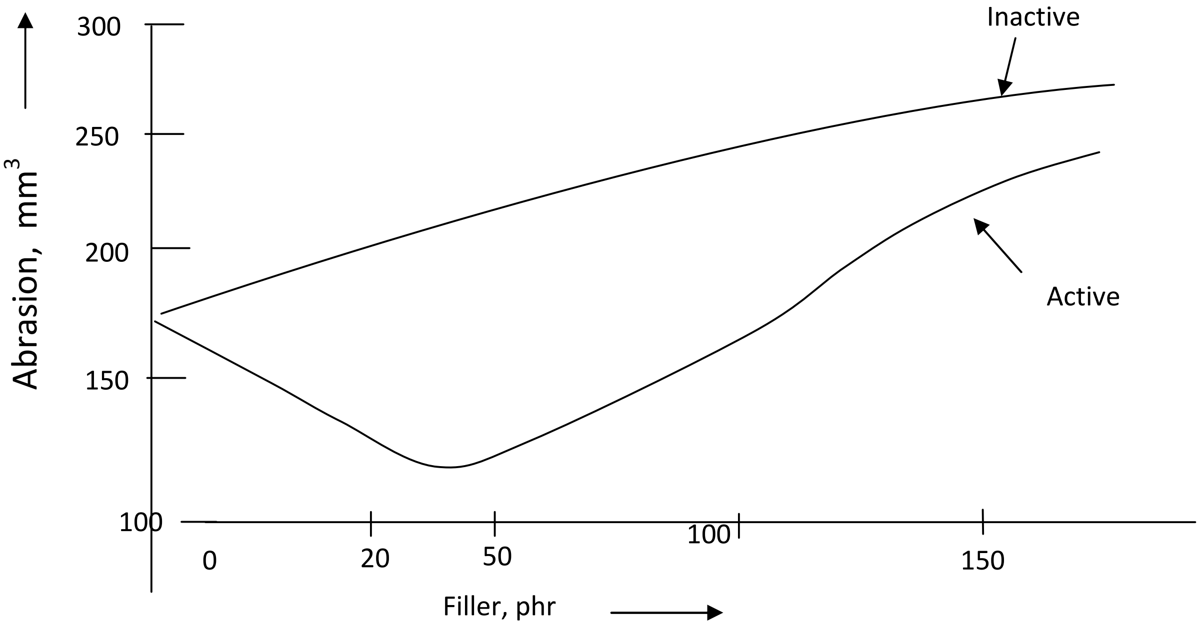


Fig 2.2: Effect of active and inactive fillers on the abrasion resistance of polymers.

C

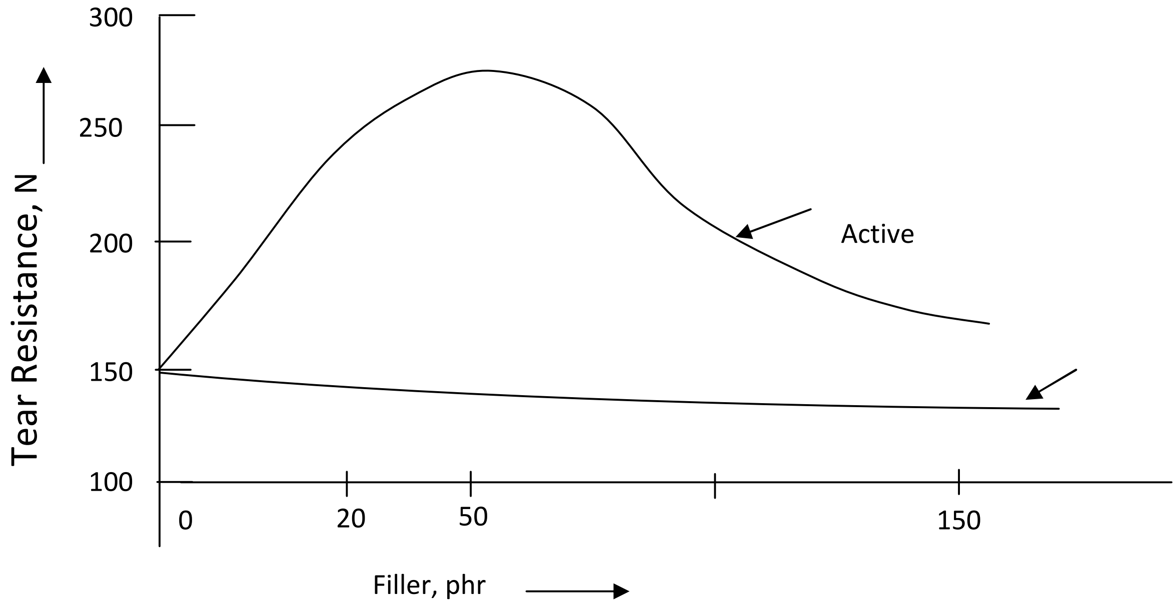


Fig. 2.2: ***Effect of active and inactive fillers on tear resistance of NR***

2.3.2 FILLER PROPERTIES

2.3.2.1 Particle Geometry

Fillers cause stiffening of polymer. The degree of stiffening is a direct function of the surface area of the filler (Bhatnagar 2005, Akpa 2008). The surface area can be determined by the particle size, particle shape and the porosity of the particles.

2.3.2.2 Particle Size

It has been observed that the increase in stiffness with decreasing particle size is linear for particles below 0.2microns (Bhatnagar 2005). The particle size is also related to tensile strength, yield strength and elongation, in the same way but the results have been eratic with larger particle sizes.

2.3.2.3 Description of Composites

Reinforced plastics are systems of at least two components-the polymer (or polymers)and the filler(or fillers). Sometimes other additives like lubricants, coupling agents, colourants etc. are also added. The term composites are applied to such systems. A composite is a material system composed of a mixture or a combination of two or more constituents that differ in form and/or composition and are insoluble in one another. This includes all filled polymers, laminates and reinforced plastics. The flow properties of these polymers have attracted large attention. The flow properties of these composites depend on voids or the crowding of filler particles.

2.3.2.4 Polymer-Filler Interaction

With the development of the composite systems like glass fibre reinforced polymers, greater attention has been given to polymer filler interactions. This can be divided into four types.

i. Simple physical inclusion of the filler particles in a non-polar polymer matrix. Here, the filler acts at a diluent and the polymer is weakened.
ii. Physical inclusion of the filler within a polymer matrix. This increases the tensile strength, stiffens the polymer and decreases elongation.
iii. Physical adhesion of the polymer to the surface of filler particles or fibres. This increases overall strength.
iv. The establishment of a true chemical bond between the polymer and individual particles of the filler, e.g. reinforcement of rubber by carbon lack (Blow and Hepborn 1982,Gent 2000).

Sinace even small amounts of fillers bring about stiffening, the first case is not applied. The second case is applicable to those composites where fillers are used to bring down cost e.g. extenders in coatings. As a matter of fact many pigment extenders are surface treated to improve welting by polymer. The third and the fourth cases have been observed in glass fibre reinforced thermo-setting plastics and carbon black reinforced rubber (Blow and Hepborn 1982, Ghent 2000). Here the primary goal of the filler is to strengthen the polymer. It has not yet been observed that the melt index and Tg of the composites are greater than those of the resin(Blow and Hepborn 1982, Gent 2000).

2.4. The use of Agricultural Wastes as Fillers (Organic Fillers)

The use of coconut fibre, palm nuts, groundnut powders etc. have been reported. (Ahmad et al 2012, Akporhonor et al 2007).The results of coconut powder showed that the coconut shell powder is most efficient as a filler for NR at 10pphr loading. The reinforcement ability of modified coconut shell powder is more when compared with the unmodified coconut shell powder. NR reinforced with modified coconut shell showed better physio-mechanical characteristics and the thermal properties of NR matrix was enhanced by the incorporation of coconut shell powder (Purushothaman et al, 2012).

Egwakhide et al, (2007), investigated the effect of coconut fibre filler on the rheological, physico mechanical and swelling properties of NR vulcanizates in diesel, kerosene and toluene. The results showed that the resistance to swelling of NR compound is dependent on the amount of filler loading.The higher the filler content, the lower the equilibrium sorption values obtained.

Ahmad, (2012) studied the effect of oil palm empty fruit bunch (OPEFB) micro filler on the free initiation and propagation in silicone rubber with different weight percentages (wt%) of filler. The loadings were 0.wt% and 1wt% respectively. It was found that OPEFB decreased the propagation of the electrical treeing development. For tree inception study, the addition of 1wt% of OPEFB increased the tree inception voltage of silicone rubber. Thus, OPEFB is a growth of electrical tree occurring in polymeric materials for high voltage application.The hardness and specific gravity of the composites were found to increase in filler loadings and were further increased on addition of MAPE (maleic anhydride-g-polyethylene) (Igwe et al, 2006).

Cuttlebone- a biomass was studied as a reinforcing filler for NR (Sirilux et al, 2008). The cuttlebone particles were obtained by crushing cuttlebone and then sieving. The density of cuttlebone is 2.70g/cm^3 and aragonite form of $CaCO_3$ crystal structure was used. The surface area and average diameter of the cuttlebone particles were measure and reinforcement effect as filler for NR was investigated. The cuttlebone particles did not prevent peroxidecross-linking reaction of NR.The mechanical properties of peroxide cross-linked NR filled with cuttlebone particles were found to be comparable with those of peroxide cross-linked NR filled with commercial $CaCO_3$ filler.

Okeiemen and Imanah, (2006) studied NR filled with agricultural waste products (cocoa pod husks and rubber-seed shell) at 50pphr. The samples were mixed on a two-roll mill, and cured using the semi-efficient vulcanization system. The authors studied the physico-mechanical properties of the composite such as tensile strength, modulus at 100% elongation, elongation at break (EAB), hardness, abrasion resistance, flex fatigue and compression set and compared the values with vulcanizates filled with commercial carbon black

(HAF) N330.and found that the agricultural wastes has poor physical and mechanical properties. The authors also investigated the effect of blending the raw and carbonized agricultural waste products with the commercial grade N330 carbon black on the physico-mechanical properties of NR compounds. It was found that the raw agricultural waste products were ineffective compared with N330 CB as a reinforcing filler for NR compound mixes and could be classified as semi-reinforcing fillers. Blends of up to 40wt% of the raw agricultural waste products and more than 60wt% of the carbonized waste products gave NR compounds with comparable physico-mechanical properties with compounds obtained with N330 carbon black.

2.5. The Importance and use of Compatibilizers

Macrophase separation in polymer blends limits their applicability as adhesives, interfacial stabilizers, coatings, membranes, ion-exchange systems, and functional materials for biomedical and also gives poor physico-mechanical strength for engineering and specialty applications. To arrest the process of phase separation in immiscible polymer blends, and also to reduce the surface tension, macromolecular compatibilizers are usually used. They localize at the interface between the immiscible homopolymers or copolymers, thereby reducing the interfacial tension and slowing down the process of phase separation, leading to a finer domain dispersion and improved mechanical strength of the interface (Willis and Favis 1988, Roe 1993, Tan 1994).

Kwanruethai et al, (2008), studied the compatibilization of NR and chlorosulphonated polyethylene (CSM) blends with zinc salts of sulphonated NR. Epoxidized natural rubber (ENR) was also used for the preparation of

NR/CSM blends. The effect of ionomer concentration on melt viscosity of the 50/50 (%wt/wt)NR/CSM blends at different shear rates was investigated. It was found that the incorporation of ionomers increased the shear viscosity of the blends, indicating an increase in interfacial interaction between NR and CSM. The maximum shear viscosity was observed when the ionomer of 10% by weight of NR was added to the blends. The tensile, tear, oil resistance properties and morphology of the various 20/80 NR/CSM blends with and without the Zn-SNR and ENR at 10% wt NR were examined. The modulus, tensile strength, tear strength and oil resistance of the compatibilized blends improved over those of the uncompatiblized blends. The blends compatibilized with Zn-SNR showed higher levels of improvement in modulus, tensile and tear strength than those of ENR. The tensile strength of 20/80 blends with Zn-SNR and ENR compatibilizers increased by 38% and 30% over the corresponding neat blends. Furthermore, the addition of ionomer and ENR resulted in decreased domain of dispersed NR phase size and improved interfacial adhesion between the NR and CSM, indicating enhanced blend compatibility. These results suggest that Zn-SNR is an effective compatibilizer for NR and CSM blends.

The effect of compatibilizer (styrene-(epoxidized butadiene)-styrene triblock copolymer) (ESBS) on cure characteristics, mechanical properties and oil resistance of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR) blends was examined (Hanafi et al, 2012). The results indicate that the increasing compositions of ENR and the presence of ESBS improve processability, tensile strength, tear strength and tensile modulus of SBR/ENR blends. The scorch time, t_2 and cure time, t_{90} decreased with increasingcompositions of ENR in the blend. The presence of ESBS exhibits a beneficial effect by increasing the scorch time of the SBN/ENR blends. It was also found that the presence of ESBS also resulted in SBR/ENR blends having an oil resistance better than similar blends without ESBS.

Immiscible blends of recycled HDPE and polyethylene terephthalate (PET) were compatibilized with maleic anhydride graft polyethylene (PE-g-MA) (Kasama et al, 1982). The effect of the compatibilizer content on mechanical, morphological, rheological and thermal properties of recycled HDPE/PET blends was studied. The blends were prepared in a twin screw extruder.Tensile strength, tensile strain at break and the impact strength improved with the addition of a compatibilizer. The compatibilized blends had a smaller size of dispersed phase compared with the uncompatibilized blends. The addition of the compatibilizer increased the melt viscosity of the compatibilized blends. The compatibilizer affected crystalline behaviour of the blends.

Compatibilization of NR/HDPE thermoplastic vulcanizate with graphene oxide (GO) through ultrasonically assisted latex mix (ULM) was studied by Yan et al, (2013). The authors found that the stacked GO platelets were successfully exfoliated by the ULM process and have good compatibilization efficiency for immiscible NR and HDP. A smaller discrete NR domains was observed in NR/HDPE blends in the presence of the GO. Moreover,the stacked GO platelets enhance the interfacial adhesion and phase compatibility, which resulted in an increase in mechanical properties of NR/HDPE blends. Compared to NR/HDPE blends, the tensile strength and tensile modulus at 300% strain for NR/HDPE/(1.5phr) GO blends were increased by 27% and 24% respectively. The authors concluded that exfoliated GO can act as both an effective reinforcing filler and compatibilizer in the immiscible NR/HDPE blend.

Chih and Chang, (2006) investigated polymer blends of polyamide-6 (PA6) and poly(phenylene oxide), (PPO) compatibilized by styrene-co-glycidy/methacrylate. The epoxy functional groups in SG copolymer can react with the PA6 amine and carboxylic end groups at interface to form compatibizer in 50/50 NR/EPDM blends.The blend properties were studied in detail. It was found that the addition of the compatibilizer improved the compatibility of NR/EPDM blends.

2.6. PHYSICAL AND MECHANICAL PROPERTIES OF POLYMER BLENDS

It has been shown that carbonization of dika nutshell powder could improve the vulcanization properties of dika nutshell powder filled-natural rubber/acrylonitrile-butadiene rubber blends (Onyeagoro, 2012). The author reported an improvement in vulcanizate properties as revealed by an increase in the tensile strength of the blend samples. The temperature at which carbonization of an agricultural by-products is carried out could affect the rheological physico-mechanical properties of the rubber vulcanizates. However, the effects of carbonization temperature on the filler properties of groundnutshell powder have been reported by (Ayo et al, 2011). They determined that thebulk density and percentage loss on ignition decreased with increase in carbonization temperature. The authors also revealed a progressive increase in iodine adsorption number as the carbonization temperature increased, whereas the filler pH changed from acidity to alkaline with increasing carbonization temperature. (Osarenmwida and Ilori, 2002) investigated the use of rice husk in rubber product. The authors investigated the hardness, tensile strength, compression, abrasion resistance and rheological properties of the product and found rice husk filler performance satisfactory. Also, the rheological, physico-mechanical and swelling properties of coconut fibre filled vulcanizate natural rubber were carried out by (Egwaikhide et al, 2007). They authors observed that the tensile strength increased to an optimum value of 7.35MPa and hardness increased with increased filler loading, while percentage compression set and abrasion resistance decreased with increased filler loading. In other reports, the use of fillers like cocoa pod husk, rubber seed shells (Okieirnen and Imanah, 2006), palm kernel husk (Egwaikhide et al, 2007) and wood flour were examined. The results obtained from these studies indicated a potential for the utilization of agricultural residues as fillers in natural rubber compounds. In a study by (Aguele and Madufor, 2012), carbonized coir showed some potential enhancement on the reinforcing or other mechanical properties of rubber composites. (Osarenmwinda and Abode, 2010) reported the possibility of utilizing low cost carbonized bagasse (waste from sugar cane), an agriculturalwaste as alternative filler material in natural rubber. The carbonization characteristics of rice husk, corncob, bagasse, coconut shell, and palm shell have been investigated by (Nakorn, et al. 2004) using a thermogravimetric analyzer and an FTIR spectrometer. It was found that the weight change behaviours during the carbonization were significantly different among the samples. The Derivative Thermogravimetry (DTG) curves during the carbonization of biomass have several distinctive peaks. These peaks seem to be caused by the decomposition of hemicellulose, cellulose, and lignin in biomass. There were significant interactions between cellulose and lignin during the carbonization. The thermogravimetric analyses of the lignin-cellulose blends clearly show that the interactions between cellulose and lignin during the carbonization contributed to an increase in the carbonization yield.

From the FTIR analyses, the increase in carbonization yields during the carbonization of lignin-cellulose blends was brought about by the cross-linking reactions between lignin and cellulose to form ester groups during the carbonization. It suggests that further study and analysis of gas formations during the carbonization of biomass is necessary for better understanding of carbonization characteristics of biomass. (Ugbesia, 2001) reported that physic-mechanical properties of natural rubber vulcanizates are greatly influenced by filler carbonization temperature and loading; and are therefore significant factors in determining their use in rubber compounding.

The investigation showed that vulcanizates exhibit high quality characteristics at filler type 300-500 (that is at filler carbonized at 300 - 500°C) and with 60phr loading. Therefore, for high quality vulcanizates using cassava peel as the reinforcing filler, carbonization should be done at 300°C for 45mins. Longan seed was carbonized to form longan seed activated charcoal. A carbonization temperature of 500°C was favourable due to the highest presence of organic carbon. Activated charcoal which was triggered by phosphoric acid at the ratio of 1.0 : 0.5 by weight of charcoal per volume of phosphoric acid prior to the carbonization process gave a higher iodine number than that being triggered after the carbonization process, particularly at carbonization temperature of 500°C (Mopoung, 2008).

In addition to the physical properties, there are certain properties known as performance or engineering properties which correlate with the performance of the polymer under varied type of loading and environmental influences such as flame retardancy impact, fatigue, high and low temperature behaviour and chemical resistance. Ideal elastic solids deform according to Hookean law which states that the stress is directly proportional to strain. The behaviour of a polymer subjected to shear or tension can be described by comparing its reaction to an external force withthat of an elastic solid under load. (Rao, 1991).

The mechanical andflame retardancy properties of samples changed significantly due to the mean agglomeration of particles sizes (surface area) and polymer-filler interactions. Reinforcement of filled natural rubber (NR)/linear low density polyethylene (LLDPE) arises from the strong interaction between filler and polymer matrix. Higher filler loading leads to a higher insoluble gel content and bound rubber in NR/LLDPE blends (Azizan et al, 2004). Addition of PVOH in starch-glycerol blends significantly improved both the tensile strength (TS) and elongation of the extruded materials. DMA analysis showed that Tg values in blends decreased with increased glycerol content. Addition of PVOH to starch-glycerol blends prevented the development of surface cracks and improved mechanical properties. As expected, the starch-glycerol extruded ribbons biodegraded rapidly in soil. Addition of PVOH to blends slowed the biodegradation process (Lijun et al. 2000).

Investigations are currently on, aimed at finding suitable reinforcing agents to replace carbon black in the compounding of rubber products. Sepiolite, kaolin, and precipitated silica were commonly used as reinforcing agents. However, their reinforcing properties are lower than those of carbon black. Because of their inorganic origin, these mineral fillers are not compatible with polymermatrices. The particle size, structure, and surface characteristics are important factors that are considered in determining the reinforcing and flame retardancy ability of filler to rubber compounds. The particle size is especially important because a reduction in particle size provides a greater surface area

(Zhang et al, 2000). Thus, the use of talc, nano-ZnO, nano-CaCO3, and nano-$A1_2O_3$ as substitutes for carbon black in rubber compounding has been suggested (Zhang et al, 2004). These fillers have small particle sizes and exhibit superior physical and mechanical properties in the vulcanizates when compared to the conventional micro- composites. They also offer new techniques, and business opportunities in the rubber industry. Different materials have been used to reinforce natural/synthetic rubber. (Arroyo et al, 2003) studied the use of octadecylamine modified mont-morillonite as substitute for carbon black in natural rubber (NR) compounds. The organo clay was reported to improve the strength of the natural rubber without having any reduction in the elasticity of the material.

Osabohien and Egboh, (2007), revealed the potentials of cherry seed shells as filler in natural rubber compounds. They reported that the cure characteristics and the physico-mechanical properties investigated showed comparable results with that of reinforcing standard carbon black filler. It has been shown that the use of rice husk (RH) in natural rubber/linear low-density polyethylene composite results in an increase in tensile modulus and hardness (Mwaikambo and Ansell, 1999).

The main disadvantage of using RH as reinforcing filler for composite material is the poor interaction between rice husk particle and polymer matrix (Avella et al, 1998). Compatibility of cellulosic fibres with non-polar matrices which are mostly hydrophobic is problematic due to high polarity and hydrophilicity in nature of cellulosic fibres. Therefore, modification of the surface of natural cellulosic fibres is critically important to increase the hydrophilicity of the fibres and enhances the adhesion with polymer matrix. Hence, modification of natural fibre surface represents the natural process used to increase the hydrophobic character or decrease the hydrophilicity of the fibres. The adhesion of RH to the matrix can be improved on minimizing the surface tension.

The use of clay in producing butadiene rubber (BR) nano-composite was reported by (Kim, 1980). The tensile and tear strengths of BR/Cloisite 2OA (clay) composites were 4.4 times, and 2 times greater than that of unfilled BR, respectively. The rebound resilience, compression set, and abrasive resistance and flame resistance of BR/Cloisite 2OA was approximately twice larger than that of BR.

Yang et al, (2013) investigated the influence of graphite particle size, and shape on the properties of acrylonitrile butadiene rubber (NBR) at 20, 40, and 60 Phr filler contents. It was found that the graphite having the smallest particle size possessed the best reinforcing ability, while the largest graphite particles imparted the lowest function coefficient of the composites among four fillersinvestigated. (Anserifer, 2001) studied the properties of natural rubberreinforced with synthetic precipitated amorphous white silica nano-filler. The flame retardance, hardness, tensile strength, and compression set were improved when the filler was incorporated into the rubber. However, the tear strength, elongation at break, and cyclic fatigue life were adversely affected. The effect of recycled rubber powder (RRP) on tensile properties and swelling behaviour of natural rubber (NR) compounds was investigated in the concentration range, 0 to 50 P1w by (Ismail et al, 2002). It was reported that increasing the RRP content produced natural rubber compounds that have better resistance to swelling and lower the elongation at break. However, the tensile stress Ml00 (stress at 100% elongation) increased slightly.

Hanafi et al, (2002), examined the cure characteristics and mechanical properties of bamboo fibre reinforced natural rubber composites as a function of fibre loading and bonding agent. The scorch time, t2 and cure time, t decreased with increasing filler loading showing better flame retardance and the presence of bonding agent. Tensile modulus and hardness of composites increased with increasing filler loading and the presence of bonding agents. The adhesion between the bamboo fibre and natural rubber was increased by bonding agent.

The synergistic effect between carbon black and organo-clay, such as mechanical and dynamic mechanical properties in rubbers (NR, epoxidized NR, styrene-butadiene rubber (SBR), etc.) was also investigated (Praveen et al,

2009).The synergistic mechanism generally explained that the coexistence ofclay and carbon black could enhance the clay-carbon black network structure hindering the movement of polymer chains and improving mechanical and flame retardant properties (Chattopadhyay, 1986).

The effect of poly (cis- 1, 4-isoprene)-graft- poly (vinyl alcohol) (PIP-g-PVA) copolyrner upon the mechanical properties of the incompatible poly (3-hydroxybutyrate)/poly (cis- 1,4-isoprene) (PHBIPIP) blend was investigated by (Jin-San et al, 1999). Graft copolymer of PIP.-g-PVA was introduced, because PVA was known to be compatible with PHB. The content of the grafted PVA in the copolyrner was approximately 18 wt% and the Tg of the copolymer occurred around 60 C, which is same as the Tg of PIP. The PHB/PIP-g-PVA blend showed two separate Tg’s. As the amount of the graft copolymer in the blend was increased, the higher Tg that was attributable to the PHB rich phase was slowly increased, whereas lower Tg remained almost constant near 60 C.

Thus, it was inferred that PIP formed a dispersed domain in the blend and that although the PVA domain was so small as not to show its own Tg, it was mixed with PHB, resulting in an increase in the Tg of the PHB rich phase. With an increase in the PIP content in the PHBJPIP blend, the breaking strength, strain at break and toughness of the blend were significantly decreased and no improvement in the impact strength was observed. On the other hand, the strain at break, toughness and impact strength of the PHB/PIP-g-PVA blend were increased with an increase in the copolymer content, however, the breakingstrength was slightly decreased. The average size of the rubbery domain in the PHBJPIP-g-PVA blend was smaller than that in the PHB/PIP blend.

Osman et al, (2010) studied the effect of maleic anhydride- grafted polypropylene (MAPP) on the properties of recycled newspaper (RNP) filled polypropylene (PP)/natural rubber (NR) composites and reported that the incorporation of MAPP reduced the water uptakes of the composites. The effects of partial or complete re-placement of carbon black (CB) and silica on the properties of paper sludge (PS) filled natural rubber composites were elucidated by (Ismail et al, 2008). PS/silica filled natural rubber composites was reported to exhibit lower maximum torque, tensile properties and fatigue life compared to the PS/CB filled natural rubber composites. (Sobhy and Tamman, 20 10) in their studies found that the tensile strength of wheat husk fibres (WHFS)/ethylene-propylenediene terpolymer (EPDM) composites was decreased as the filler content increased.

Rahmadini et al, (2010) investigated the effect of surface modification of rice husk (RH) with sodium hydroxide (NaOH) and liquid epoxidized natural rubber (LENR) on mechanical properties of the natural rubber (NR)/ high density polyethylene (HDPE) reinforced RH composites. The FTIR spectra showed the changes on peaks of LENR coated RH as rubber surface treatment in this investigation at 10% wt LENR in toluene solution. The SEM micrograph indicated that the surface of rice husk changed after treatment process.

Modification of RH with NaOH 5% followed by 10% LENR showed the optimum tensile stress, modulus and impact strength as compared to untreated RH, NaOH treated and LENR treated RH composite. A significant increase of the strength was observed upon fibres addition when using LENR as compatibilizer. The changes were due to the increase of hydrophobicity and compatibility of the rice husk surface which improved the adhesion properties of rice husks and wettability of the fibre which leads to improved mechanical properties of the composite.

Recently (Ukeme, 2014) reported that the mechanical properties of polystyrene(PS)/Polypropylene (PP) blends are dependent on blend composition (ratio of PS/PP) and styrene-b-(ethylene-co-butylenes)-b-styrene (SEBS) content. The impact strength and elongation at break of the uncompatibilized PS/PP blends increased with PP content. However, the tensile strength and flexural modulus decreased with PP content. The impact strength and elongation at break of the PS/PP blends increased with SEBS content, at the expense of tensile strength and flexural modulus. The improvement in impact strength and elongation at break with the addition of SEBS are due to the improved interfacial adhesion between the PP dispersed phase (PP) and matrix phase (PS). The effectiveness of SEBS in enhancing the compatibility of the blends depends on the blend composition.

2.7.0 FLAME RETARDANTS IN POLYMERIC MATERIALS

Flame retardants are a key component in reducing the devastating impact of fires on people, property and the environment. They are added to potentially flammable materials, including textiles and plastics. The term ‘flame retardant’refers to a function, not a family of chemicals. A variety of different chemicals, with different properties and structures act as flame retardants and these chemicals are often combined for effectiveness.Bromine, phosphorus, nitrogen, chlorine, magnesium, silicon, oxides, hydroxides, magnesium chloride, magnesium oxide, magnesium hydroxide, diammonium phosphate, sodium chloride, trisodium phosphate, ammonium chloride.

Potassium carbonate, calcium chloride, sodium tetraborate, potassium bromide, ammonium polyphosphate, zinc chloride, ammonium trilydrate, ammonium sulphate, ammonium sulphamate, boric acid, phosphoric acid, diammonium phosphate, sodium chloride, trisodium phosphate are commonly used flameretardantsin polymeric materials.

Flame retardants are added to different materials or applied as a treatment to materials (e.g. polymers) to prevent fires from starting, limit the spread of fire and minimize fire damage. Some flame retardants work effectively on their own; others act as ‘synergists’ to increase the fire protective benefits of other flame retardants (Laoutid et al, 2015).Most times a variety of flame retardants is necessary because materials that need to be made fire-resistant are very different in their physical nature and chemical compositions, so that they behave differently during combustion (Laoutid et al, 2015). The elements in flame retardants also react differently with fire. As a result, flame retardants have to be matched appropriately to each type of material.Flame retardants work to stop or delay fire, but, depending on their chemical makeup, they interact at different stages of the fire cycle.

Igwe and Obuneme, (2011)reported that the rate of burning of different snail shell filled NR vulcanizates. The researcher said that for any given particle size of snail shell powder considered, the rate burning of the vulcanizates was observed to decreased with increase in filler content at snail shell powder content above 5pphr. In other words the researchers found that the snail shell powder is inefficient as a filler in retarding the rate of burning of NR vulcanizates at a filler content less than 5pphr, CB was observed to reduce the rate of burning of rubber vulcanizates at the filler content investigated. Igwe et al noted the decreases in the burning rate of snail shell powder filled rubber vulcanizates with increases in filler content and at any given filler particles size was very marginal and may point to the fact that the flame retardant property of snail shell powder in the vulcanizate is not particularly good. Also the rate of burning of snail shell powder filled NR vulcanizates decreases with decreases in filler particle size. This they attributed to the envisaged greater dispersion of the smaller sized filler in vulcanizates, which resulted in greater absorption of energy and hence less tendency for the vulcanizates to burn. This study shows that CB is superior to snail shell powder in retarding the rate of burning of NR vulcanizates.

Sirquera and Soares, (2003) studied the properties of PP and ACM with special attention on compatibilization and dynamic vulcanization and their effects on mechanical and temperature characteristics of the blends. The researchers found that the mechanical properties and temperatureandflame resistance increased with increasing compatibilizers level.

Ali,(2012) studied the effects of heat on zinc borate ($2ZnO.3H_2O.3.5H_2O$) and antimony pentoxidte (SB_2O_3), araldite composite and concluded that the flame retardancy will be increased by the addition of 10% SB_2O_3 because of the phase transformation which happened in internal structure of the oxide which caused with the zinc borate enhanced flame retardancy of the composite material and this retardant action increased with increased antimony pentoxide content 20% and 30%. The flame retardancy is reduced when mixing is increased to 4.1and 5.1 from 3-1. The retardantaction decreases with the increase of antimony pentoxide percentage of 40% and 50% and tests show that the surface was starting to decompose and fracture after exposure to 3000^{o}Cflame temperature and above. (Al-Mamori et al, 2011).

Obidiegwu, (2012) investigated the effects of wood fibres on the flammability properties of LDPE, test results showed that ignition time and auto-combustion times increased with increasing fibre content and the flame propagation rate decreased with increasing filler content.

Polymers and polymers of vinyl chloride and vinylidene chloride are widely used as plastics, fibres and flame retardants. PVC is a thermoplastic that is partially syndiotactic and irregular with low crystallinity. PVC use as a result of the chloride group which is a halogen and a flame retardant (Burgess, 1982, Brown et al, 2000). When unplasticized PVC is mixed with little epoxy resin, as plasticizer and nitrile rubber, chlorinated PE, ABS resin or methyl methacrylate butadiene-styrene, terpolymer, or styrene-acrylonitrile copolymer or poly(methacrylate), we get a rigid vinyl. Jeziorsky and Wenzler, (1982), copolymerizing little amounts of vinyl acetate with vinyl chloride produces materials with higher softening point and lower solubility and better fabrication or workability (Billmeyer 2005).

Flame retardants are the most useful material. Used in imparting flame resistance to plastics. They must be used with a source of available chlorine to be effective. Examples are antimony trioxide the phosphates, ester plasticizers, magnesium hydroxides magnesium chlorides, etc. The major factor in reducing flammability of materials appear to be (a) elimination of volatile fuel by cooling, (b) production of a thermal barrier by charring, thus eliminating fuel by reducing heat transfer and (c) quenching the chain reaction in the flame by adding suitable radical scavengers (Blake 1982).

2.7.1 The Fire Cycle

i. The initial ignition source can be any energy source (e.g. heat, incandescent material, a small flame).
ii. The ignition source causes the material to burn and decompose (pyrolysis), releasing flammable gases.
iii. If the solid materials do not break down into gases, they remain in a condensed phase. During this phase, they will slowly smoulder and, often, self-extinguish, especially if they “char”, meaning material creates a carbonated barrier between the flame and the underlying material.
iv. In the gas phase, flammable gases released from the material are mixed with oxygen from the air. In the combustion zone or the burning phase, fuel, oxygen and free radicals combine to create chemical reactions that cause visible flames to appear. The fire then becomes self-sustaining because, as it continues to burn the material, more flammable gases are released, feeding the combustion process (Laoutid et al, 2015).

2.7.2 The Action of Flame Retardants

When flame retardants are present in the material, they can act in three ways to stop the burning process. They may work to:

i. Disrupt the combustion stage of a fire-cycleincluding avoiding or delaying “flashover” or the burst of flames that engulfs a room and makes it much more difficult to escape.
ii. Limit the process of decomposition by physically insulating the available fuel sources from the material source with a fire-resisting “char”layer.
iii. Dilute the flammable gases and oxygen concentrations in the flame formation zone by emitting water, nitrogen or other inert gases (Laoutid et al, 2015).

2.7.3 PRODUCTS REQUIRING FLAME RETARDANTS

Today, flame retardants are used in predominantly four major areas:

2.7.4 Electronics and Electrical Devices

i. Television and other electronic device casings
ii. Computers and laptops, including monitors, keyboards, and portable digital devices.
iii. Telephones and cell phones
iv. Refrigerators and air conditioners
v. Washers and dryers
vi. Vacuum cleaners
vii. Electronic circuit boards

viii. Electrical and optical wires and cables
ix. Small household appliances
x. Battery chargers

2.7.5 Building and Construction Materials

i. Electrical wires and cables, including those behind walls
ii. Insulation materials (e.g. polystyrene and polyurethane insulation foams).
iii. Paints and coatings which are applied to a variety of building materials, including steel structure, metal sheets, wood, plaster and concrete.
iv. Structural and decorative wood products
v. Roofing components
vi. Composite panels
vii. Decorative fixtures

2.7.6 Furnishings

i. Natural and synthetic filing materials and textile fibres.
ii. Foam upholstery
iii. Curtains and fabric blinds
iv. Carpets

2.7.7 Transportation (Airplanes, Trains, Automobiles)

i. Overhead compartments.
ii. Seat covers and fillings
iii. Seats, headrests and armrests
iv. Roof liners

v. Textile carpets
vi. Curtains
vii. Sidewalls and ceiling panels
viii. Internal structures, including dashboards and instrument panels.
ix. Insulation panels
x. Electrical and electronic cable coverings
xi. Electrical and electronic equipment
xii. Battery cases and trays
xiii. Car bumpers
xiv. Stereo components
xv. GPS and other computer systems

2.8.0 Potassium Bromide (KBr) and Magnesium Chloride ($Mg(Cl)_2$)

Bromine and chlorine, because of their low bonding energy with carbon atoms, can readily be released and take part in the process, in free-radical combustion mechanism reactions occurring in the gas phase. (Alexandre 1991)

Thermally induced polymer decomposition releases very reactive free-radical species such as $H^{\cdot}$ and $OH^{\cdot}$ which maintain combustion by a cascade-chain mechanism in the gas phase Halogenated flame retardant are able to react with these, stopping the chain decomposition and therefore the combustion of the polymer (Laoutid et al 2015),

$R_X \longrightarrow R^{\cdot} + X^{\cdot}$ where x may be Br, Cl

$X^{\cdot} + RH \longrightarrow H_2 + X^{\cdot}$

$HX + H^{\cdot} \longrightarrow H_2 + X^{\cdot}$

$HX + OH^{\cdot} \longrightarrow H_2O + X^{\cdot}$

HX the effective flame retardant species is regenerated by the reaction of X^{+} with RH. Also being non-flammable, HX can have a physical action on the combustion mechanism (protective gaseous coating, dilution of fuel gases). It also catalyzes the oxidation of the solid phase and the oxidation products tend to cyclize, which leads to formation of a solid protective layer. It should be noted that $X^{\cdot}$ is much less reactive than $OH^{\cdot}$ and $H^{\cdot}$ (Laoutid et al, 2015).

Halogenated flame retardants are characterized by high molecular weight and good thermal stability and mainly used in styrenic polymers, polyolefins, polyesters and nylons (Laoutid et al, 2015).

The incorporation of either KBr or $Mg\ (Cl)_2$ into PMMA charges the thermal degradation pattern of polymer. (Zhubanov et al 1976, Zutty 1963, Janovic 1999)

2.9.0 Magnesium hydroxide ($Mg\ (OH)_2$

To be used as a polymer flame retardant, a metal hydroxide need to decompose endothermally and release water at a temperature higher than the polymer processing temperature range and around the polymer decomposition temperature. $Mg(OH)_2$ undergoes endothermal degradation at a high temperature (> 300^{o}C), which is interesting with respect to the extrusion and injection moulding processes of some polymers (Laoutid et al, 2015).

The reaction below shows the decomposition of $Mg(OH)_2$.

$2Mg\ (OH)_2 \longrightarrow 2MgO + 2H_2O$(1300KJ/Kg).

It has to be noted that the flame retardant action of magnesium hydroxide is very effective up to 400°C. Beyond this temperature, the exothermic character of degradation predominates(Well 2004). Metallic hydroxides like Mg $(OH)_2$ are likely to have a catalytic effect on the combustion of the carbonized residues produced, which is probably responsible for the incandescence phenomenon observed during several flame retardant tests (Delfosse 1989). Mg(OH) is used to enhance fire retardancy in ethylene vinyl acetate copolymer (EVA) (Qui 2003 and Shen 1988).

Table 2.1: Comparing the Properties of Some Flame Retardants.
(Source: CJSC Nikomag 2016 40067 Volgogrod, Str 40 let VLKSM 57)

Index Denomination	**Magnesium hydroxide**	**Aluminum trihydrate**	**Bromine-contain**
Decomposition temperature ^{o}C	340-380	180	Up to 400
Smoke density decrease at combustion	3-9 times	2-5 times	Smoke density increases
Electric conductivity (10% in U_2O) on $\mu S/cm$	≤ 350	≤ 200	Not rated
Heat absorption at decomposition	1220	1075	None
Whiteness (Elrepho 351nm)	> 96	> 94	Not rated
Smoke toxicity at decomposition	Does not form toxic or pungent gases	>94	Form bromine toxic gas
Consumption rate %	Up to 40	Up to 50	Up to 10
Finished product recycling technology level, %	90-100	50-60	10-20

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Natural Rubber (NR) of Nigeria Standard Rubber Grade 10 (NSR10) having the characteristics listed in table 3.10 was obtained from Rubber Research Institute of Nigeria, Benin City, Edo State.

Table 3.1: Properties of Nigeria Standard Rubber (NSR10)

Parameters	
Dirt content retained on 45 μm sieve (%)	0.02
Ash content (%)	0.32
Volatile matter (%)	0.40
Nitrogen (%)	0.23
Initial plasticity (P_o)	32.0
Plasticity Retention Index (PRI)	67.0
Mooney Viscosity ML (1+4),100^{o}C	70.0

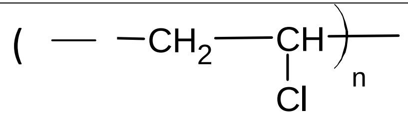
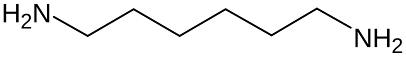
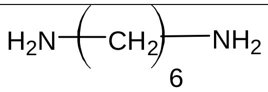
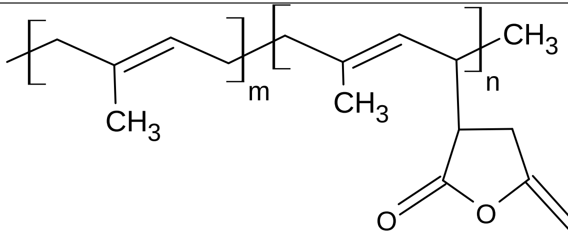
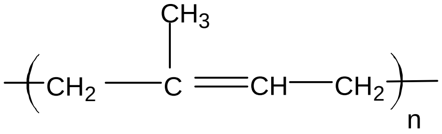
Dikanut (*Irvingia Gabonensis*) shells were collected from a farm yard in Auchi, Edo State, Nigeria.Poly-vinyl chloride, PVC has the following characteristic;(specific gravity 1.35-1.45(g/cm^3), refractive index 1.52-1.55, melt flow index(MFI 26g/min)high tensile strength of 4500N/m2 = 4.5KN/m2 elongation of 40%. The PVC is self-extinguishing, light reaction to sunlight, resistance to strong acids and bases, transparent and soluble in organic solvents, melt flow index of 26g/min, melt temperature of 140-160°C and heat decomposition temperature of 200-250°C.Hexamethylene diamine (HMDA), maleic anlydride graft polyisoprene (MAPI), Triethylene tetraamine (TETA) were obtained from Rovet chemicals Limited, Benin City, Nigeria.

Table 3.2: Shows the properties of maleic-anhydride-g-polyisoprene

Parameters	°C
Molecular weight average (Mw)	25000
Viscosity {cp,20wt % in toluence (30 Brookfield)}	10-50
Refractive index	n20/D152
Density (g/mol at 25°C)	0-92

All the compounding ingredients used were of commercial grades. All the reagents were used without further purification. The structures of PVC, HMDA, MAPI, TETA and NR are presented in Table 3.3.

Table 3.3.Chemical structures of PVC, HMDA, MAPI, TETA and NR.

Component	Structure
PVC	 $\left(-CH_2-\underset{Cl}{CH}-\right)_n$
HMDA	 or 
MAPI	
TETA	$NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$
NR	 $\left(-CH_2-\overset{CH_3}{C}=CH-CH_2-\right)_n$

3.1.1 Equipment

i. Brabender mixer
ii. Grinding machine
iii. Two roll mill
iv. Milling knife
v. Sample trays
vi. Sample dishes
vii. Oven
viii. Daylight
ix. Mould press
x. Mould release
xi. Stop watch
xii. Spanners
xiii. Screw drivers
xiv. Scrappers
xv. Sandpaper

3.2 METHODS

3.2.1 Preparation of the Dikanut Nutshell Powder

After collection, the dikanut shells were washed thoroughly and dried in a microwave over at a temperature of 120^oC. The dried shells were ground to fine powder and sieved through a mesh size of 100μm, 150μm, 200μm, 250μm,300μm, 350μm.The fine particles that passed through the mesh were collected as the dikanut shell powder (DNS).

3.2.2. CHARACTERISTICS OF DIKANUT SHELL POWDER

3.2.2.1 pH Determination

The pHof the DNS was determined in accordance with ASTMD 1512-05 method, by immersing 1.0g sample in 20.0cm^3 beaker. The mixture was stirred for 15minutes and the pH meter was then inserted into the solution to obtain the readings directly. After several readings the average was obtained.

3.2.2.2 Particle Size

The DNS powder was passed through a sieve of 100μm, 150μm, 200μm, 250μm, 300μm, 350μmmesh. The particles that passed through the mesh were taken as having the particle size of 100μm, 150μm, 200μm, 250μm, 300μm, 350μm mesh sizes.

3.2.2.3 Bulk Density Determination

The Bulk density was determined by the tapping procedure described by (Ahmedna et al, 1997). Accurately weighed (about 150)samples were transferred into a cylinder of uniform cross-sectional area and then tapped several times until there was no change in volume occupied by the material, the volume was then recorded and the bulk density calculated as follows:

$$\text{Bulk density} = \frac{\text{Mass of Sample}}{\text{Volume of Sample}} \quad (3.1)$$

3.2.2.4 Moisture Content Determination

The moisture content of the sample was determined by using the method prescribed by ASTMD 1509. A quantity (50g) of the sample was weighed and its initial weight recorded. The sample was then dried to a constant weight at a temperature of 125^{o}C in a microwave oven. The sample was removed from the oven and allowed to cool. The cooled sample was then removed and weighed again, and the weight recorded as the final weight of the sample.

$$\text{Moisture content (\%)} = \frac{\text{Initial weight} - \text{final weight of the sample}}{\text{Initial weight of the sample}} \quad (3.2)$$

3.2.2.5 Determination of Iodine Value

The iodine value was determined by a method described by ASTM 7384.0.1M sodium thiosulphate solution was titrated against 20.0$cm^3$of the sample aliquot solution (prepared by centrifriging 0.5g of powdered sample separate in 25.0cm^3 of 0.488cm^3 iodine dire solution) using 5.0 $cm^3$of freshly prepared starch solution as the titrate the blank was determined and the procedure carried out in triplicate and the average of the values obtained were calculated and recorded.

The volume of sodium thiosulphate employed in aliquot solution is recorded as volume S, while, that used in blank solution is recorded as B.

$$\text{Iodine value} = \frac{B-S}{B} \times 300.14 \qquad (3.3)$$

The iodine adsorption is equal to the inverse of the iodine value.

3.2.2.6 Determination of Loss on Ignition

Loss on ignition refers to the mass loss of a combustion residue whenever it is heated in an air or oxygen atmosphere at high temperature. The loss on ignition of the samples was determined in accordance with the procedure described by ASTMD 7348-13. 10g of the sample was placed in a crucible and put in the furnace, after 2hrs, cooled and weighed. It was heated in the furnace cooled weighed. It was put back in the furnace, heated, cooled and reweighed until a constant weight was obtained.

$$\text{Loss on ignition} = \frac{Initial\ weight - final\ weight\ of\ sample}{Initial\ weight} \qquad (3.4)$$

3.3.0 Preparation of the Composite Samples

Before the melt mixing, PVC was dried in a microwave oven at 100^{o}C for 12hours, the NR was dried at 80^{o}C, while the PVC was first melted in a Brabender mixer (PLE 331) with a rotational speed of 75-85 rpm at 120-160^{o}C for about 5minutes; NR and other compounding ingredients, except the vulcanizing agents and accelerator were added and allowed to mix for 10minutes.

Thereafter, the blend produced was transferred to a two-roll mill set at 120^{o}C, with a rotational speed of 37rpm and a nip clearance or setting of 2mm, which converted the mix to flat sheets. The temperature of the two-roll mill was reduced from 120^{o}C to 70^{o}C, and the nip reduced to 1.5mm.This was followed by addition of the vulcanizing agent. Reduction of temperature was done in order to avoid premature curing of the samples.

The composite samples were then cured by putting them in round shaped mould cavities using the Daylight Press. They were clamped at a pressure of 10Mpa at a temperature of 120^{o}C for 5mins into the standard specimens ready for flame retardant tests.

The formulation used in compounding the composite samples is shown below in table 3.4.

Table: 3.4. Recipe for Compounding

	Uncompatibilized	**KBr**	**Mg(Cl)$_2$**	**Mg(OH)$_2$**
Materials	**Uncompatibilized**	**Compatibilized**	**Compatibilized**	**Compatibilized**
NR	100Pphr	100Pphr	100Pphr	100Pphr
PVC	30.0	30.0	30.0	30.0
Zinc Oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
MAPI/ TETA	0/0	0.5//0.0 1.0/0.2 1.5/0.4 2.0/0.6 2.5/0.8 3.0/1.0	0.5//0.0 1.0/0.2 1.5/0.4 2.0/0.6 2.5/0.8 3.0/1.0	0.5//0.0 1.0/0.2 1.5/0.4 2.0/0.6 2.5/0.8 3.0/1.0
Sulphur	5.0	3.0	3.0	3.0
MBT	1.0	1.0	1.0	1.0
TMTD	1.5	1.5	1.5	1.5
CBS	1.0	1.0	1.0	1.0
TMQ	1.5	1.5	1.5	1.5
WAX	4.0	4.0	4.0	4.5
DNS	0,5,10,15,20,25	0,5,10,15,20,25	0,5,10,15,20,25	0,5,10,15,20,25
KBr	0,5,10,15,20,25	0.5,1.0,1.5,2.0,2.5,3.0	0.5.1.0,1.5,2.0,2.5,3.0	0.5,1.0,1.5,2.0,2.5,3.0
Mg(Cl)$_2$	0,5,10,15,20,25	0.5,1.0,1.5,2.0,2.5,3.0	0.5.1.0,1.5,2.0,2.5,3.0	0.5,1.0,1.5,2.0,2.5,3.0
Mg (OH)$_2$	0,5,10,15,20,25	0.5,1.0,1.5,2.0,2.5,3.0	0.5.1.0,1.5,2.0,2.5,3.0	0.5,1.0,1.5,2.0,2.5,3.0
CB	0,5,10,15,20,25	0,5,10,15,20	0,5,10,15,20	0,5,10,15,20
Mesh size of DNS	100μm, 150μm, 200μm, 250μm, 300μm, 350μm			
Mesh size of CB	100μm, 150μm, 200μm, 250μm, 300μm, 350μm			

3.4. FIRE ENDURANCE TEST

Fire endurance test was carried out in accordance with ASTM E 108-11. Blends of uniform sizes were cut and weighed on an analytical balance, having an accuracy of 0.0001g. The cut samples were 0.1m in length and were each exposed to flame at intervals of 12seconds and the temperatures recorded.

3.4.1 Ignition Time

The ignition time was recorded as the time between the initial supply of the flame from the heat source and the appearance of flame on the substrate or sample.

3.4.2 Auto-combustion Time

Auto-combustion time is the time that elapsed between an initial supply of flame and a self-sustaining combustion of composite samples.

3.4.3 Flame Propagation rate

Flame propagation rate (FPR) is the rate of spread of fire through the substrate. The flame propagation time (FPT) is the time between an initial supply of flame and the combustion of a distance marked N. FPR is the ratio of the distance from the sample and the FPT.

$$FPR = \frac{N}{FPT} \tag{3.5}$$

3.5. Characterization of Dikanut Shell Powder (DNS) and Carbon Black Powder and Carbon (CB)

Characterization of Dikanut Shell (DNS) in terms of the moisture content, pH, surface area, ash content and loss on DNS was done.The results are presented in

Table 3.5:The physical properties of DNS

Parameters	Values	
	DNS	CB
pH of slurry at 28°C	5.40	8.5
Particle size (ıt 28°C μm)	100, 150, 200, 250, 300, 350	100, 150, 200, 250, 300, 350
Bulk density (g/cm^3)	0.80	0.70
Loss on ignition (%)	40.4	92.80
Moisture content (%)	2.20	0.02
Iodine adsorption number (mg/g)	20.40	83.90

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Flammability Tests Results

The results of the (i) Flame ignition time, (ii) Auto-acceleration time and(iii) Flame propagation rate tests are in tables 4.1 – 4.24 and figures 4.1 – 4.24.

Table 4.1Shows the Ignition Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	5	10	14	15
24	10	20	28	30
36	15	30	32	45
48	20	40	46	60
60	25	50	58	72
72	30	60	72	86

Table 4.2 Shows the Auto-acceleration Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	5	7	10	12
24	10	17	21	26
36	15	27	30	38
48	20	37	44	51
60	25	47	56	63
72	30	57	68	76

Table 4.3 Shows the Flame Propagation Rate Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	5	3.0	2.1	2.0
0.8	10	4.3	3.0	2.5
0.6	15	3.5	2.9	2.4
0.4	20	3.3	2.7	2.3
0.2	25	3.1	2.7	2.2
0.1	30	3.0	2.5	2.1

Table 4.4 Shows the Ignition Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	5	5	8	12
24	10	15	17	24
36	15	25	26	37
48	20	35	39	45
60	25	45	48	54
72	30	55	59	65

Table 4.5 Shows the Auto-acceleration Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	5	3	5	10
24	10	12	14	20
36	15	20	22	30
48	20	30	33	36
60	25	39	42	48
72	30	48	53	56

Table 4.6 Shows the Flame Propagation Rate Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	Filler (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	5	0.6	3.8	2.3
0.8	10	0.1	6.0	3.0
0.6	15	3.0	2.8	2.0
0.4	20	3.3	2.7	2.5
0.2	25	3.1	2.5	2.5
0.1	30	2.5	2.4	2.0

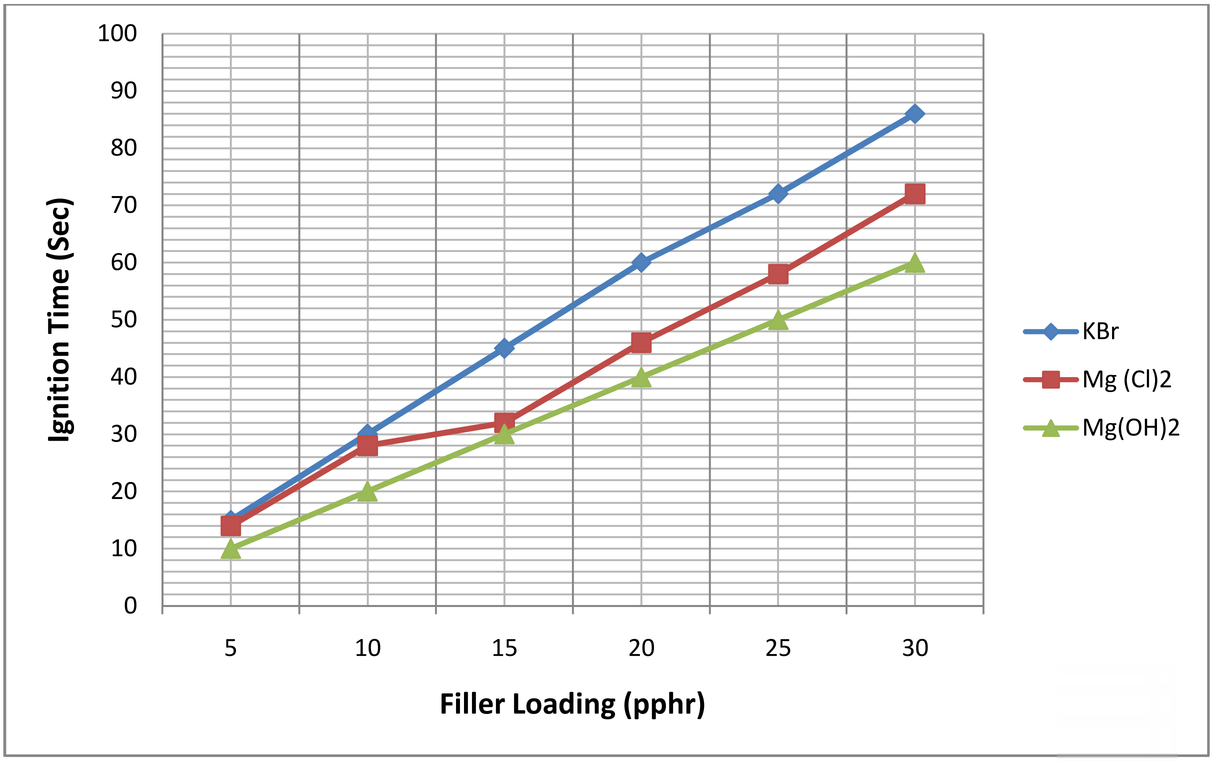


*Fig. 4.1: Graph of ignition time versus CB filler loading*at mesh size of$150\mu m$.

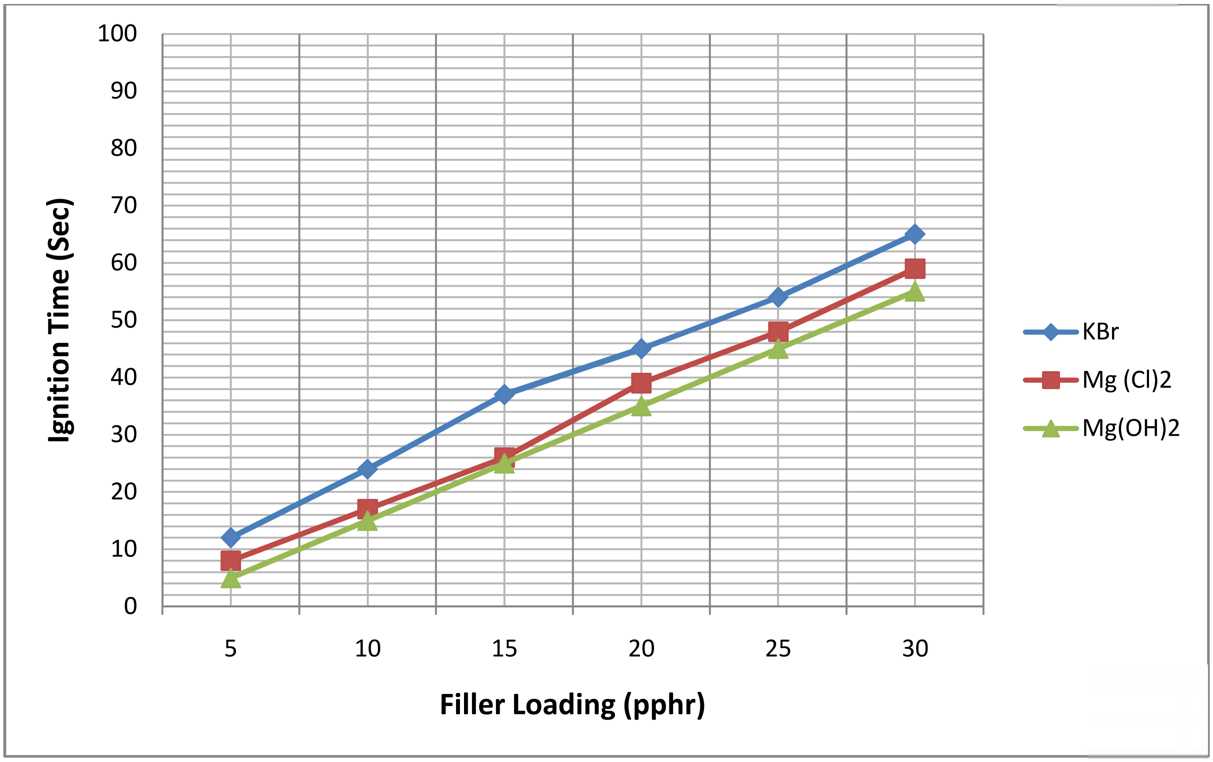


Fig. 4.2: Graph of ignition time versus DNS filler loading at mesh size of $150\mu m$.

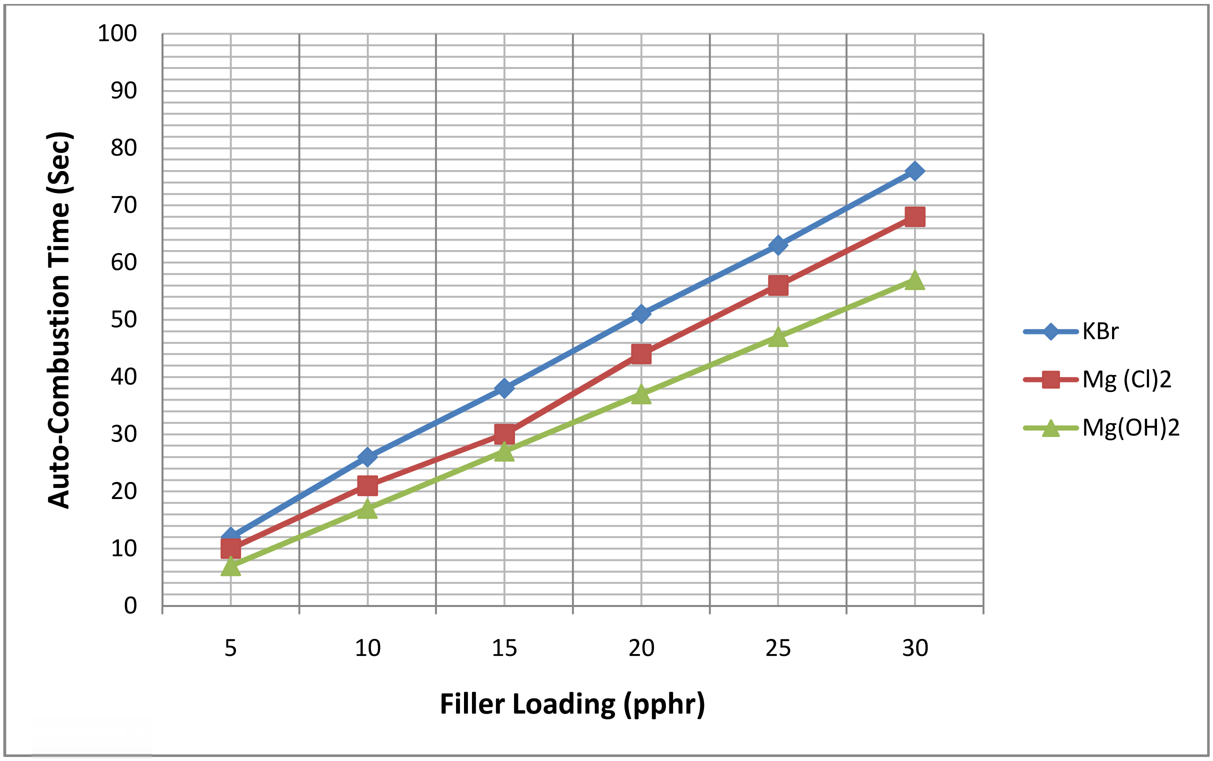


Fig. 4.3: Graph of Auto-combusting time versus CB filler loading **at mesh size of $150\mu m$.**

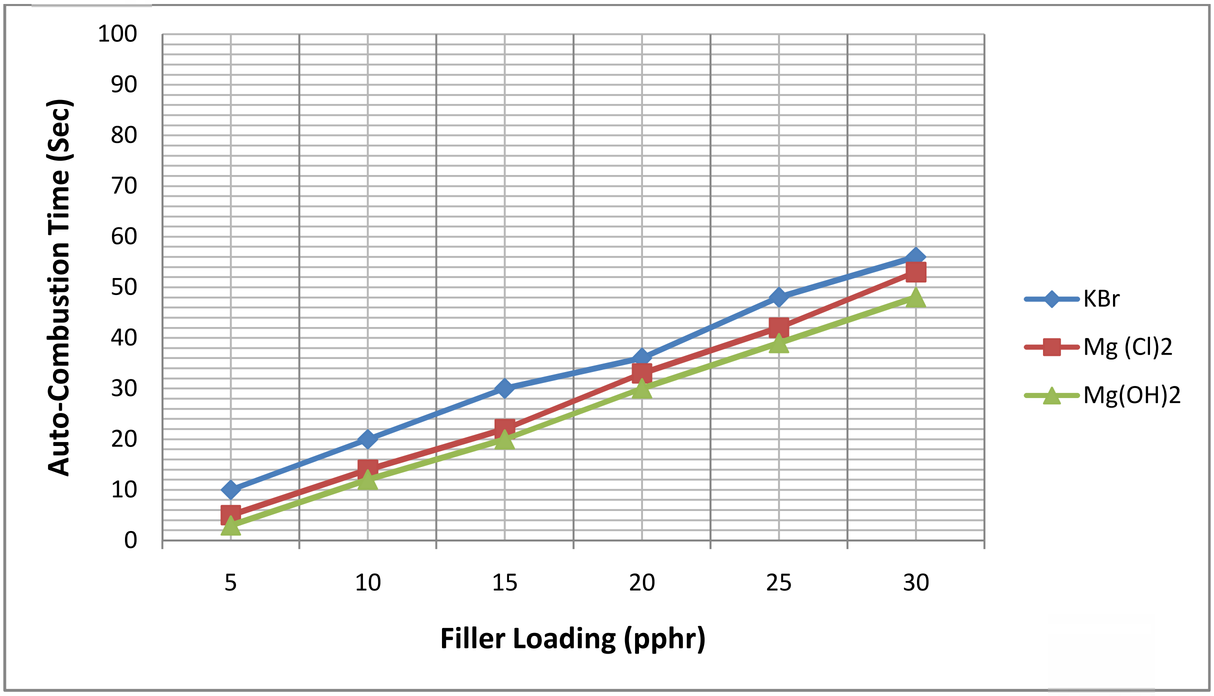


Fig. 4.4: Graph of Auto-combusting time versus DNS filler loadingat mesh size of $150\mu m$.

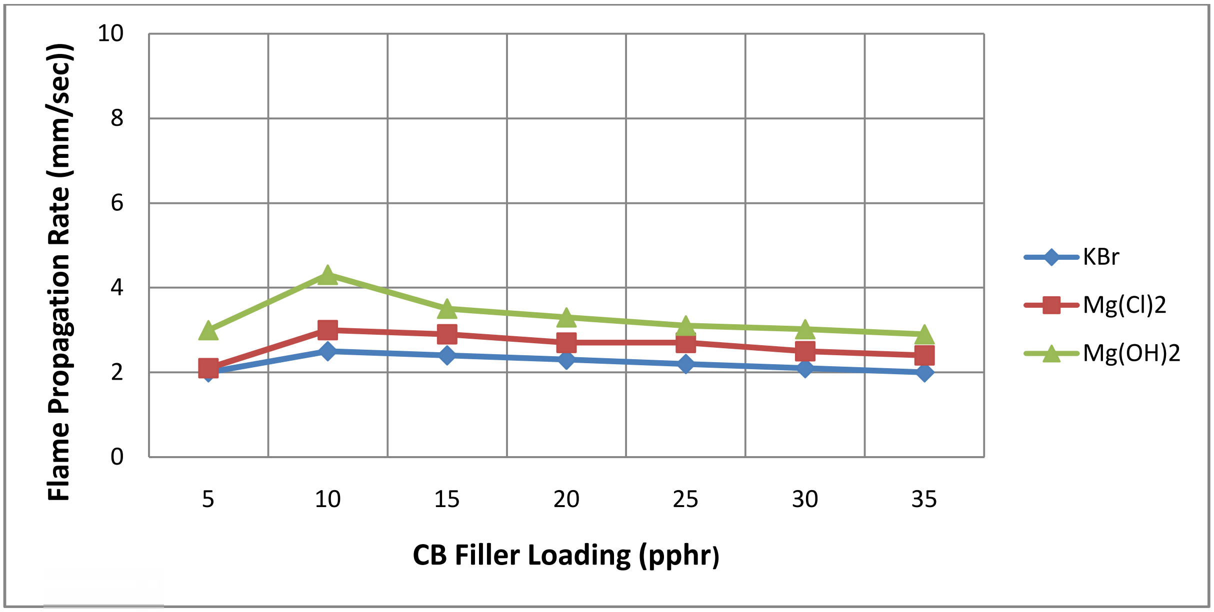


Fig. 4.5: Graph of flame propagation rate versus CB filler loading**at mesh size of $150\mu m$.**

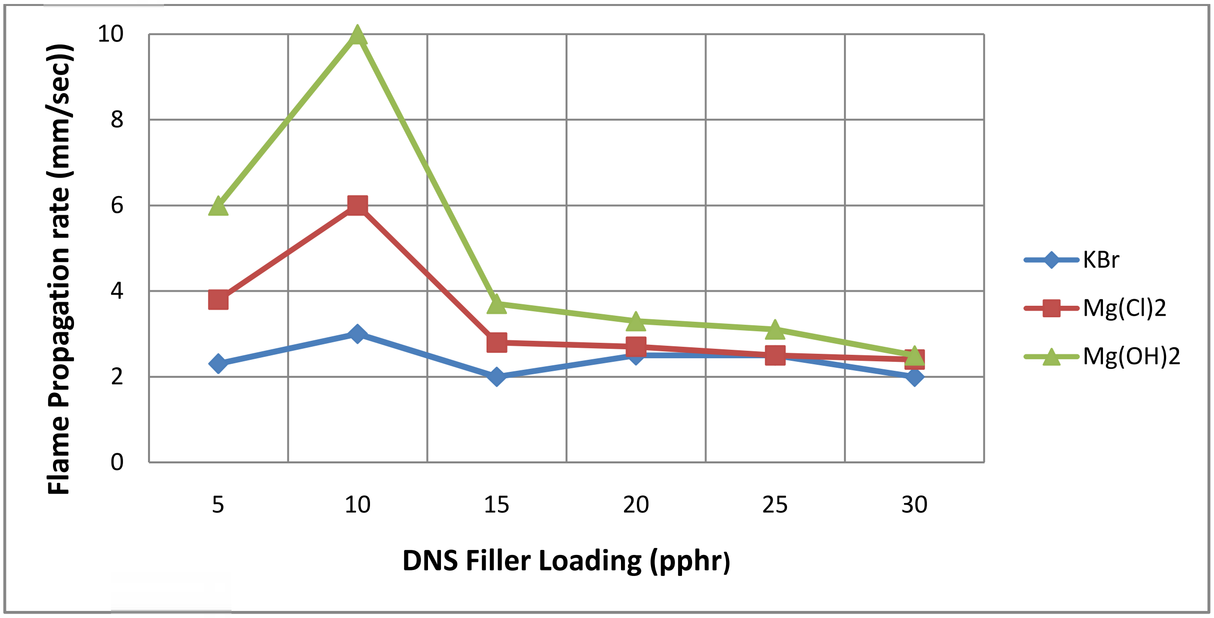


Fig. 4.6: Graph of Flame Propagation rate versus DNS filler loading**at mesh size of $150\mu m$.**

Table 4.7 Shows the Ignition Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	8	11	13
24	1.0	17	19	24
36	1.5	25	28	36
48	2.0	34	39	50
60	2.8	45	50	63
72	3.0	53	58	69

Table 4.8 Shows the Auto-acceleration Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	8	11	13
24	1.0	17	19	24
36	1.5	25	28	36
48	2.0	34	39	50
60	2.8	45	50	63
72	3.0	53	58	69

Table 4.9 Shows the Flame Propagation Rate Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	0.5	3.8	2.7	2.3
0.8	1.0	3.6	4.3	2.7
0.6	1.5	3.3	2.5	2.0
0.4	2.0	3.2	2.7	2.2
0.2	2.5	2.9	2.5	2.5
0.1	3.0	3.0	2.3	2.0

Table 4.10 Shows the Ignition Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	6	8	11
24	1.0	12	14	18
36	1.5	17	21	27
48	2.0	24	27	35
60	2.8	29	36	42
72	3.0	36	44	56

Table 4.11 Shows the Auto-acceleration Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	3	5	8
24	1.0	9	11	15
36	1.5	14	17	23
48	2.0	21	25	30
60	2.5	26	33	37
72	3.0	32	42	50

Table 4.12 Shows the Flame Propagation Rate Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	FR (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	0.5	5.0	3.8	2.7
0.8	1.0	10.0	6.0	3.8
0.6	1.5	4.3	5.5	4.0
0.4	2.0	4.3	3.6	3.9
0.2	2.5	4.6	3.6	3.2
0.1	3.0	4.6	3.8	3.0

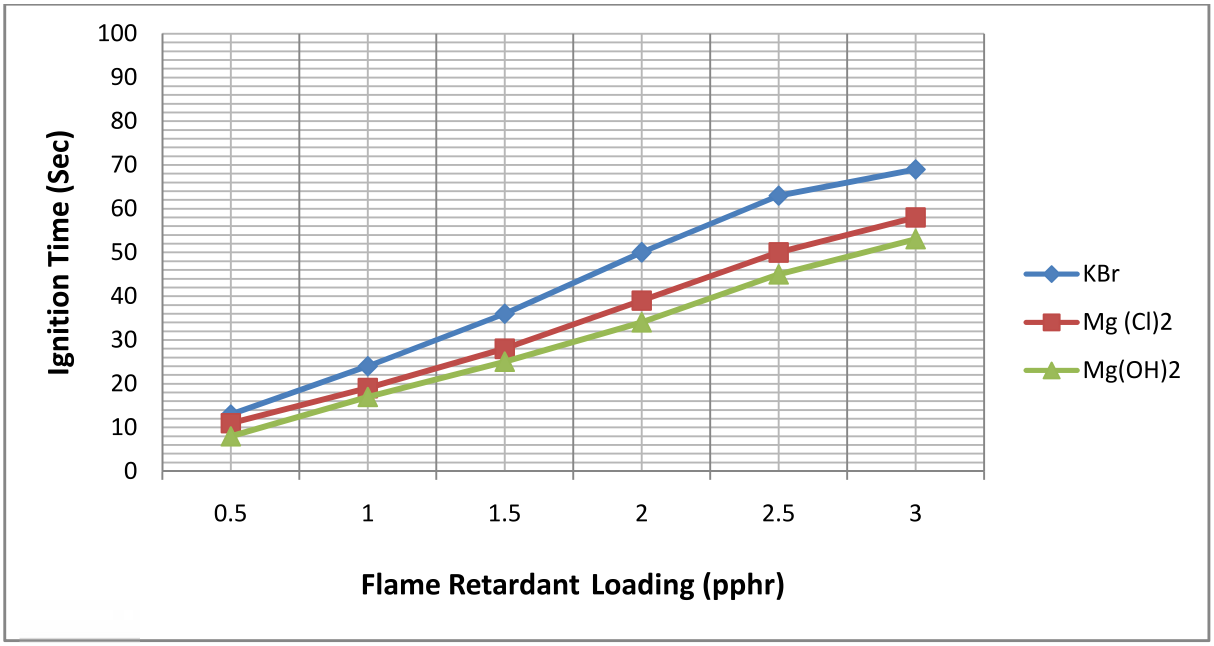


Fig. 4.7: Graph of ignition time versus Flame Retardant loading for CBat mesh size of $150\mu m$.

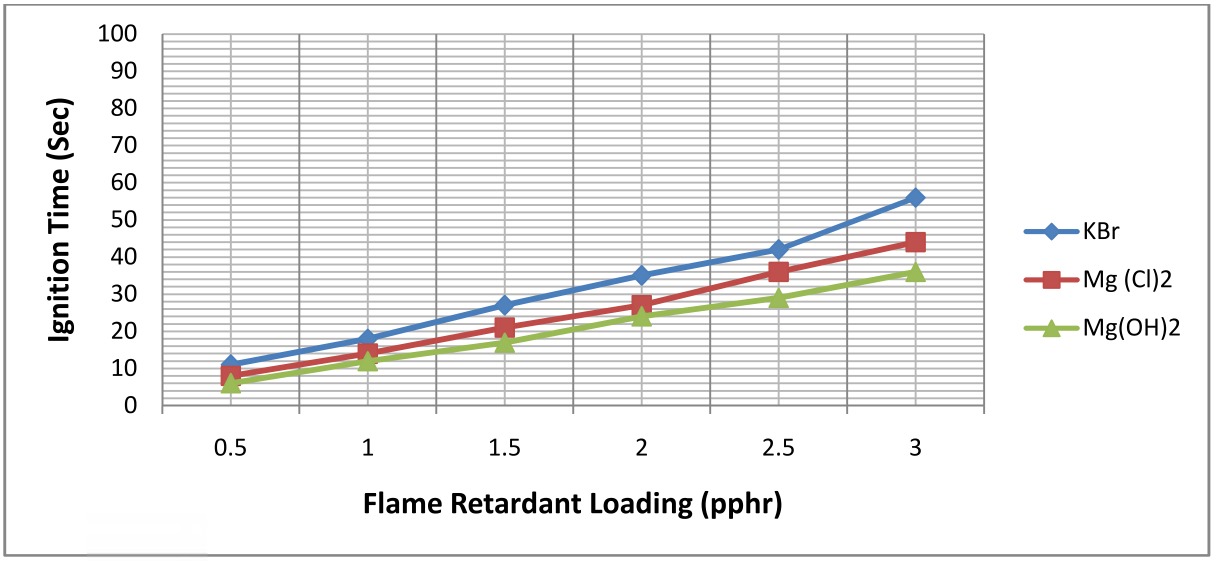


Fig. 4.8: Graph of ignition time versus Flame Retardant loading for DNS at mesh size of $150\mu m$.

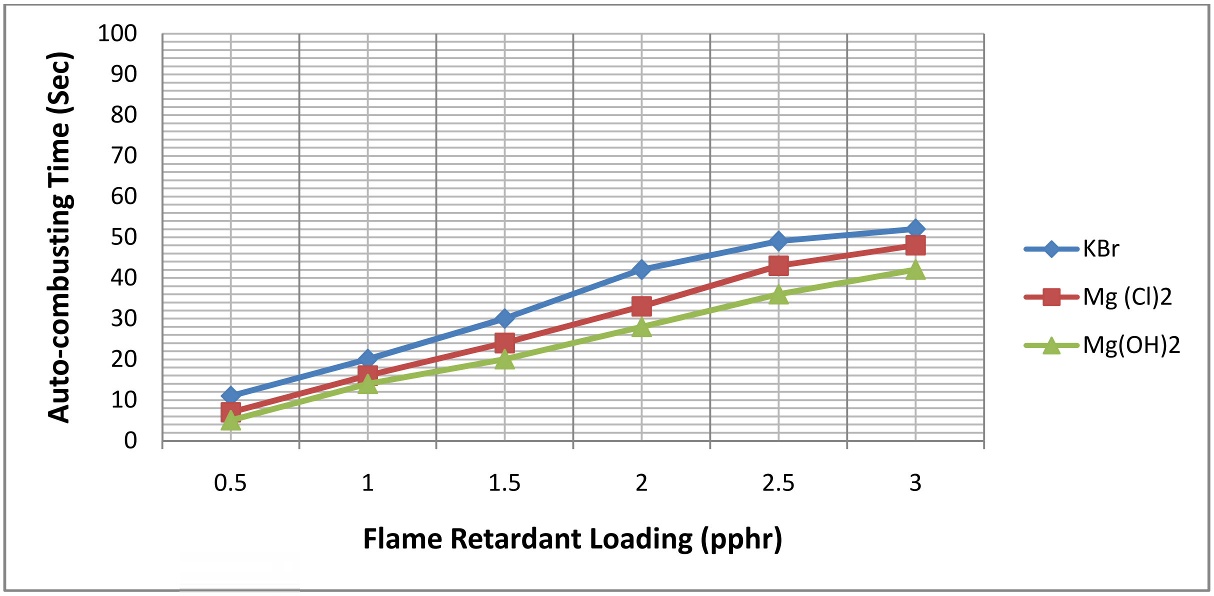


Fig. 4.9: Graph of Auto-combusting time versus Flame Retardant loading for CBat mesh size of $150\mu m$.

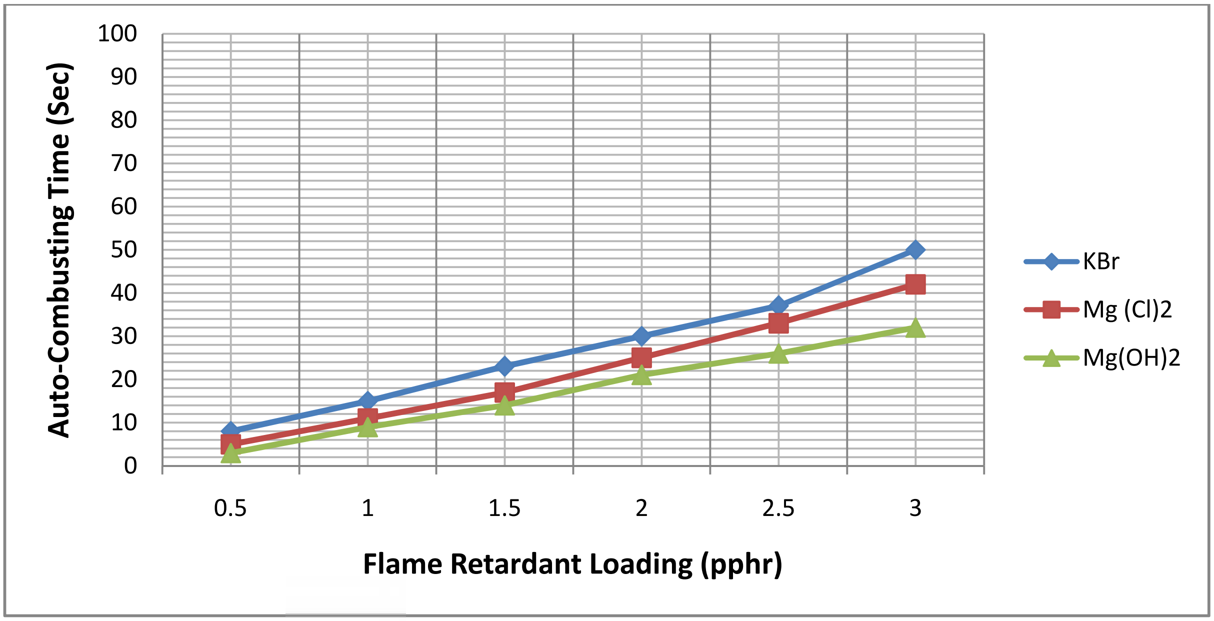


Fig. 4.10: Graph of Auto-combusting time versus Flame Retardant loading for DNSat mesh size of $150\mu m$.

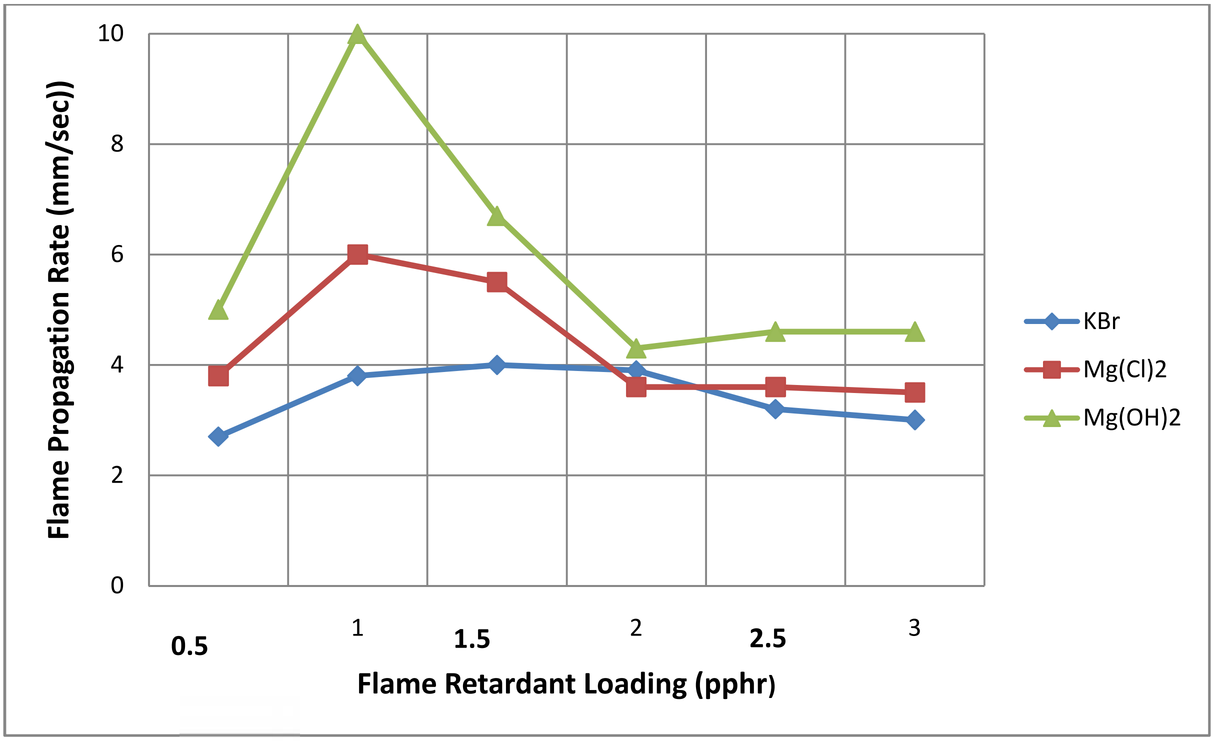


Fig. 4.11: Graph of Flame Propagation rate versus Flame Retardant loading for CBat mesh size of $150\mu m$.

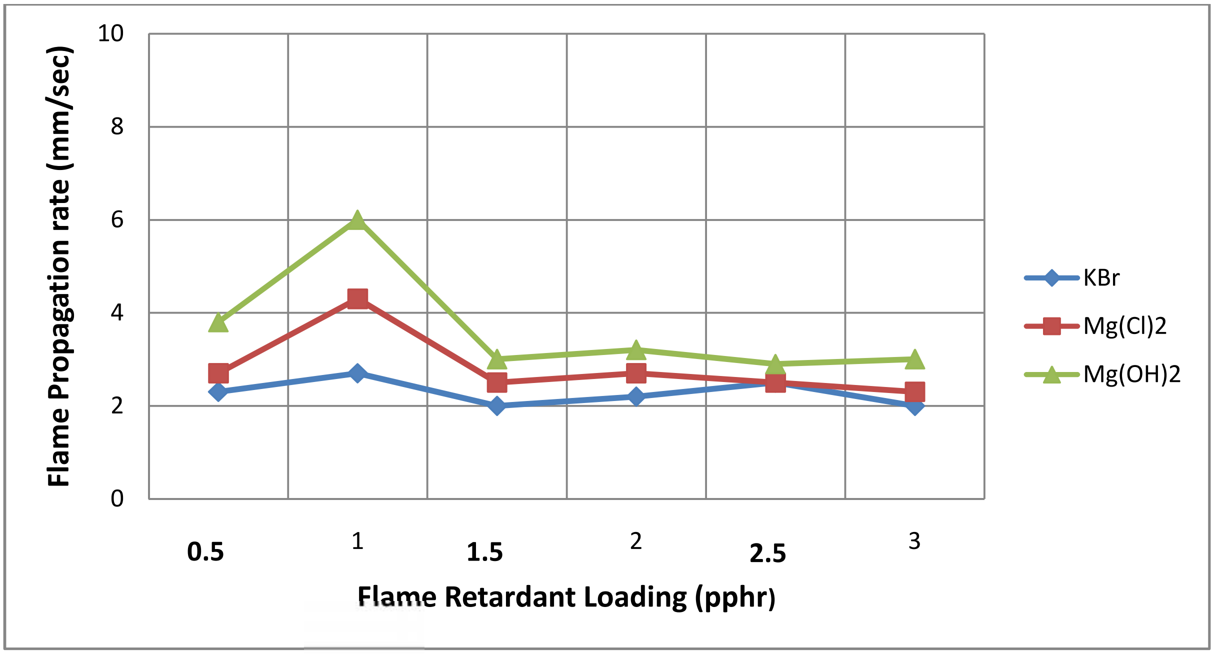


Fig. 4.12: Graph of Flame Propagation rate versus Flame Retardant loading for DNS at mesh size of $150\mu m$.

Table 4.13 Shows the Ignition Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	19	22	28
24	1.0	23	28	34
36	1.5	34	37	40
48	2.0	45	49	54
60	2.8	56	60	63
72	3.0	58	65	72

Table 4.14 Shows the Auto-acceleration Time Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	14	18	24
24	1.0	20	24	30
36	1.5	28	32	37
48	2.0	37	41	48
60	2.5	46	50	56
72	3.0	54	58	64

Table 4.15 Shows the Flame Propagation Rate Tests Results for CB at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	0.5	1.6	1.4	1.1
0.8	1.0	2.6	1.9	1.5
0.6	1.5	3.0	1.9	2.0
0.4	2.0	2.4	1.5	1.9
0.2	2.5	2.6	2.4	2.1
0.1	3.0	2.0	2.3	1.8

Table 4.16 Shows the Ignition Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	16	18	23
24	1.0	20	23	29
36	1.5	26	31	37
48	2.0	33	38	45
60	2.8	41	47	53
72	3.0	50	58	67

Table 4.17 Shows the Auto-acceleration Time Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	0.5	12	13	20
24	1.0	17	19	24
36	1.5	23	27	33
48	2.0	32	36	41
60	2.5	41	44	50
72	3.0	46	55	62

Table 4.18 Shows the Flame Propagation Rate Tests Results for DNS at mesh size of $150\mu m$.

Time (Sec)	MAPI (pphr)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	0.5	1.9	1.7	1.3
0.8	1.0	2.5	2.3	1.5
0.6	1.5	3.5	3.0	2.5
0.4	2.0	4.0	3.3	2.7
0.2	2.5	3.8	2.3	2.0
0.1	3.0	3.6	1.8	1.5

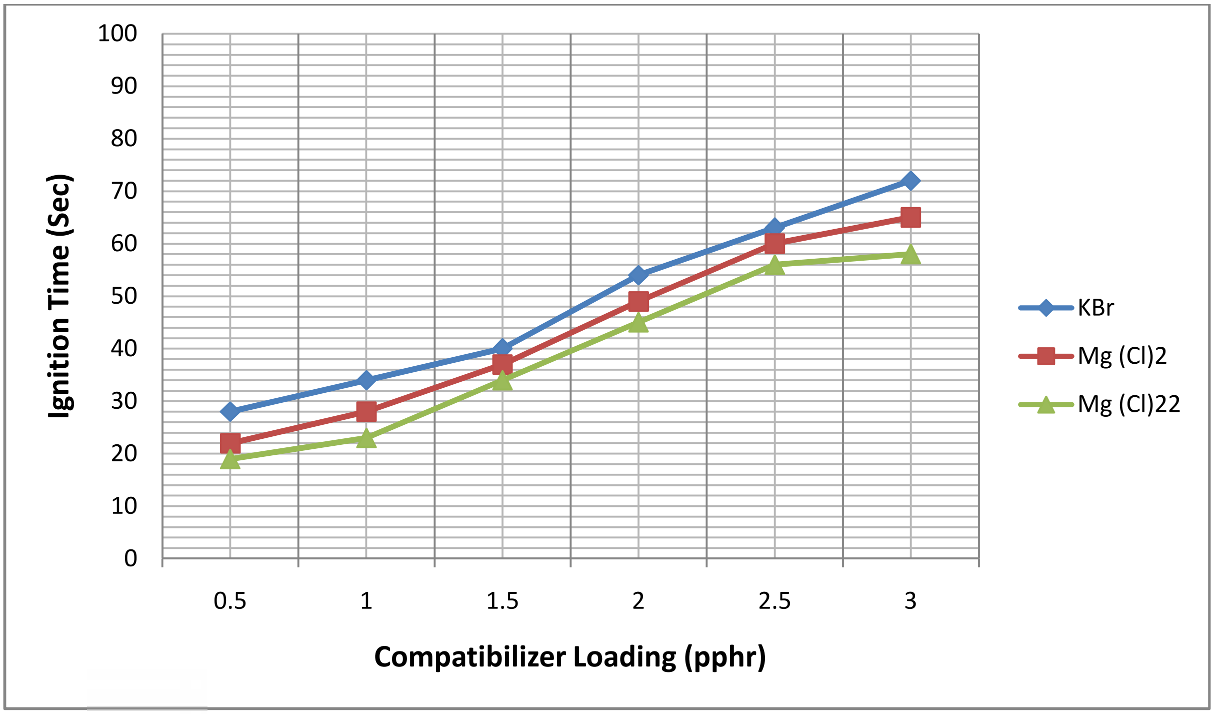


*Fig. 4.13: Graph of ignition time versus compatibilizer loading for CB*at mesh size of $150\mu m$.

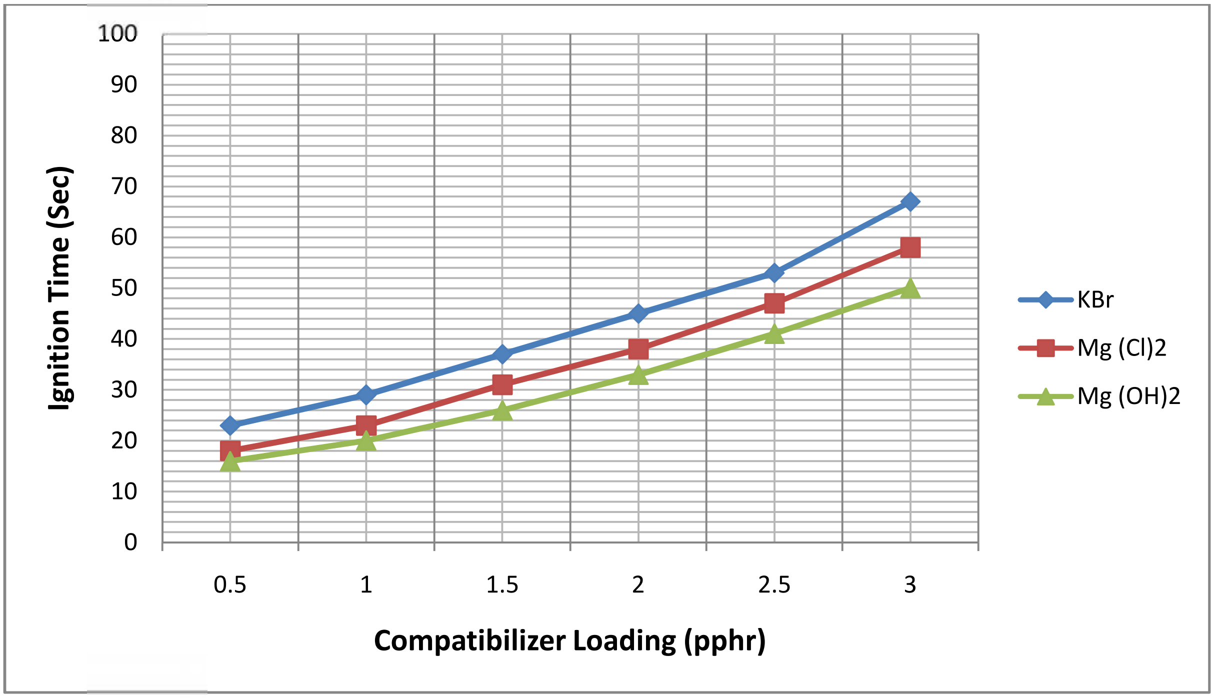


*Fig. 4.14: Graph of ignition time versus compatibilizer loading for DNS*at mesh size of $150\mu m$.

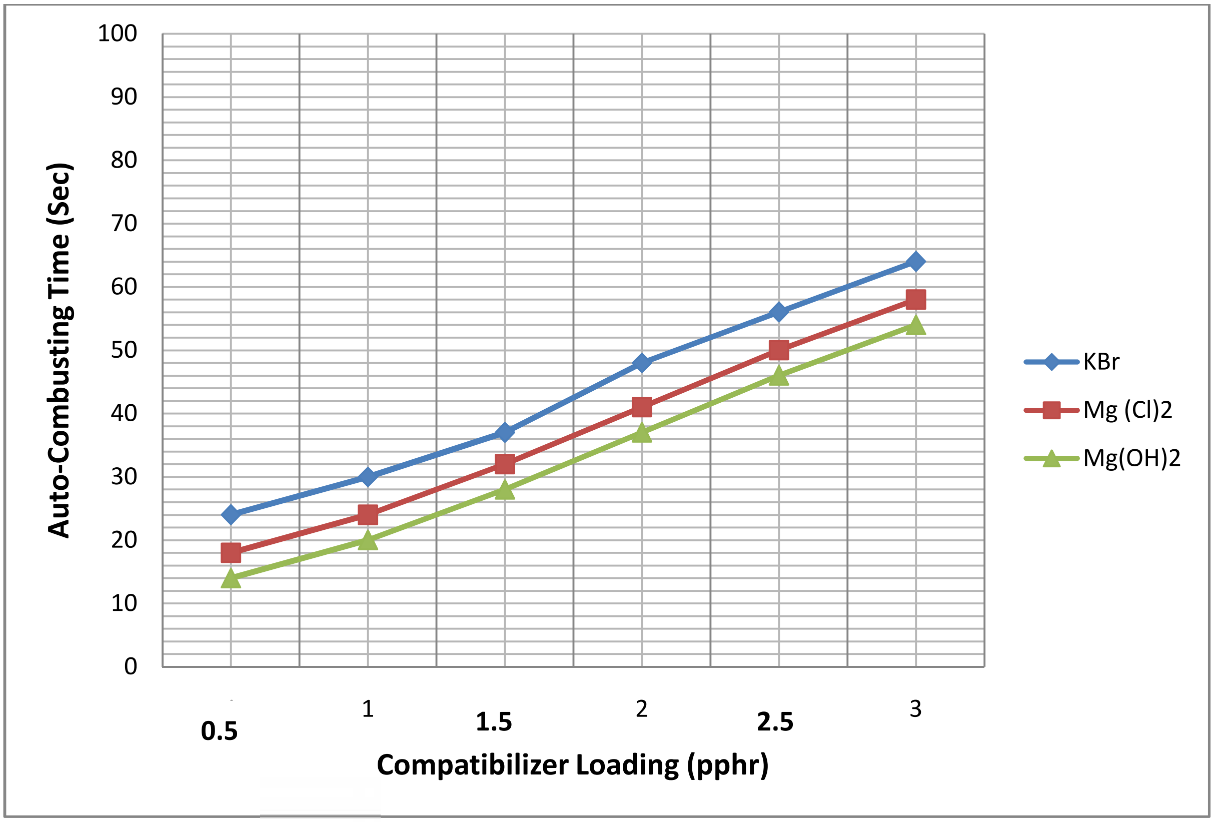


*Fig. 4.15: Graph of auto-combusting time versus compatibilizer loading for CB*at mesh size of $150\mu m$.

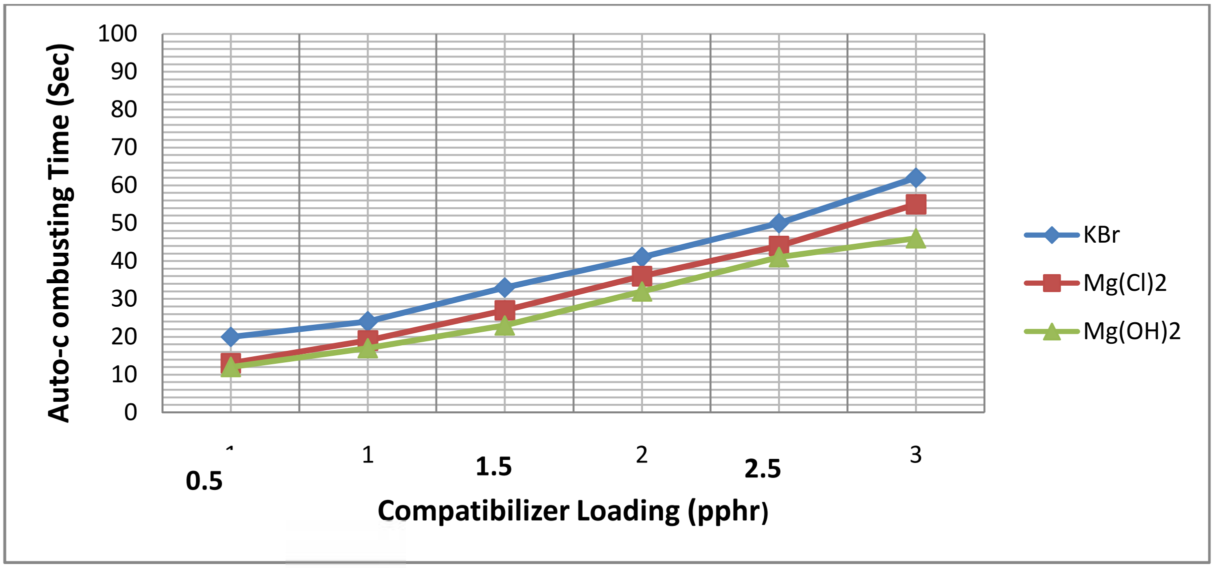


*Fig. 4.16: Graph of auto-combusting time versus compatibilizer loading for DNS*at mesh size of $150\mu m$.

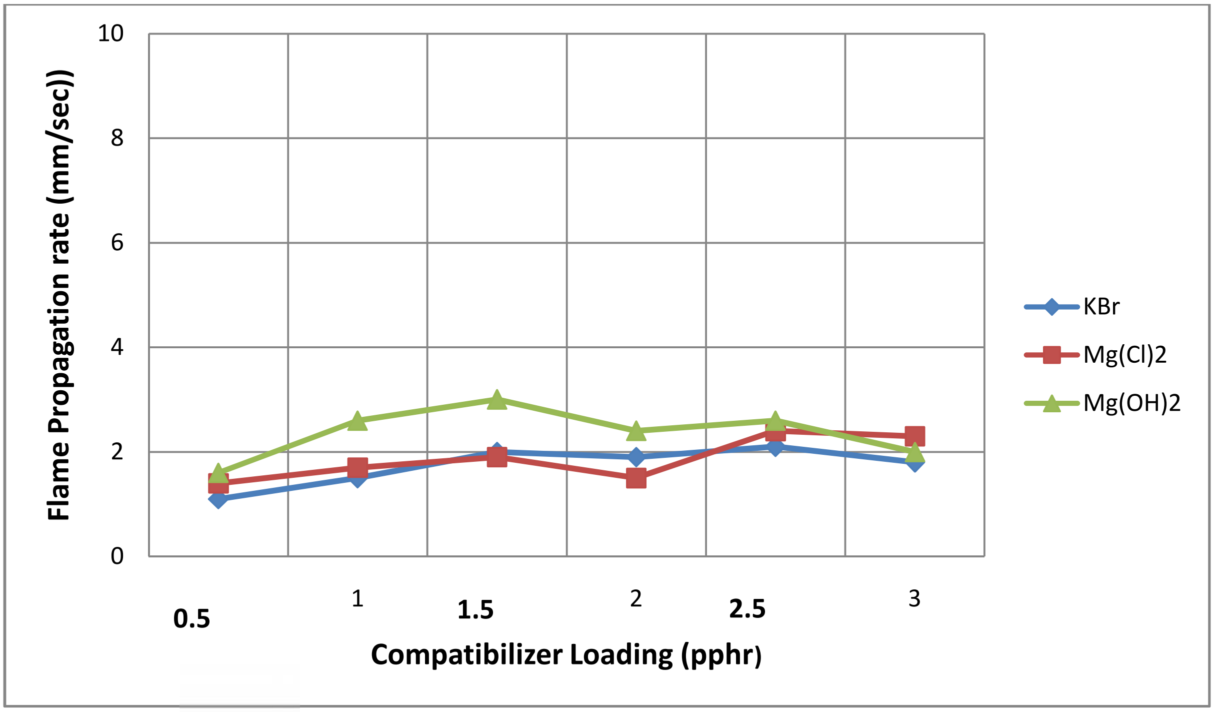


*Fig. 4.17: Graph of flame propagation rate versus compatibilizer loading for CB*at mesh size of $150\mu m$.

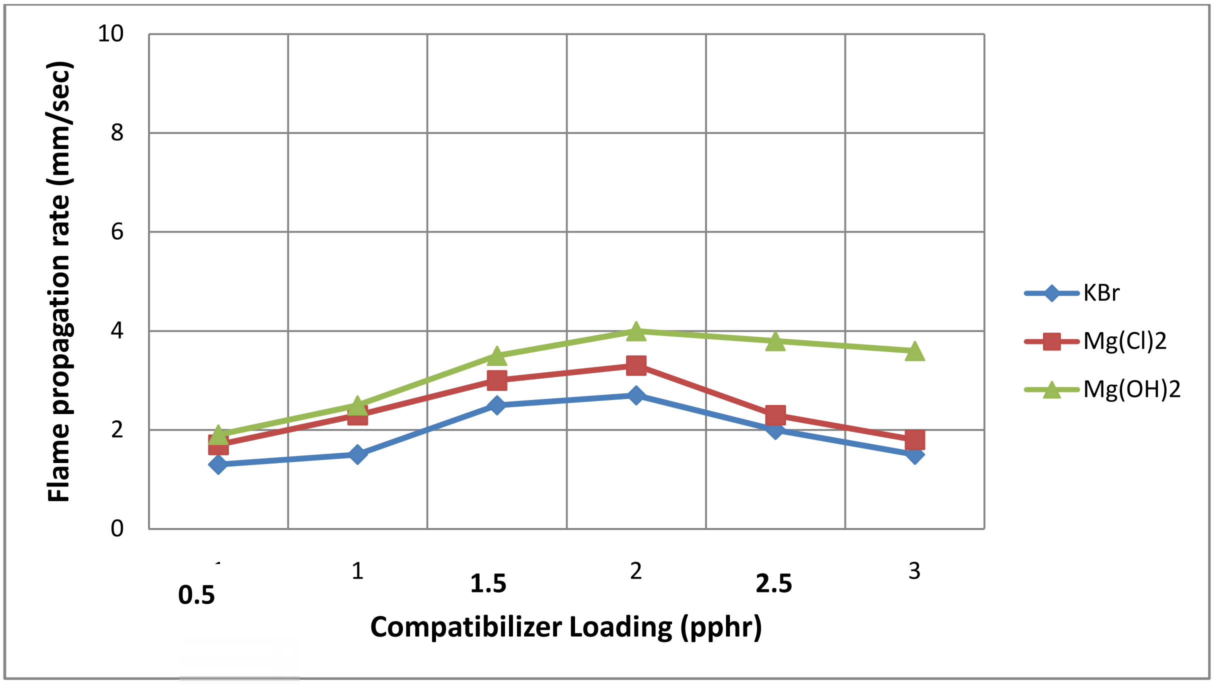


*Fig. 4.18: Graph of flame propagation rate versus compatibilizer loading for DNS*at mesh size of $150\mu m$.

Table 4.19 Shows the Ignition Time Tests Results for various mesh size ofCB ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	100	22	26	31
24	150	25	35	38
36	200	36	41	45
48	250	47	54	56
60	300	58	63	68
72	350	63	68	75

Table 4.20 Shows the Auto-acceleration Time Tests Results for various mesh size ofCB ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
12	100	20	24	29
24	150	23	33	36
36	200	34	39	43
48	250	45	52	54
60	300	56	61	66
72	350	61	66	73

Table 4.21 Shows the Flame Propagation Rate Tests Results for various mesh size ofCB ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	Mg $(OH)_2$	Mg $(Cl)_2$	KBr
1.0	100	1.4	1.2	0.9
0.8	150	1.5	1.3	1.0
0.6	200	2.6	1.8	1.7
0.4	250	2.8	2.3	2.1
0.2	300	3.0	2.6	2.4
0.1	350	3.3	3.0	2.6

Table 4.22 Shows the Ignition Time Tests Results for various mesh size of DNS ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	$Mg(OH)_2$	$Mg(Cl)_2$	KBr
12	100	18	22	27
24	150	21	31	34
36	200	32	37	44
48	250	43	50	52
60	300	54	59	64
72	350	59	64	71

Table 4.23 Shows the Auto-acceleration Time Tests Results for various mesh size of DNS ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	$Mg(OH)_2$	$Mg(Cl)_2$	KBr
12	100	17	20	25
24	150	20	29	32
36	200	30	35	42
48	250	41	48	50
60	300	52	57	62
72	350	57	62	69

Table 4.24 Shows the Flame Propagation Rate Tests Results for various mesh size of DNS ($\mathbf{100 - 350\mu m}$).

Time (Sec)	Particle size (μm)	$Mg(OH)_2$	$Mg(Cl)_2$	KBr
1.0	100	1.7	1.4	1.1
0.8	150	1.8	1.5	1.2
0.6	200	1.9	2.1	1.9
0.4	250	2.0	2.6	2.1
0.2	300	2.9	2.8	2.3
0.1	350	3.0	3.3	2.5

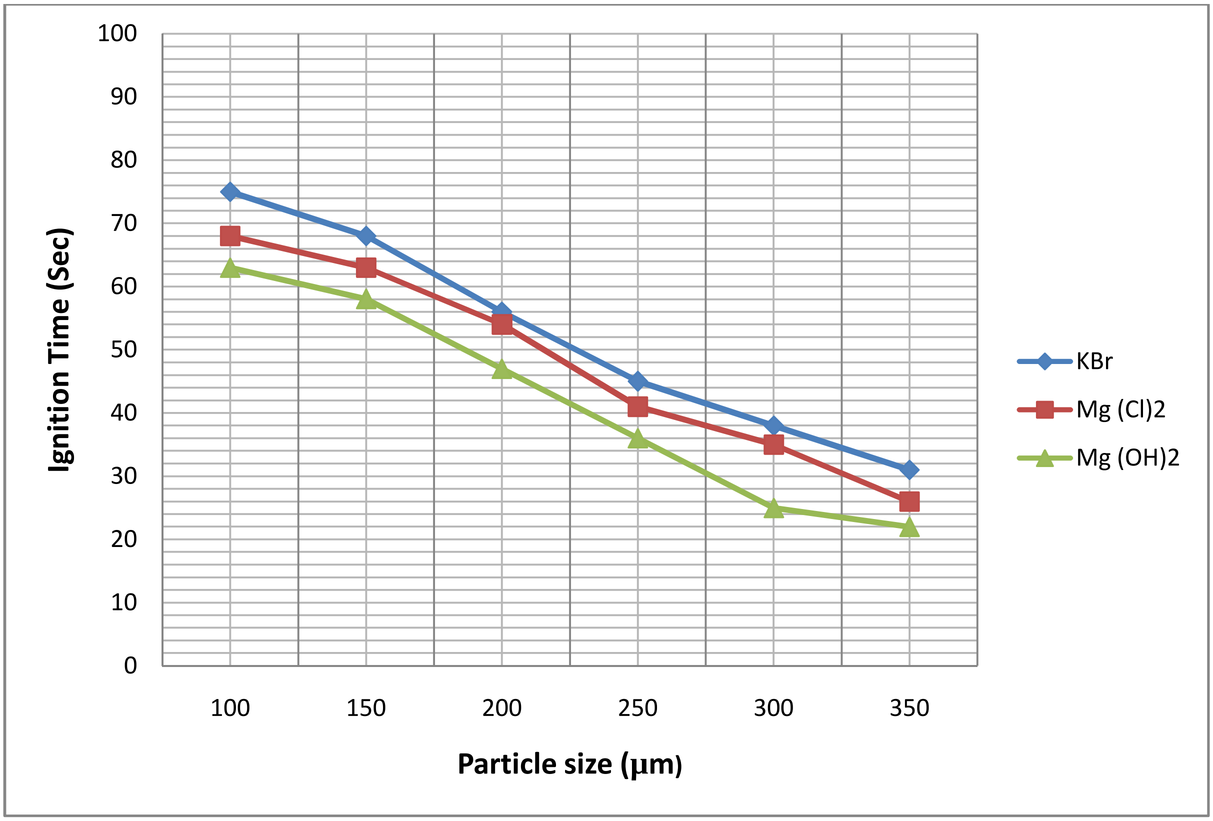


Fig. 4.19: Graph of ignition time versus CB particle size

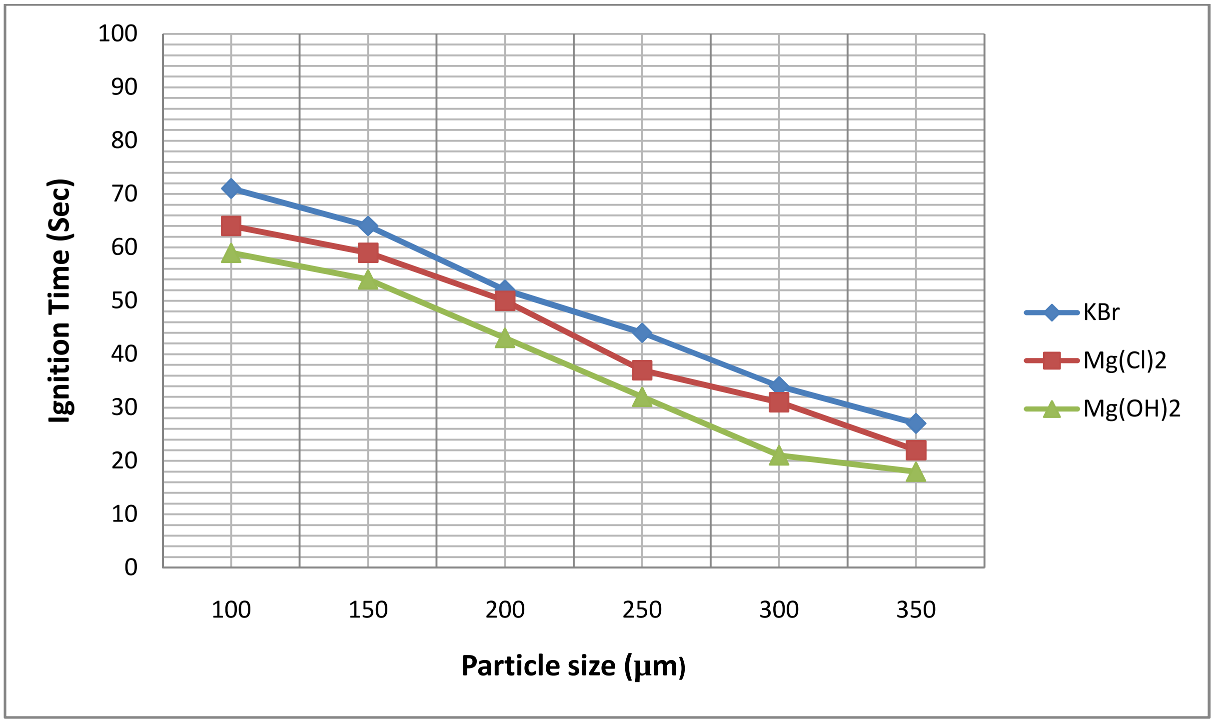


Fig. 4.20: Graph of ignition time versus DNS particle size

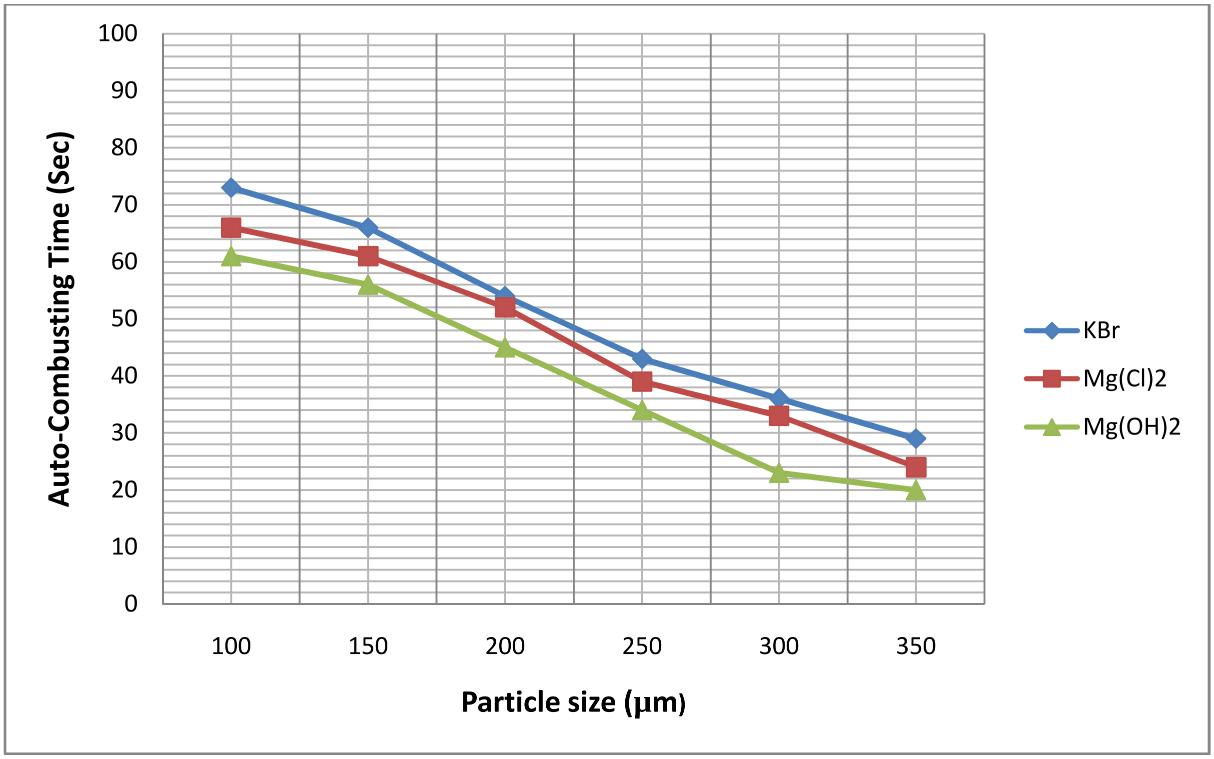


Fig. 4.21: Graph of Auto-combusting time versus CB particle size µm

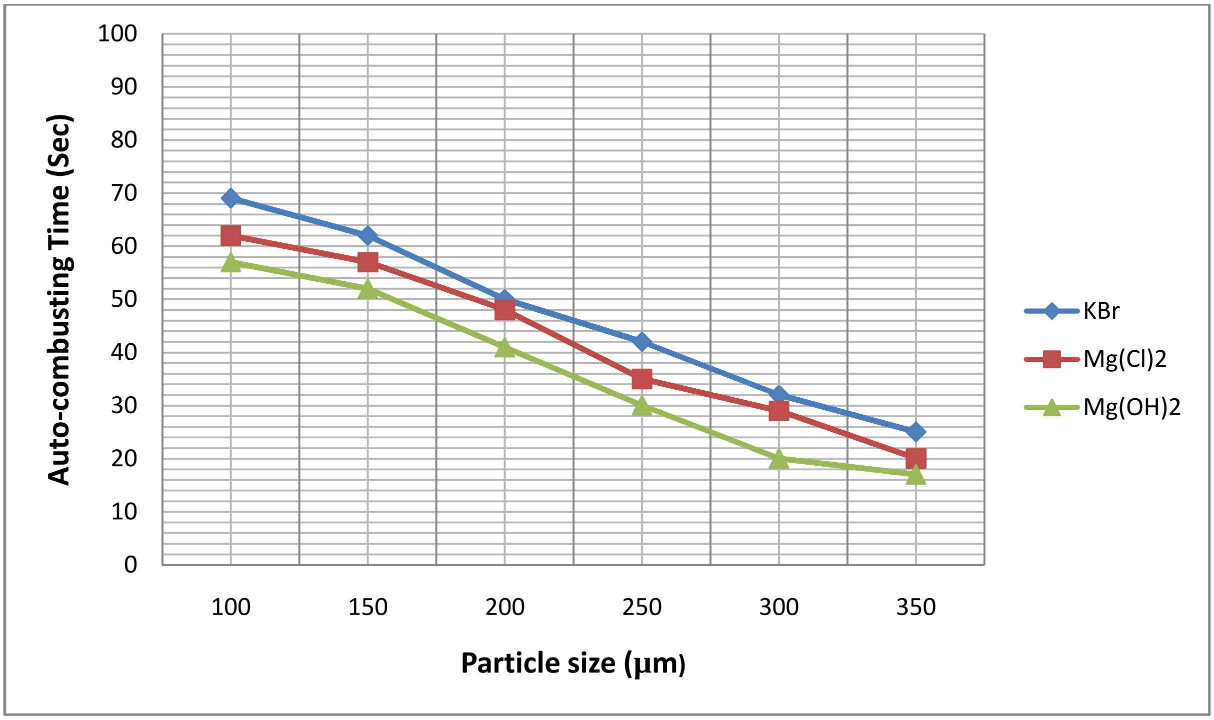


Fig. 4.22: Graph of auto-combustion time versus DNS particle size

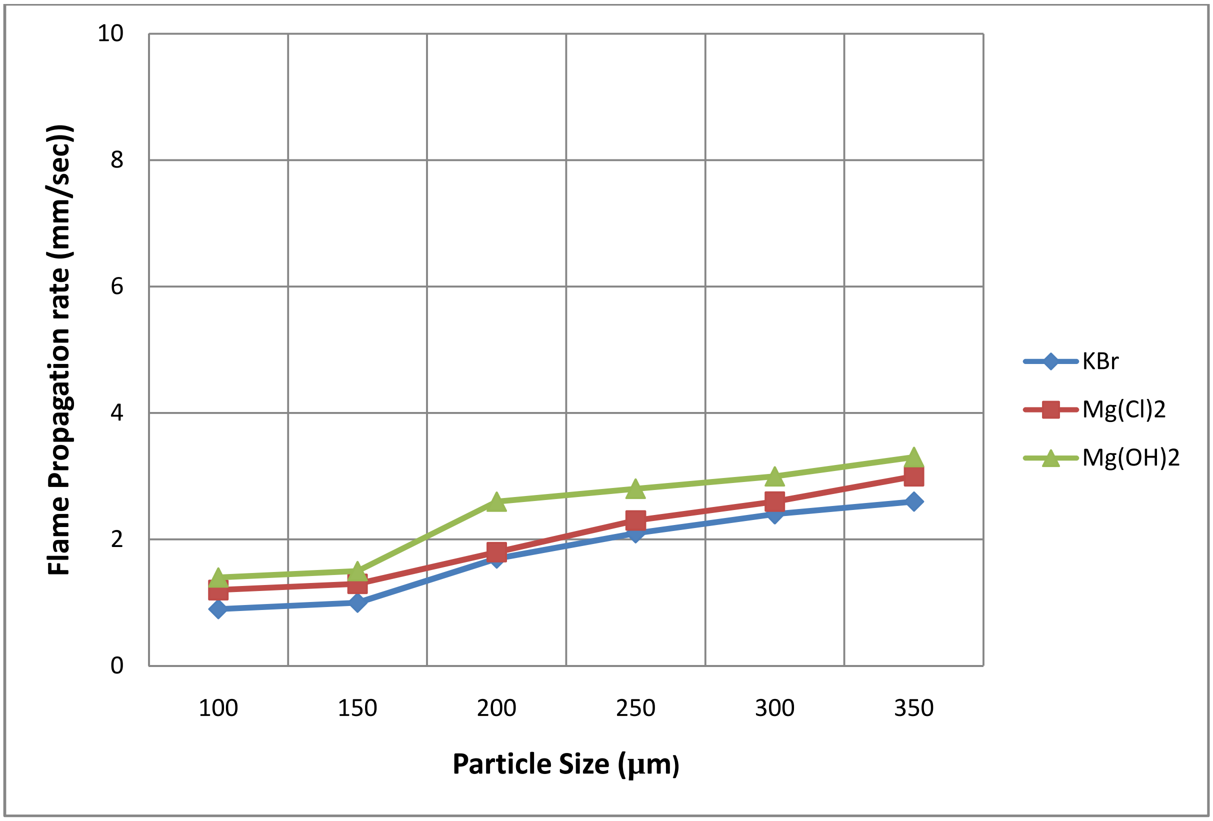


Fig. 4.23: Graph of Flame Propagation rate versus CB particle size

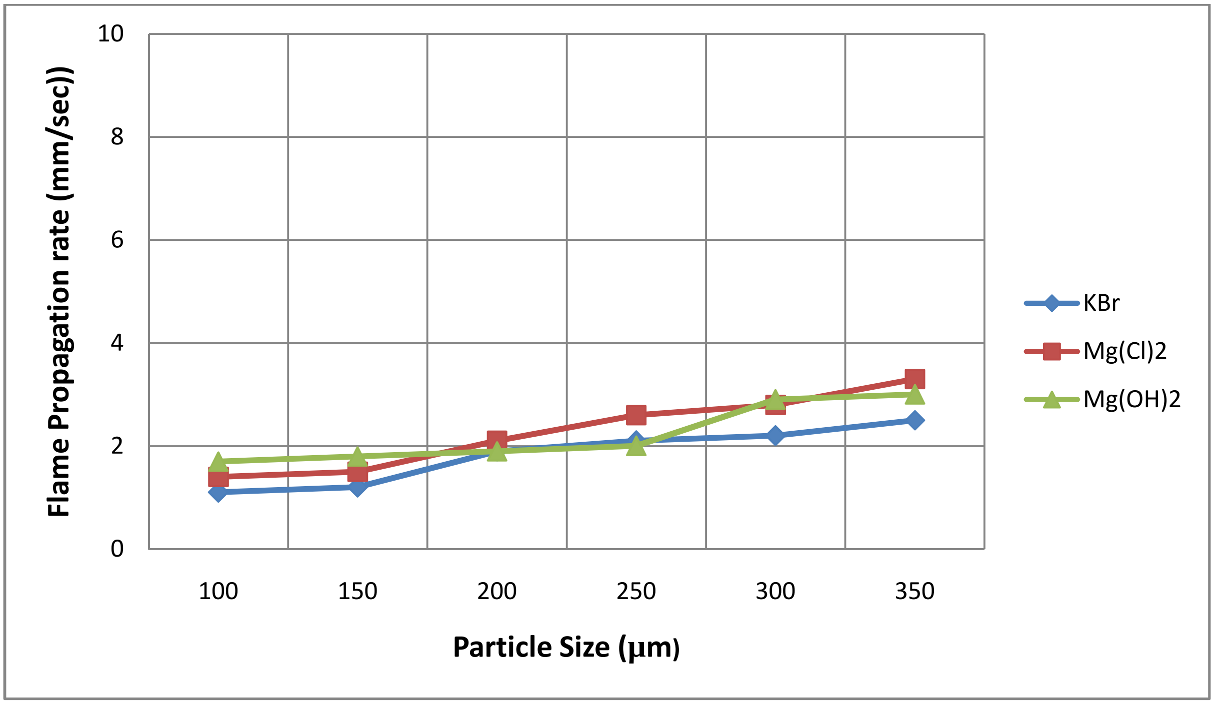


Fig. 4.24: Graph of Flame Propagation rate versus DNS particle size

Figure 4.25 illustrates the possible reactions that should take place at the interphase of these blends during the melt processing.

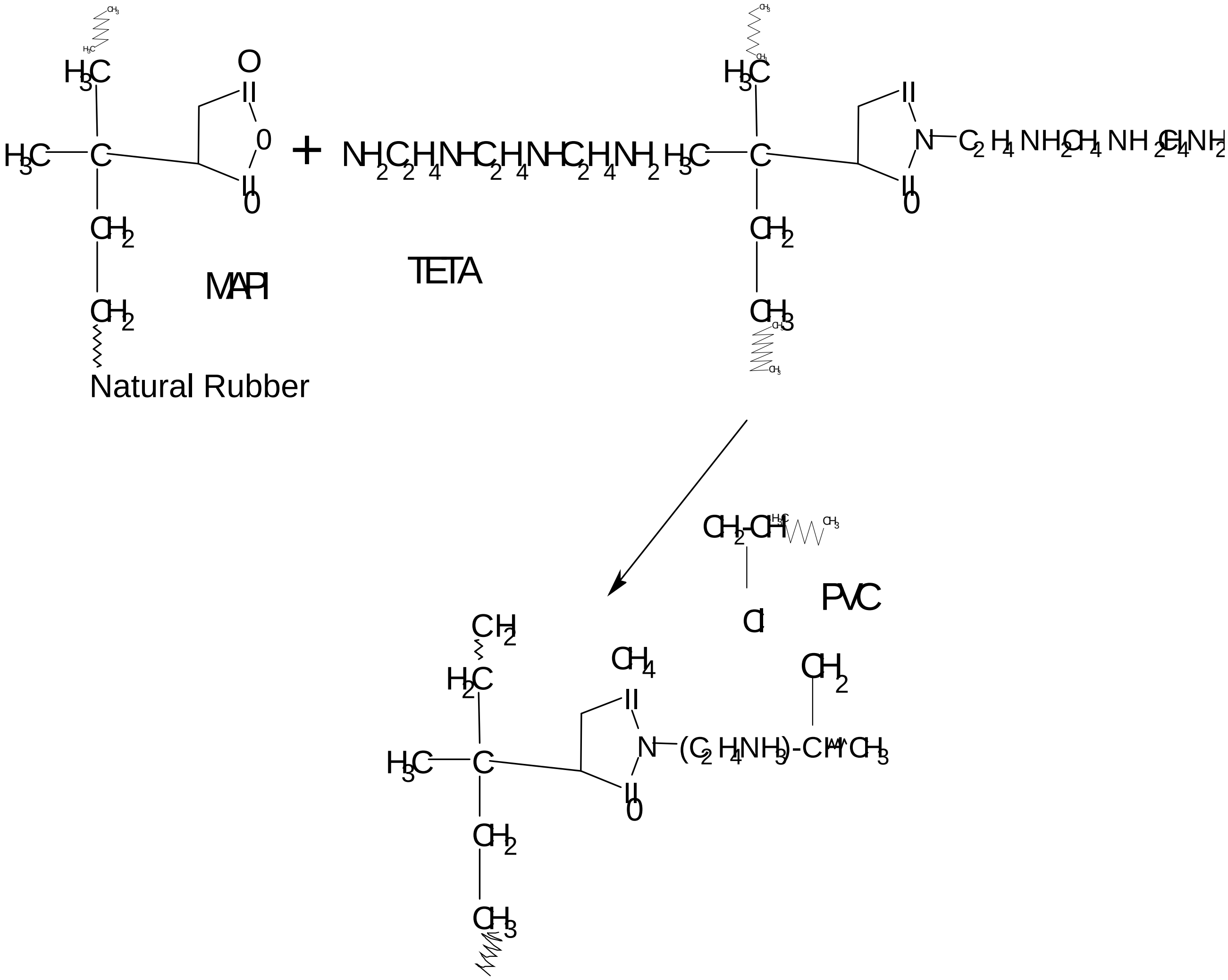


Fig. 4.25: Possible Reactions that Occur at the Interphase of the Compatibilized NR/PVC Blends

4.2 Discussion

From figures 4.1 and 4.2, the ignition times of the substrates or test pieces increased with increasing filler content for both CB and DNS filled composites.For NR/PVC/CB, the ignition time increased more than that of NR/PVC/DNS, at lower filler loading (5 and 10pphr), both composites showed low ignition times as the filler loading increased (20 and 30pphr), the ignition times became longer with NR/PVC/CB having the best flame resistance properties of over 500%, 300%, and 200% for KBr, $Mg(Cl_2)$ and $Mg(OH)_2$ respectively, compared to that of NR/PVC/DNS which was 260%, 200% and 150% for KBr, $Mg(Cl_2)$ and $Mg(OH)_2$ respectively. Increasing filler loading makes thematerial more difficult to burn because of dense packing of the molecularstructure and hence ignition time increases with increasing filler loading.

In figures 4.3 and 4.4, the results of the auto-combusting times also show increase with increasing filler loading for both composites, though lower than ignition times due to the fact that the temperature of substrates increase after initial ignition because of increase in internal energy or heat content. Hence, the material easily burns, the auto/combusting times generally increase with increasing filler content with NR/PVC/CB substrates having higher values than NR/PVC/DNS. Values forNR/PVC/CB were 380%, 280% and 130% for KBr, $Mg(Cl_2)$ *and*$Mg(OH)_2$ *at 30 pphr while NR/PVC/DNS substrates gave 180%, 120% and 100% for KBr,* $Mg(Cl_2)$ *and* $Mg(OH)_2$ *at 30 pphr filler loading.*

The flame propagation rate (FPR) shown in figures 4.5 and 4.6 corroborates the ignition and auto-combusting time of the substrates flame resistance. The result shows that the rate of flame propagation greatly decreased with increasing filler loading. The spread of flame was highly reduced with NR/PVC/CB blends havingthe values 280%, compared to 150% for that of NR/PVC/DNS blends at 25 pphr. (Obidiegwu 2012, Laoutid et al 2015, Majid et al., 2015).

The results of the ignition times are presented in figures 4.7 and 4.8. They show that in both NR/PVC/CB and NR/PVC/DNS samples, the ignition times increased markedly with increases in flame retardant loading. Ignition times for NR/PVC/CB substrates where higher than those of NR/PVC/DNS. KBr had anincrease of about 400%, followed by $Mg(Cl_2)$ with 250% and least Mg $(OH)_2$with about l50% at 3.0 pphr. On the other hand in comparison with NR/PVC/DNS,KBr had an increase of 250%, $Mg(Cl)_2$ about 220% and $Mg(OH)_2$ about 150%. This shows that NR/PVC/CB has better flame resistant properties than NR/PVC/DNS composites. (Laoutid et al 2015).

The auto-combusting times are presented in figures 4.9 and 4.10 of about 220% for KBr, 170% for $Mg(Cl)_2$ and 120% for Mg(OH) in the NR/PVC/CB composites at 3pphr while, for NR/PVC/DNS composites it was an increase of about 180% for KBr, 140% for $Mg(Cl)_2$ and 100% $Mg(OH)_2$NR/PVC/CB thus shows better resistance to burning than NR/PVC/DNS. (Ferguson, R.S 1970).

The flame propagation rate (FPR) shown in figures 4.11 and 4.12 below, further shows the flame retardant properties of the flame retardants used. The results showed that the flame propagation rate decreased with increasing flame retardant loading thus indicating that the rate of spread of flame reduced with increasing flame retardant content. NR/PVC/CB blends show a reduction in flame propagation rate of about 200%, while NR/PVC/DNS show a reduction of about 120%.

From the results presented in figures 4.13 and 4.14, the ignition times of both NR/PVC/CB and NR/PVC/DNS increased with increasing compatibilizer (MAPI) loading. At lowloadings of 0.5 and 1.5 pphr, the substrates showed little increases in ignition times,however at higher loadings of MAPI, (i.e. 2.5 and 3.0 pphr) the increases were as high as300%, 200% and 150% at 3 pphr for KBr, Mg $(Cl)_2$ and $Mg(OH)_2$ respectively in theNR/PVC/CB composite, those for KR/PVC/DNS composite though were lower at about 260%, 150% and 120% at 3pphr for KBr, $Mg(Cl)_2$ and $Mg(OH)_2$ respectively. The increase in ignition times observed has to do with better mixing and molecular interaction of the blends at higher compatibilizer levels of 3 pphr.(Onyeagoro et al., 2013, Ismail and Harunezan 2001, Kiaw 2000).

The results of the auto-combusting times are shown in figure 4.15 and 4.16. The time before the sample becomes auto-combusting increase with increasing MAPI levels for all the samples, though NR/PVC/CB showed higher increases, and hence better fire resistance, for NR/PVC/CB, KBr had about 500%, $Mg(Cl)_2$ about 400% and $Mg(OH)_2$, about 250% at 3pphr. In comparison with NR/PVC/DNS composite, KBr had about 400%, $Mg(Cl)_2$ about 300 and $Mg(OH)_2$ about 200% increase at 3pphr level of MAPI. (Arrayapraneel and Rempel2007, Roe 1993).

The flame retardance rate reduction lends credence to the fire resistance properties of the composites as influenced by the use of MAPI as compatibilizer. NR/PVC/CB and NR/PVC/DNS both showed reduction of about 300% and 150% respectively in the flame retardancy rate at 3pphr compatibilizer loading for both NR/PVC/CB and NR/PVC/DNS blends.

The results obtained are shown in figures 4.19 and 4.20. The ignition times oftest samples increased with decreasing filler particle size. This is because thesmaller particle sizes have a structure with better aggregate molecular parking, thereby reducing the volume of voids in the bulk material. Since the volume of voidsaffects the space available for mixing within the composite, the smaller sizes,therefore increases the physical, mechanical, flame retardant properties, theenergy at rupture and the resilient energy (Akpa 2008). Hence, the ignition time of NR/PVC/CB and NR/PVC/DNS all increased with reduction in filler particle size. For NR/PVC/CB, KBr increased 300%, $Mg(Cl)_2$ 200% and $Mg(OH)_2$, 100% while NR/PVC/DNS, showed lower flame resistance in KBr showing an increase of 200% $Mg(OH)_2$ 100% and $Mg(OH)_2$ 80% respectively all at 150µm particle size.

Also, the auto-combusting times increased because of the better reinforcing by smaller particle sizes. NR/PVC/CB composite had the highest increaseieKBr 250%,$Mg(Cl)_{2,}$ 200% and $Mg(OH)_2$, 150% at 150µ The increase for NR/PVC/DNSwas lower than that of NR/PVC/CB at KBr, 200% $Mg(Cl)_2$ 150% and $Mg(OH)_2$ about 100% at 150µ.

The results of the flame propagation rate for NR/PVC/CB and NR/PVC/DNSare as shown in figures 4.24 and 4.25. There was a reduction *in* the flame propagation rate of about 150% for blends of NR/PVC/CB *at*150µ and of about 70% for blends of NR/PVC/DNS at 150µ.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The following conclusions were drawn from this study:

Increasing the DNS and CB filler contents in the composites increased the ignition time, auto-combustion time and reduces flame propagation rate. Reducing the particle size of the filler showed a corresponding increase in ignition time, auto-combustion and reduces the flame propagation rate of the composites. This is due to the fact that larger particle size leads to less close-knit filler-matrix interaction and bonding. As the flame retardant loadings increased, the flame retardancy rate of the composites increased for all the three flame retardants studied. Although, the composite samples filled with DNS showed lower flame retardance temperatures than those filled with CB, DNS filled composites can be used for high volume products, where high engineering specifications are not required as in shoe soles, and floor coverings. Increasing the compatibilizer levels also increased the flame retardancy rate of the composites for both DNS and CB filled composite samples studied. This is due to better polymer filler interaction due to more molecular mixing facilitated by the compatibilizer and have less voids/volume free of occupation. DNS is a biodegradable agricultural by product and this confers biodegradability on the NR/PVC/DNS bio-composites. This helps to reduce the effect of solid non-bio-degradable waste on the environment. NR/PVC/DNS composite also helps to ameliorate the effects of waste on climate change by a reduction of burning of such wastes. NR/PVC/DNS biocomposites also reduces the cost of rubber products usually and makes them cheaply more affordable than NR/PVC/CB composites that are more expensive due to the high cost of CB. CB is a petrochemical filler, which is not renewable and also pollutes the environment. It is also very costly. Of the three flame retardants used, KBr, $Mg(Cl)_2$ and $Mg(OH)_2$, KBr and $Mg(Cl)_2$ are poisonous because of the presence of bromine (Br) and chlorine (Cl). Thus, $Mg(OH)_2$ is therefore the recommended flame retardant, because it is non-toxic, abundant and cheap.

5.2 Recommendations

More research should be done on the use of biological waste products such as dikanut shell, groundnut shells, husks, cassava peelings, yam peelings, coconut shells and a host of other agricultural byproducts as fillers for the production of industrial goods where high specifications are not necessary and the possibility of exporting such by-products overseas to other countries for the earning of hard currency.

5.3 Contribution to knowledge

i. The study showed that dikanut shell powder significantly improved the flammability properties of the blend.
ii. The flame propagation rates of the blends greatly reduced with increased dikanut shell(DNS) and carbon black (CB) filler loading.
iii. Composites with carbon black showed superior flame resistant qualities than dikanut based blends.

iv. NR/PVC/DNS composites can be used in commodities such as shoe soles, foot mats, car exhaust hangers etc because of its good abrasion resistance, though a filler level of 10pphr.

v. The use of low cost dikanut shell powder (DNS) to replace the expensive non-renewable conventional fillers like carbon black and culverin carbonate in the polymer industry will greatly reduce the cost of rubber goods. While DNS costs about ₦2,000 for a 25kg bag, CB costs about ₦10,000 for the same 25kg bag.

vi. DNS powder is biodegradable and hence environmentally friendly and renewable; this will encourage agriculture and provide more food and jobs.

vii. Mg(OH) is preferable flame retardant than either of KBr and $Mg(CL)_2$ because both are toxic and inimical to human health and also notenvironmental friendly.

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