

**PHYSICO-MECHANICAL PROPERTIES OF
COMPATIBILIZED NATURAL RUBBER/RECYCLED POLY (ETHYLENETEREPHT
HALATE)/DIKANUT SHELL POWDER BIO-COMPOSITES**

By

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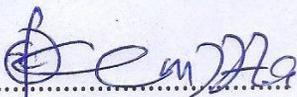
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CERTIFICATION

This is to certify that this research work entitled" **PHYSICO-MECHANICAL PROPERTIES OF COMPATIBILIZED NATURAL RUBBER/RECYCLED POLY(ETHYLENE TEREPHTHALATE)/DIKANUT SHELL POWDER BIO-COMPOSITES**" was carried out by **UZOR, CAROLYN CHINOMSO (20134873528)** in partial fulfillment for the award of the Degree of M.Sc. in Polymer Science and Engineering, Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, Imo State. Under my supervision.



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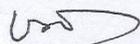
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DEDICATION

I dedicate this research work to my mum, Mrs. Anthonia Uzor, who through her struggles ensured that my M.Sc. programme was a reality and a success.

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LIST OF ABBREVIATION, SYMBOLS AND NOTATIONS

NR	Natural Rubber
PET	Poly (ethylene terephthalate)
DNS	Dikanut Shell
SG	Styrene-Co-glycidyl methacrylate
PA	Polyamide
GMA	Glycidyl Methacrylate
MBS	Methyl methacrylate-butadiene styrene
PEG	Polyethylene Glycol
AFM	Atomic Force micrograph
PTMSP	Poly(1 trimethylsilyl-1-propyne)
EVA	Poly(ethyl-1-Vinyl acetate)
DCP	Dicumyl Peroxide
HMDA	Hexamethylene diamine
PB	Polymer Blend
VARTM	Vacuum Assisted Resin Transfer Moulding
VARIM	Vacuum Assisted Resin Infusion Moulding
SCRIM	Seemann Composites Resin Infusion Moulding Process
VBRTM	Vacuum Bag Resin Transfer Moulding
VARI	Vacuum Assisted Resin Infusion Process
ISAF	Intermediate Super Abrasion Furnance

HSR	High Styrene Rubber
LDW	Lime Stone dust waste
PCC	Precipitated Calcium Carbonate
NPCC	Nano Precipitated Calcium Carbonate
Zn- SNR	Zinc Salt of Natural Rubber
ESBS	Styrene - (epoxidized butadiene)-Styrene
PE-g-MA	Maleic Anhydride grafted Polyethylene
GO	Graphene Oxide
APP	Atatic Polypropylene
IPP	Isotatic Polypropylene
ABS	Acrylonitrile Butadiene Styrene
MAPP	Maleic Anhydride -g- Polyethylene
LLDPE	Linear Low Density Polyethylene
HDPE	High Density Polyethylene
ENR	Epoxidized Natural Rubber
T _g	Glass Transition Temperature
EPDM	Ethylene Propylene diene Monomer
CSM	Chlorosulfonated Polyethylene
SEM	Scanning Electron Microscope
PC	Polycarbonate
SBR	Styrene Butadiene Rubber

MAPI	Maleic Anhydride-g-Polyisoprene
DSC	Differential Scanning Calorimetry
PPO	Poly (phenyl oxide)
SAN	Styrene Acrylonitrile
ZnO	Zinc Oxide
PP	Polypropylene
PS	Polystyrene
IPN	Interpenetrating polymeric Network
FTIR	Fourier Transform Infra- red
TMTD	Tetra Methyl Thiuram disulphide
MBT	Mercapto Benzoyl thiazol
T	Temperature
ΔH_{mix}	Enthalpy of mixing
ΔS_{mix}	Enthropy of mixing
ΔG_{mix}	Gibb free energy of mixing
ULM	Ultrasonically assisted latex milk

ABSTRACT

Blends of natural rubber(NR) and recycled poly(ethylene terephthalate) (PET) filled with dikanut shell powder (DNS), were prepared by reactive compatibilization in a two roll mill, using maleic anhydride grafted polyisoprene (MAPI) and hexamethylene diamine (HMDA) as dual compatibilizer. Dikanut shell powder was prepared at a particle size of 150 μ m. A constant blend composition of NR/PET: 70/30 was used with varying filler and compatibilizer ratios of DNS/MAPI/HMDA: 0/0/0, 10/0/0, 15/0/0, 20/0/0, 0/2/0.5, 10/2/0.5, 15/2/0.5, 20/2/0.5, 10/2/0, 10/2/0.3, 10/2/0.5, 10/2/0.7. The effects of filler loading and compatibilizer content on physico-mechanical properties such as tensile strength, modulus, percentage elongation and compression set of NR/PET/DNS composite were investigated. The results show that, tensile strength, modulus, and compression set values increased with increasing filler loading for both compatibilized and uncompatibilized composites. These properties also showed increasing trend with increasing compatibilizer content. However, for compression set, a decreasing trend was observed with increasing compatibilizer content. Percentage elongation showed a decreasing trend with increasing filler loading for both compatibilized and uncompatibilized composites. It also exhibited a decreasing trend with increasing compatibilizer content.

Keywords: *Natural* rubber, recycled poly(ethylene terephthalate), dikanut shell powder, compatibilization and bio-composites.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

The growing environmental awareness throughout the world has given impetus to the design of environmental- friendly materials. As a result, natural fibres have attracted more and more interest as reinforcements for both thermoplastic and thermosetting polymer composites. Bio-composites derived from natural fibres and traditional thermoplastics or thermosetts can maintain a balance between economy and environment allowing them to be considered for applications in the fields of automotive, aerospace, building, furniture and packaging industries (Deepa *et al.*, 2011). These materials provide high durability, design flexibility and light weight which make them attractive materials in these applications. The desired property improvements obtained through polymer blending include impact strength, heat distortion temperature, flame retardancy, permeability characteristics, processability and relatively low cost (Findiket *al.*,2004).

Since, no one polymer has all the properties required in many application areas, polymers are commonly blended to improve their performance and processing characteristics (Tillekeratine and Scott, 2006).

Natural rubber (NR) vulcanizates display high mechanical strength, outstanding resilience, excellent elasticity, abrasion resistance, low heat buildup and good dynamic properties. However, natural rubber is known to have poor wet grip properties and poor weather resistance because of reactive double bond in its structure. Recent investigations have reported that blending natural rubber with another polymer could improve oil, ozone and chemical resistance (Kwanruethai et al.,2008). Basically, the performance of rubber blends is largely governed by various factors such as the nature of the rubber (Stephen *et al.*, 2006, Sirqueiraet *al.*, 2003, Sirisinhaet *al.*, 2004). Blend compositions (Naskaret *al.*, 2001), phase morphology of rubber blends (Sirisinhaet *al.*, 2003) and interfacial crosslinking in rubber blends (Naskaret *al.*, 2004). For instance, improved oil and thermal aging resistance were observed with blends of NR and chlorinated polyethylene (CPE) (Sirisinhaet *al.*, 2004), blends of NR with carboxylated styrene butadiene rubber (XSB) (Stephen *et al.*, 2006) and EPDM (Sirqueiraet *al.*, 2003) were reported to have better aging and ozone resistance. Phase morphology was improved in blends of NR and nitrile rubber (NBR) which resulted in an increased oil resistant property of blends (Sirisinhaet *al.*, 2003). The oil resistance and mechanical properties of NR/XNBR (natural rubber/ carboxylated nitrile rubber) blends was found to be strongly dependent on blend ratio and the degree of interfacial crosslinking between NR and XNBR components.

Other reports on the mechanical properties of polymer blends include natural rubber/ vinyl alcohol blend (Sa-Ad Riyajan, 2012), natural rubber/ ethylene-vinyl acetate rubber blend (Koshy *et al.*, 1992, Koshy *et al.*, 1993), natural rubber/ linear low density polyethylene blend (Ahmad *et al.*, 2004). Particulate filler can increase the strength of an amorphous rubber more than 10-fold (Madani and Aly, 2010). Small particles possess large surface area for effective rubber-particle interaction and close particle-to-particle spacing in the rubber.

The growing trend in the use of lignocellulosic filler in the manufacture of polymer composite systems is due to their abundance, low density, high specific properties and non-abrasive nature. They are also non-toxic, renewable and biodegradable.

Dikanut shell powders are natural fillers and represent environmentally-friendly alternative to conventional reinforcing filler.

Dikanut shell (*IrvingiaGabonensis*), known locally as "ogbono", is found mostly in African countries such Nigeria, Senegal, Angola, Democratic Republic of Congo. Dikanut shell is rich in fat and protein. It is used as a thickening agent in foods, due to its high mucilage content. The shells are a by-product of the nut-processing and do not have any known domestic/industrial use. They are currently discarded as waste, which could be found in waste-bins and farm yards in most localities and big cities hence, causing environmental

pollution either through incineration, filling up water ways and or landfills. Utilizing dikanut shell as reinforcing filler offers an effective, innovative and alternative solution to indiscriminate dumping of agro-waste. The main disadvantage of using dikanut shell powder as reinforcing filler is the poor interaction between the dikanut shell powder particles and rubber matrix. This is due to the high hydrophobicity of the rubber matrix and polarity of lignocellulosic filler (dikanut shell powder).

Natural fibres have difficulties associated with surface interactions between hydrophilic fiber and hydrophobic thermoplastic, (Deepa *et al*, 2011). This results to difficulties in compounding these materials and poor mechanical properties.

Reports exist on the modification of the polar natural fiber surface by grafting with compatibilizing and coupling agents before the compounding step and the modification of the polymer matrix with a polar group. The compatibilizer provides adequate interaction between the phases.

The blending of natural rubber which is non polar with poly (ethylene terephthalate) (PET) which is polar gives phase separation due to differences in polarity. In this regard, maleic -anhydride- grafted-poly isoprene is considered to be a potential compatibilizer for the blend system. It is well known that in PET the carboxyl terminal group do

not react with anhydride readily, while the reaction between hydroxyl group of PET and dikanut shell powder (DNS), a cellulosic filler is insignificant without the presence of a catalyst (Onyeagoroet *al.*, 2013), that is, secondary interaction is expected. However, hexamethylene diamine is known to react with polyester terminal (carboxyl groups) to compatibilize effectively many polyester related blend. Hexamethylene diamine (HMDA) is capable of producing PET-co-HMDA-co-MAPI copolymer at the interface which is able to function as an effective compatibilizer.

PET is a low cost commodity polymer with excellent properties, such as solvent resistance and electrical insulation, hence, its wide applications in the packaging industry. However, low impact resistance particularly at low temperature is the major disadvantage of PET and this has limited its applications. The usual method to overcome this drawback is to add a second rubber phase to the PET matrix, so that the rubber particles act as effective stress dissipating agents (Onyeagoroet *al.*, 2014).

1.2 Problem Statement

In the vulcanization of rubber, carbon black is the main filler in use. However, because of the origin of carbon black from petroleum, carbon black causes pollution and is costly. It is also non-renewable.

Hence, investigations are now aimed at finding suitable reinforcing agents to replace carbon black in the compounding of rubber products.

Agricultural by-products in Nigeria are currently being discarded as waste and could be found littered around in the environment, with attendant environmental concerns. Agricultural by-products such as dikanut shell can be properly utilized in the industries, as reinforcement agents in rubber/ thermoplastic blends.

Natural rubber (NR) being highly abundant in nature around the world, has many applications such as tyres, condoms, shoe soles, cars etc. due to its excellent tensile, damping properties and elasticity properties. But NR has a very poor wet-grip properties and weather resistance. Dikanut shell powder is cellulosic and hydrophilic, its blend with NR which is polar, though bio-degradable, is expected to be phase separated due to difference in polarity and also NR and PET are immiscible and incompatible, due to difference in polarity. However, in order to obtain useful material that combines the solvent resistance of PET with excellent mechanical properties of natural rubber, a suitable compatibilizer/ coupling agent is utilized in the blend. Only secondary interaction is obtained when MAPI alone is used as compatibilizer in NR/PET/DNS bio-composites, hence insignificant property improvement is expected. The carboxyl terminal group of PET do not react with the anhydride of MAPI while the reaction between hydroxyl group of PET and dikanut shell

powder (DNS) filler (cellulosic filler) is insignificant without the presence of a catalyst. Hexamethylene diamine reacts with polyester terminal carboxyl group for effective compatibilization. It also reacts readily with anhydride. If used as the second component of the compatibilizer, hexamethylene diamine (HMDA) is capable of producing PET-co-HMDA-co-MAPI copolymer at the interface which will function as an effective compatibilizer.

1.3 Objectives of the Study

The main objective of the study is to evaluate the physico-mechanical properties of compatibilized Natural Rubber/recycled Poly(ethylene terephthalate)/dikanut shell powder bio-composites.

The specific objectives are to:

- 1.) produce improved compatibilized natural rubber/recycled poly (ethylene terephthalate) / dikanut shell powder bio-composites for the production of bio-composites.
- 2.) determine the effect of compatibilizer and filler loading on mechanical properties of dikanut shell powder- filled natural rubber/ poly(ethylene terephthalate) blends.

1.4 Justification of the Study

Agricultural by-products which are abundant and renewable are being discarded as waste. Utilizing these by-products as bio-composites for the production of useful products, will drastically minimize the use of costly carbon black which is most commonly used as reinforcement in rubber compounding.

The current economic situation in the country has made it imperative to diversify the nation's petroleum dependent economy.

The benefit of this study is to minimize the overhead cost of rubber articles by replacing carbon black expensive, non-renewable petroleum-based-reinforcing filler with a cheap, renewable, abundant and bio-degradable dikanut shell as alternative.

1.5 Scope of the Study

This study is limited to:

- I. the determination of the physico-mechanical properties of dikanut shell filled natural rubber/ recycled poly(ethylene terephthalate) blend.
- II. investigation on the effect of compatibilizer and filler loading on some mechanical properties of dikanut shell filled natural rubber/ poly (ethylene terephthalate) blend.

CHAPTER TWO

LITERATURE REVIEW

2.1 Compatibilizer

The micro-phase separation in polymer blends limits their applications as adhesives, interfacial stabilizers, coatings, membranes, and functional materials for bio-medical applications. To prevent phase separation in immiscible polymer blends, macro-molecular compatibilizers are added. These macro-molecular compatibilizers reduce interfacial tension and slow down the process of phase separation by localizing at the interface between the immiscible homopolymers, leading to finer dispersion and improved mechanical strength of the interface.

Chih-Roncet *al.*, (2006) investigated polymer blends of polyamide-6 and poly (phenylene oxide) compatibilized by styrene-co-glycidyl methacrylate. The epoxy functional groups in Styrene-Co-glycidyl methacrylate(SG) copolymers can react with the poly amine (PA6) and carboxylic end groups at interface to form various SG-g-PA6 copolymers. These in-situ found copolymers tend to anchor alongside the interface to function as compatibilizer of the blends. The styrene and the SG segments of the grafted copolymers are miscible (or near miscible) with Poly (phenyl oxide) (PPO); whereas

the PA6 segments are structurally identical with PA6 phase. The compatibilized blend, depending on quantity of the compatibilizer addition and glycidyl methacrylate (GMA) content in the SG copolymer, resulted in smaller phase domain, higher viscosity and improved mechanical properties. Optimum content of 5wt% GMA in SG copolymer produced the best compatibilization of the blends. This study demonstrates that SG reactive copolymers can be effective in compatibilizing polymer blends of PA6 and PPO.

Kwanruetha *et al.*, (2008) studied compatibilization of natural rubber (NR) and chlorosulfonated polyethylene (CSM) blends with zinc salts of sulfonated natural rubber. 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 rate was investigated. It was found that the incorporation of ionomers increased shear viscosity of the blends, indicating an increase in interfacial interaction between the NR and CSM. The maximum shear viscosity was observed when the ionomer of 10% by weight of NR was added into the blends. The tensile strength, tear, oil resistant 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, 100% modulus, tensile strength, tear strength and oil resistance of the compatibilized blends improved over those of the uncompatibilized 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. Also 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.

Arayapraneel and Rempel,(2007) studied properties of NR/EPDM blends with or without methyl methacrylate-butadiene-styrene (MBS) as a compatibilizer. EPDM was blended with natural rubber with various blend ratios, after which the processing, cure characteristics, and mechanical properties of the NR/EPDM blends were determined. The morphology of NR/EPDM blends was investigated by scanning electron microscopy. The effect of methyl-methacrylate- styrene (MBS) as a compatibilizer in a 50/50 NR/EPDM blend on blend properties was studied in detail. It was found that addition of the compatibilizer improved the compatibility of NR/EPDM 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 were examined by Hanafi *et al.*, (2001). The results indicate that the increasing compositions of ENR and the presence of ESBS improved processability, tensile strength, tear strength and tensile modulus SBR/ENR blends. The scorch time, t_2 and cure time t_{90} decreased with increasing compositions of ENR in the blend. The presence of ESBS exhibits a beneficial effect by increasing the scorch time and decreasing the cure time of the SBR/ENR blends. It was also found that the presence of ESBS also resulted in SBR/ENR blends having an oil resistance better than the similar blends without ESBS.

Immiscible blends of recycled high density polyethylene (HDPE) and poly (ethylene terephthalate) (PET) were compatibilized with maleic anhydride grafted poly ethylene (PE-g-MA) (Kasama *et al.*, 2006). The effect of the compatibilizer content on mechanical, morphological, rheological and thermal properties of recycled HDPE/PET blends was investigated. The blends were prepared in a twin screw extruder. Tensile strength, tensile strain at break and impact strength improved with addition of the compatibilizer. The compatibilized blends had a similar size of phase compared with uncompatibilized blends. The addition of the compatibilizer increased the melt viscosity of the compatibilized blends. The compatibilizer affected the crystallinity behaviour of the blends.

Compatibilization of natural rubber (NR)/ high density polyethylene (HDPE) thermoplastic vulcanizate with graphene oxide (GO) through ultrasonically assisted latex mix (ULM) was studied by Yan *et al.*, (2012). The authors found that the stacked GO platelets were successfully exfoliated by ULM process and have good compatibilization efficiency for the immiscible NR and HDPE. A smaller NR domain was observed in NR/HDPE blend in the presence of the GO. The stacked GO platelets enhance the interfacial adhesion and phase compatibility, which resulted in an increase in mechanical property of NR/HDPE blends. Compared to the NR/HDPE, the tensile strength and tensile modulus at 300% strain for NR/HDPE/ (1.5 phr) GO blend were increased by ~ 27% and ~ 24%, respectively. The authors concluded that exfoliated GO can act as both the effective reinforcing filler and compatibilizer in the immiscible NR/HDPE blends.

2.2 Methods of Compatibilization

I. Physical Process

In this process, temperature, shear and time of mixing are major factors. Increasing the temperature may increase or decrease the thermodynamic miscibility. Higher temperature lowers the viscosity and miscibility is observed. Increase in shear force causes changes in

the morphology, directional shear force can convert spherical domains into rod-like or fibrillar, which can contribute in mechanical reinforcement or reduction in permeability.

II. Polymer Modification

Polymers are commercial materials and are readily available in the market. For physical compatibilization, the commercial polymer product should be modified according to the requirement for miscibility in immiscible blends. Modification can be done in two manners:

- a) During polymerization and
- b) After polymerization.

Modification during polymerization can occur by controlling the molecular weight, by random and block copolymerization and also by attaching terminal functional groups. Modification after polymerization occurs by addition and substitution reaction. Modification of polymer has become a major route to obtain structural and functional polymers with the desired physical and chemical properties at lower cost than developing completely new polymer (Meister, 2000).

III. Additives

This is adding one or more, such as monomeric additives which includes surfactants, fillers, solvents, fibres and plasticizers in polymer blends compatibilization. There are no chemical reactions in this process.

IV. Reactive Processing

Jun, 2000 reported reactive blends of starch/PLA with a reactive agent during the extrusion process. The effects of the reactive blending were investigated and significant improvements were confirmed by measuring the tensile strength and elongation at break, IR spectra and (Differential Scanning Calorimetry) DSC. In reactive processing, the immiscible polymers along with block or graft copolymer are introduced in twin screw extruder, where chemical reaction between the block or graft copolymer and immiscible polymers take place, resulting in polymer alloy with good interfacial adhesion and stabilized morphology. Different ways of reactive processing are:

- a) by reaction between primary polymers like High Impact Polystyrene (HIPS), and Acrylonitrile butadiene styrene (ABS), Urea-formaldehyde (UF) and Poly ethylene(PE) resins.
- b) by addition of monomeric reactants like maleic anhydride grafted polymer(MAH), peroxides, ionomers etc.

- c) by reaction between functional groups of polymer via $-C=C$ bond, amine group, hydroxyl group, amide group, sulphonic acid group etc.
- d) by addition of reactive polymers like ionomers, Maleic anhydride-grafted-polymer, etc.
- e) Interpenetrating Polymeric Networks (IPNs)

2.3 Composite

Composite is defined as a material that consists of two or more chemically and physically different phases separated by a distinct interface. The different systems are combined judiciously to achieve a system with more useful structural or functional properties non attainable by any of the constituents. There has been a growing interest in the use composites materials in structural applications ranging from aircraft and space structures to automotive and marine applications instead of conventional materials.

A variety of manufacturing methods can be used according to the end-use design requirements. Vacuum assisted resin infusion techniques have become popular in manufacturing of these composites. the most popular terms to describe vacuum infusion processes are: VARTM-Vacuum Assisted Resin Transfer Moulding (Koefoed,2003; Correia *et al.*, 2004), VARIM-Vacuum Assisted Resin Infusion Moulding (Khattag, 2005), SCRIMPTM-Seeman Composites

Resin Infusion Moulding Process (Bohet *et al.*, 2005), VBRTM-Vacuum Bag Resin Transfer Moulding (Kang *et al.*, 2001), VARI-Vacuum Assisted Resin Infusion process (Tzetzis, 2008) etc. All of them involve basically the same technology, and describe methods based on the impregnation of a dry reinforcement by liquid.

2.4 Types of Fillers for Composites

The filler used in polymer materials can be classified into reinforcing and non-reinforcing type (Onyeagoroet *al.*, 2014).

I) **Reinforcing Fillers**

Reinforcing fillers are fillers which increase some of the mechanical properties such as tensile strength, hardness and abrasion resistance of the polymer product. They achieve performance enhancement by forming strong chemical bonds with polymer, that is strong filler-polymer interactions. Carbon black and silica are the most commonly consumed reinforcing fillers in the rubber industry, (Onyeagoroet *al.*, 2014). For instance, carbon black imparts strength and toughness to rubbers; it improves resistance to tearing, abrasion and flex- fatigue of rubbers and also increases traction and durability. Silica and other types of fillers have a weaker polymer-filler interaction and are extensively used where a high degree of reinforcement is not

essential. Reinforcing filler has the ability to change the viscosity of a compound and the vulcanizate properties with an increasing amount of filler loading.

II) Non –Reinforcing Fillers

These fillers cause reduction in strength properties but may increase hardness and modulus of the polymer product. They slightly increase the viscosity of the compound and actually diminish the mechanical properties of the vulcanizate. They are generally applied as extenders to reduce cost. Examples are china clay, kaolin and calcium carbonate.

2.5 Mechanical Behaviours of Polymers

The mechanical behaviour of polymeric components are dominated by its visco-elasticity. A brittle polymer deforms elastically before fracture, a plastic polymer deforms elastically and then yields into a region of plastic deformation, while an elastic polymer shows total elastic deformation at large strain levels. Thermoplastics go through a brittle or ductile transition when heated through their glass transition temperature (T_g). Thermoplastics when below their glass transition temperature deform mainly by elastic deformation, this means they are brittle and above T_g , they deform by plastic deformation, this means they are ductile.

Temperature plays a major role on the strength of a thermoplastic. A thermoplastic loses its strength when heated, because the secondary bonds between the molecular chains become weaker. There is a significant drop in strength when heated through its T_g , because the secondary bonding forces are fully overcome.

Heated thermosets degrade or char above their maximum use temperature. Both thermosets and thermoplastics that are well below their T_g exhibit brittle behavior. When polymers are in brittle state the polymer chains are locked (interlocking network) this makes plastic flow difficult.

2.6 Mechanical Behaviour of Filled and Reinforced Polymers

Fillers are intentionally inserted in polymers to make them stronger, lighter or less expensive. Fillers affect the mechanical behaviour of a polymeric material. Example, long fibres make the polymer stiffer and denser, whereas, foaming makes it more compliant and much lighter. A filler such as calcium carbonate, decreases the polymer's toughness while making it considerably cheaper to produce.

Reinforced plastics are matrix polymers whose properties have been enhanced by introducing a reinforcement of higher stiffness and strength. Such a material is usually called a Fiber-Reinforced-Polymer (FRP) or a Fiber-Reinforced-Composite (FRC). The purpose of introducing a fiber into a matrix is to transfer the load from the weaker material to the stronger one.

The mechanical properties of polymer composites involve its behaviour under stress. These properties show how strong the composite or the polymer is, how much it can be stretched before breaking; how stiff it is; if the composite holds up well under repeated stresses. when considering how a composite or polymer can be used.

Mechanical properties of polymer blends are controlled generally by many factors such as the nature of polymer (George, 1993); blend composition (Valsamiset *al.*,1998); phase morphology (Findiket *al.*, 2004) and interfacial adhesion (Satheet *al.*, 1996). The phase morphology depends on processing factors such as type of mixer; blending rate; blending temperature, component rheology; interfacial tension and crosslinking agent (Madani and Badawy, 2005).

Blends of natural rubber have been reported to be compatible with desirable mechanical properties. Hanafi and Hairunezam, (2001) reported on “the Effect of a Compatibilizer on curing characteristics, mechanical properties and oil resistance of Styrene butadiene rubber/epoxidized natural rubber blend”. The results show that the increasing composition of epoxidized natural rubber (ENR) and the presence of styrene epoxidized butadiene styrene (ESBS), improved

processability, tensile strength, tear strength and tensile modulus of styrene butadiene rubber (SBR)/epoxidized natural rubber (ENR) blends.

2.7 POLYMER BLEND

Polymer blend is the mixture of at least two or more polymers or copolymers. Polymer blending makes it easy to achieve / develop new polymer products which has the combined excellent properties of more than one existing polymer. Polymer blending is mostly carried out in processing machines, such as twin screw extruders, which are considered standard industrial equipments.

2.8 TYPES OF POLYMER BLENDS

I) Heterogeneous Polymer Blend.

These blends have a coarse phase morphology, sharp interphase and poor adhesion between the blend phases. Each component exhibits its own glass transition temperature (T_g). These blends are useless without being blended with compatibilizers.

Examples of this type of blend are polyamide (PA)/ acrylonitrile-butadiene-styrene terpolymer (ABS). The polyamide provides good heat and chemical resistance, good tensile properties, good flow and good paintability while ABS lowers the moisture absorption, improves the dimensional stability and provides low cost and low temperature impact strength. Polyamide (PA)/ ethylene propylene-

diene terpolymer (EPDM). This blend is called “super blend nylons”. Polyamide (PA)/ poly (dimethylphenylene oxide) (PPO), here the polyamide provides good processability, good chemical resistance and paintability while PPO exhibits low moisture absorption, good dimensional stability and stiffness at higher temperatures. Polypropylene (PP)/ Polyamide (PA). PP lowers both moisture absorption and cost. These blends are of great commercial use when sufficiently and effectively compatibilized.

II) Compatible Polymer Blend.

In Compatible polymer blend, part of one blend component is dissolved in the other. This type of blend exhibits a fine phase morphology and satisfactory properties. It is also referred to as partially miscible blend. Both blend phases are homogenous, and have their own Tg. The Tg of each phase is the average Tg of the components of blend of each phase.

Example of this type of blend is the polycarbonate (PC)/ acrylonitrile-butadiene-styrene terpolymer (ABS) blends, which combine the heat resistance and toughness of PC with the low temperature impact, processability, stress cracking resistance and low cost of ABS. In these blends, PC and poly(styrene-co-acrylonitrile) (SAN) phase of ABS partially dissolve in one another, creating wide interphase and good interfacial adhesion.

III) Homogenous Polymer Blend.

In this type of blend, the change in enthalpy (heat of mixing) is less than zero ($\Delta H_{\text{mix}} < 0$). This is due to specific interactions, which lead to the production of homogenous blend, these interactions range from strongly ionic to weak and non-bonding interactions, such as hydrogen bonding, ion-dipole, dipole-dipole and donor- acceptor interactions (Olabisi *et al*, 1979). Homogeneous miscibility in polymer blends require a negative free energy of mixing: $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$. The mixing must be exothermic. Both blend components lose part of their properties and the final properties is the average properties of both blend components. This type of blend exhibits only one glass transition temperature (T_g), which is between the T_g of both blend components in close relation to the blend composition.

Example of this type of blend is the blend of polystyrene (PS) and poly (dimethylphenylene) (PPO). This blend is miscible over a very wide temperature range and in all proportions. This blend combines The heat resistance, the inflammability and the toughness properties of PPO and the good processability and the low cost of PS.

2.9 Miscibility of Polymer Blends

The miscibility behaviour of polymers is strongly dependent on temperature. Each polymer pair is characterized by an interaction parameter.

The properties of polymer blends that show immiscibility systems, are not only dependent on blend composition but also on degree of dispersion, particle size, and phase interaction between the components of the blend (Datta and Lohse, 1993). Many polymer pairs that are immiscible and incompatible, show high interfacial tension that leads to rough phase structure, poor adhesion at the interface and poor mechanical properties. Zhang *et al.*, (1997) investigated the miscibility, crystallization and melting behaviour and phase morphology of poly(3-hydroxybutyrate) (PHB) and ethyl cellulose (EC) blends prepared by casting films. The blend showed composition- dependent glass transitions. The temperature position increased with a decrease in PHB content in the blends, and a maximum value of EC component. After cooling using DSC, a low temperature T_g corresponding to that of the PHB phase in the blends was found. This T_g remained almost unchanged at about 5 or 9° C for all the blends. The hydrogen bonding of the hydroxyl groups of EC was found to be stronger than that of the hydroxyl group in EC with carbonyl groups in PHB. Unlike PHB component, the blends displayed no crystallization when cooled from the melt during the DSC non-isothermal crystallization. The growth of PHB spherulite was delayed by EC content. No evidence of phase separation of the blends was observed by SEM studies.

2.10 Advantages of Blending.

The advantages of blending include:

- I) To produce materials with full set of desired properties at the lowest cost.
- II) Develop broad property range materials.
- III) To improve specific properties.
- IV) For quick formulation changes for customer satisfaction.
- V) To improve processability, product uniformity and reduce scrap.
- VI) inherent recyclability (Utracki, 2002).

2.11 Methods of Blending

To control the properties of blend, knowing the choice of method of blending is of great importance. Methods of preparation of blends can be classified into:

- I) Melt mixing:** Is the mixing of polymers in the molten state under shear.
- II) Solvent casting:** This involves the dissolution of polymers in a common solvent and casting a film from solution.
- III) Co-precipitation:** Involves dissolving polymers in a common solvent and the subsequent removal of solvents.
- IV) Latex blending:** This is the mixing of lattices of different polymers and spraying the mixture before drying.

- V) **Inter-penetrating Polymer Networks (IPN) Technology:** Is the polymerization of one monomer dissolved in a solvent containing a polymer.

2.12 Thermodynamics of Polymer Blends

Rules governing the equilibrium behaviour of mixtures by the free energy of mixing are (Robert, 2009)

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (\text{i})$$

Where $\Delta G_{\text{mix}}, \Delta H_{\text{mix}}, T\Delta S_{\text{mix}}$ are the Gibbs free energy, energy, enthalpy and entropy of mixing at temperature, T, respectively.

Thermodynamic equation for miscible system (single phase) requires the free energy of mixing to be negative (Leszek, 2009):

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \leq 0 \quad (\text{ii})$$

Thermodynamic equation for immiscible system requires the free energy of mixing to be positive (Leszek, 2009).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} > 0 \quad (\text{iii})$$

Thermodynamics is the key to understanding the behaviour and properties of polymer blend (Leszek, 2009).

2.13 Factors Affecting the Miscibility of Polymer Blend

Generally, the mixing of two polymers lead to a two-phase system because polymers are thermodynamically immiscible and incompatible. This leads to high interfacial tension and poor interfacial adhesion (Favis *et al.*, 1988).

Some of the factors that govern/ interfere the process of polymer blending are:

I) Polarity

Polymers with similar structures or polarity are likely to be miscible polymer blends (Gaylord *et al.*, 1976; Paul and Newman 1978). While polymers with dissimilar structures or polarity produce immiscible blends.

II) Ratio of Polymers for Blending

For immiscible polymers, it is possible that a small quantity of polymer maybe soluble in large amount of other polymer.

III) Molecular weight

Low molecular weight polymers permit greater random molecular movements on mixing, thus leading to gain in entropy, which subsequently results to miscibility, while polymers of different molecular weight results in immiscibility.

IV) Specific Group Attraction

Polymers attached to each other by hydrogen bond, ion-dipole, donor acceptor, transition metal complexes etc. are likely to impart

miscibility in blends (Utrackiet *al.*, 1999; Xanthos and Dashl, 1991). When two polymers repel each other, they separate into different phases (incompatibility) and the interphase could be very weak and can fail under any kind of mechanical or thermal stress (Paul and Newman, 1978; Lui and Baker, 1992).

V) Crystallinity

When polymers in blend crystallize, they form two separate crystalline phases and it is rare for two polymers to co-crystallize in a single crystalline phase (Chen *et al.*, 1993). Practically, miscibility of polymer blends is the compatibility of polymer blends.

2.14 Recycling

Recycling is the process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. Recycling reduces waste, environmental, air pollution (incineration), water and land pollution (from land filling), hence contributing to a green economy. The use of natural resources in the world is expected to quadruple by 2050 and at the current rate of depletion, the world cannot satisfy demand for resources from virgin materials alone, (Shailendra *et al.*; 2013). The overall success of recycling stream is driven by appropriate public policies, efficient and well organized value chain, and conscious consumers. Shailendra *et al.*; (2013) studied on increased mechanical recycling target for plastics

in Europe and the results showed that, the best strategy to move Europe towards sustainability for plastics was making recyclable plastics available to recyclers, This lead to achieving 62% recycling rate, recovery of residuals for energy production (recoveryof energy from 7.5 million tonnes of residual waste) and diversion of more than 42million tonnes of plastic waste from landfill.

Recycling offers an alternative solution for handling plastic waste. Although there exist easy and inexpensive separation methods for these plastics, yet a mechanical recycling method which involves blending of the plastics gives rise to secondary materials with interesting properties (Onyeagoro, et al; 2013). Blends of polyolefins display good mechanical and permeation characteristics.

2.15 Plastics Recycling Value Chain

The market structure of plastics recycling involves collection, sorting, processing and converting (that is incorporation of recycled plastics into new products).

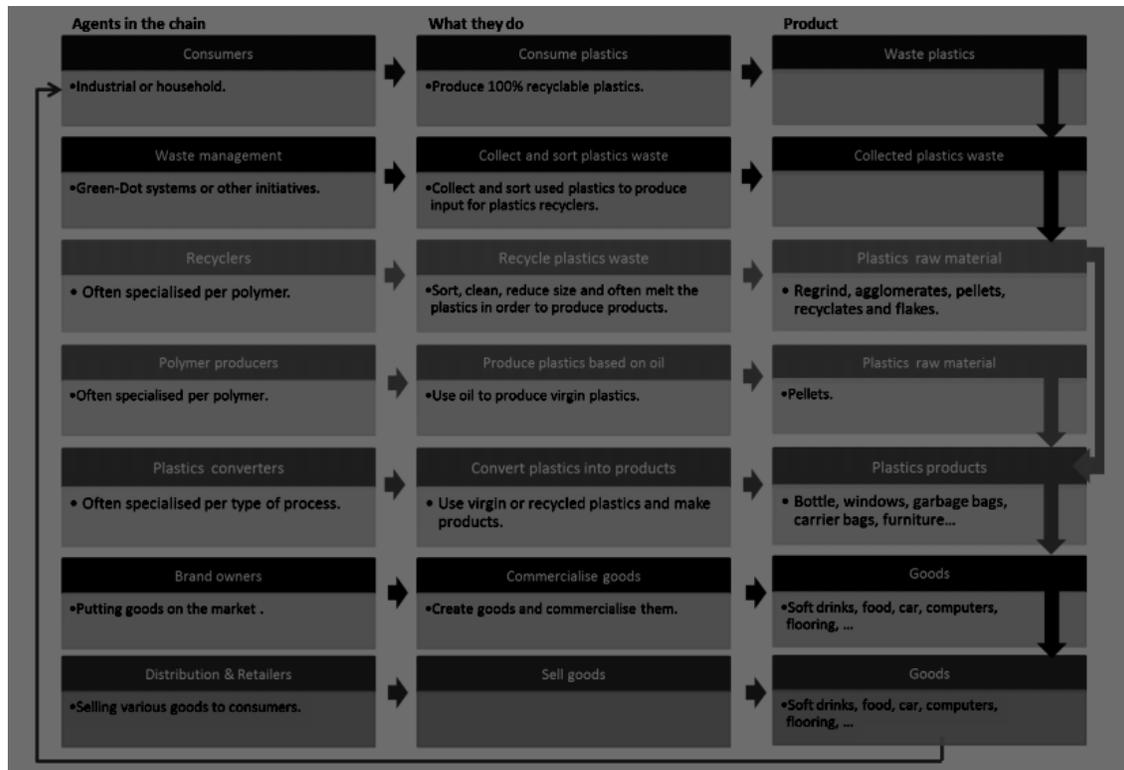


fig. 1.1 overview of the plastics recycling chain value(Shailendra, 2013)

A major challenge in producing recyclate is that most plastic types are inherently immiscible at the molecular level and have different processing requirements. For example, a small amount of PVC contaminant present in a PET stream will degrade the recycled PET resin and vice versa;(Shailenderal et al; 2013). This makes recycling more difficult. The cleaner and fewer the different types of plastic, the less mechanical treatment is required and the quality of the recycled plastic products improved. Sorting and separation thus affect the cost of recycling and the quality of recyclate. Sorting plastic waste at an early stage may be the most significant activity in the recycling loop. Bio-based plastics (those derived from renewable

sources) are generally not a problem for mechanical recycling as they are designed to keep their properties. Bio-degradable plastics, on the other hand, lose their properties and create a lower melt index (the degradation of the organic part) which lowers the quality of therecyclate. Greater penetration of biodegradable products in non-biodegradable plastic streams is thus a threat to plastic recycling.

Masud et al; (1997), reported that decrease in polymer properties with increase in the number of processing cycles are not severe. However, sharp decrease in mechanical properties with excessive processing may be predicted when the molecular weight is under a critical value.

Masud et al; (1997), measured the intrinsic viscosities and molecular weights of recycled PET and discovered that they decreased with further reprocessing. This indicates that the molecular chains of PET undergo thermal degradation on further processing.

It is found that during reprocessing, mechanical properties of PET showed slight decrease and the weight-average molecular weight, M_w , dropped more notably; also blends of 20W/W% recycled PET with virgin PET showed practically the same mechanical properties with its M_w slightly lower than virgin PET. The results suggest that mechanical blending can be used for recycling purposes without sacrificing useful properties of the virgin PET and to reduce raw material cost. (Masoud et al; 1997).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Natural rubber conforming to Nigeria Standard Rubber Grade 10 (NSR10) having the characteristics listed in Table 3.1 was obtained from Rubber Research Institute of Nigeria, Benin City;

Table 3.1 Characteristics of Nigeria Standard Rubber Grade 10 (NSR10)
Parameters

Dirt content retained on 45 μ sieve (%)	0.02
Ash content(%)	0.32
Volatile matter (%)	0.40
Nitrogen (%)	0.23
Initial plasticity(p ⁰)	32
Plasticity after ageing for 30min at 140 ⁰ C(P ³⁰)	24
Plasticity Retention Index(PRI)	67
Mooney viscosity ML(1+4), 100 ⁰ C	70

Molecular weight average(M_w)	350,000
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Dikanut (*irvingiaGabonensis*) shells were obtained from agricultural farm yard in Auchi, Edo state, Nigeria. Poly (ethylene terephthalate) bottles with recycled code 1, (specific gravity of 1.38g/cm^3 , melting point of 260°C and melt flow index of 20g/min), were picked in Owerri, Imo State environs, washed, ground into pellets and air dried. Hexamethylene diamine (HMDA), and maleic anhydride grafted polyisoprene (MAPI) with the properties shown in Table 3.2 were purchased from Rovert Chemicals Limited, Benin City, Nigeria.

Table 3.2 properties of Maleic anhydride-g-polyisoprene

Parameters

Molecular weight average (M_w)	25000
Viscosity (cp, 20wt% in toluene (30°C Brookfield) (lit))	10-50
Refractive index (lit)	n ₂₀ /D152
Density (g/mol at 25°C lit)	0.92

All rubber compounding ingredients: zinc oxide, stearic acid, MAPI, HMDA, Sulphur, MBT, TMTD and wax, used were of commercial grades.

Equipment:

- i. Brabender plastic mixer
- ii. Two roll mill

3.2 Methods

Preparation of Dikanut Shell Powder

The dikanut shells were washed and dried in air to remove sand particles and moisture. Thereafter, portion of the dikanut shells were milled to fine powder and sieved through a mesh size of $150\mu\text{m}$. The fine particles that passed through the mesh were collected as dikanut shell powder and were stored in sealed plastic container and kept in a desiccator until required.

3.3 Characterization of Dikanut Shell Powder

I) pH Determination

The pH of the sample was determined according to ASTM D1512-05 method by immersing 1.0g sample in 20.0cm^3 of de-ionized water in a 250cm^3 beaker. The mixture was stirred for 15minutes and the pH meter was inserted into the solution to obtain readings. The average of the readings was taken.

II) Particle Size Determination

The dikanut shell powder was passed through a sieve of 150 μ m mesh. The particles that passed through the mesh were taken as having particle size of 150 μ m.

III) Bulk Density Determination

Bulk density was determined by the tapping procedure described by (Ahmednaet *al.*, 1997). 10g of Sample was transferred into a cylinder of uniform cross-section area and then tapped several times until there was no change in volume occupied. The volume was recorded and the bulk density calculated as in equation 3.1.

$$\text{Bulk density} = \frac{\text{mass of sample}}{\text{volume}} \quad (3.1)$$

IV) Moisture Content Determination

The moisture content was determined by adopting the method described in ASTM D1509. 10g of sample was weighed and recorded as initial weight. The sample was dried to a constant weight at a temperature of 125 $^{\circ}$ C in an oven. The sample was removed from the oven and allowed to cool. The cooled sample was weighed and recorded as final weight of sample. Moisture content was calculated as shown in equation 3.2.

$$\text{moisture content} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100 \quad (3.2)$$

V) Iodine Value Determination

The method used for surface area measurement of the fillers is iodine adsorption number (Ahmednaet *al.*, 1997). 0.1 molar sodium thiosulphate solution was titrated against 20.0cm³ of the aliquot solution (prepared by centrifuging 0.5g of the powdered samples separately in 25.0cm³ of 0.488cm³ iodine solution) using 5.0cm³ of freshly prepared starch solution as indicator. Similarly, the quantity of thiosulphate needed to titrate the blank was determined and 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.

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

Iodine adsorption number is equal to the inverse of iodine value.

VI) Determination of Loss on Ignition

Loss on ignition refers to the mass loss of a combustion residue wherever it is heated in an air /oxygen atmosphere to high temperature. The loss on ignition of the samples was determined gravimetrically in accordance with the procedure described in ASTM D7348. The sample was placed in a crucible and placed in a furnace

and heated again to a constant weight. The loss on ignition was obtained as expressed in equation 3.4.

$$\text{Loss on Ignition} = \frac{(\text{Initial weight} - \text{Final weight})}{\text{Initial weight}} \quad (3.4)$$

3.4 Preparation of the Composite Sample

Recycled poly (ethylene terephthalate) (PET), was dried in air for about a week. The natural rubber was dried at 50°C before using. PET was first melted in Brabender Plastic Mixer (PLE 331) with a rotational speed of 80 rpm at 260°C for about 2minutes, followed by addition of natural rubber. The compounding ingredient, except the vulcanizing agent and accelerator were charged into the mixer. After about 8minutes of mixing, the blend produced, was transferred to a two roll mill set 170°C with a rotational speed of 35rpm and nip clearance of 2mm which converted from an irregularly shaped mass to flat sheets. The temperature of the two roll mill was reduced from 170°C to 90°C, followed by the addition of accelerator and vulcanizing agent to prevent premature curing of the composite. The composites were compressed with a hot plate under 10Mpa pressure at 140°C.

The formulation used in preparing the composites samples are shown in Table 3.3.

Table 3.3: Compounding Recipe of NR/PET/DNS Bio-composites.

Materials	Uncompatibilized	Compatibilized	Compatibilized
NR	70	70	70

PET	30	30	30
Zinc oxide	5	5	5
Stearic acid	2	2	2
MAPI/HMDA	0/0	2/0.5	2/0, 2/0.3, 2/0.5, 2/0.7
Sulphur	3	3	3
MBT	1.5	1.5	1.5
TMTD	1	1	1
Wax	4	4	4
DNS	0, 10, 15, 20	0, 10, 15, 20	10

MBT = MercaptoBenzothiazole

TMTD = Tetramethythyuramdisulphide

DNS = Dikanut shell.

3.5. Determination of Physico-mechanical properties of the Composites

I) TensileStrength (Mpa)

Tensile properties were determined on a mosanto tensile tester (model 1/m) with a cross test speed of 200mm/min using dumb bell test pieces measuring 30mm x 4mm x 3mm according to ASTM D

412-87 method A. The recorded value for each tensile parameter is the average of three measurements.

II) **Percentage Elongation(%)**

Percentage elongation was calculated by dividing the maximum elongation of the gauge length ($l-l_0$) by the initial gauge length(l_0)of the test piece then multiplied by 100.

$$\text{Percentage elongation} = \frac{l-l_0}{l_0} \times 100$$

III) **Modulus (Mpa)**

Modulus was determined according to the ASTM E 111-97 Standard Test Method for Young's Modulus.

IV) **Compression Set (%)**

The compression set (%) of the samples was measured according to ASTM D395-03(2008). The different blend samples were subjected to a standard compressive load of 1.8KN in air. 24hours at test temperature of 70°C. The compression set was measured after 30 minutes of discharge from compression set machine.

3.6 Statistical Analysis of Data

The average value was taken for each sample in the various mechanical tests carried out. Mean total length of test samples was 30mm, with cross sectional area of 12mm². The total number of test samples was 12.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterization of Dikanut Shell (DNS)

Characterization of dikanut shell fibre in terms of the moisture content, pH, surface area, ash content and loss on ignition was necessary because the above parameters play an important role in determining the distribution and dispersion of the fibres in natural rubber and curing characteristics of the vulcanizates.

Table 4.1 shows the physical characteristics of dikanut shell powder

Table 4.1 Physical Characteristics of Dikanut shell powder (DNS)

PARAMETERS	VALUES
pH Slurry at 280 ^o c	5.40
Particle size (μm)	150
Bulk density(g/cm ³)	0.80
Loss on ignition (%)	6.40
Moisture content (%)	2.2
Iodine adsorption number(mg/g)	20.40

The physical properties of dikanut shell fibre show that the pH of the slurry is slightly acidic, 5.40. The weight loss on ignition is 6.40% for dikanut fibre. The weight loss on ignition is a measure of the carbon content lost during combustion and measures the effectiveness of the fibre, the higher the values, the greater the reinforcing potential (Okieimen et al., 2003).

The Iodine adsorption number 20.40mg/g was obtained. One important application of iodine adsorption number is that it elicits the surface area of the material. It is a parameter that indicates the macrostructure of fillers and reflects the reaction and adsorption abilities.

The bulk density is principally influenced by the particle size, and structure of the fiber. The lower the particle size, the lower the

density. Therefore, the better the interaction between the polymer matrix and the reinforcing fibre(Ayo et al., 2011).

The moisture content of 2.2% was obtained. The lower the moisture content, the lower the degree of defect arising from shrinkage during curing at elevated temperature (Egwaikhide et al., 2007(a)).

EFFECTS OF FILLER LOADING ON PHYSICO-MECHANICAL PROPERTIES OF NR/PET/DNS COMPOSITES.

4.2 TENSILE PROPERTIES (Mpa)

The influence of filler on mechanical properties of reinforced elastomers has been extensively reported in literature. In this study, a constant blend composition of NR/PET: 70/30wt% was used with varying filler and compatibilizer blends of DNS/MAPI/HMDA: 0/0/0, 10/0/0, 15/0/0, 20/0/0, 0/2/0.5, 10/2/0.5, 15/2/0.5, 20/2/0.5, 10/2/0, 10/2/0.3, 10/2/0.5, 10/2/0.7, wt% respectively.

Table 4.2: Tensile Strength for both Compatibilized and Uncompatibilized blend compositions.

TENSILE STRENGTH (Mpa)		
Compatibilized	Uncompatibilized	Filler loading (pphr)
4.3	3.1	0
5.5	2.4	10

6.8	3.1	15
7.2	4.4	20

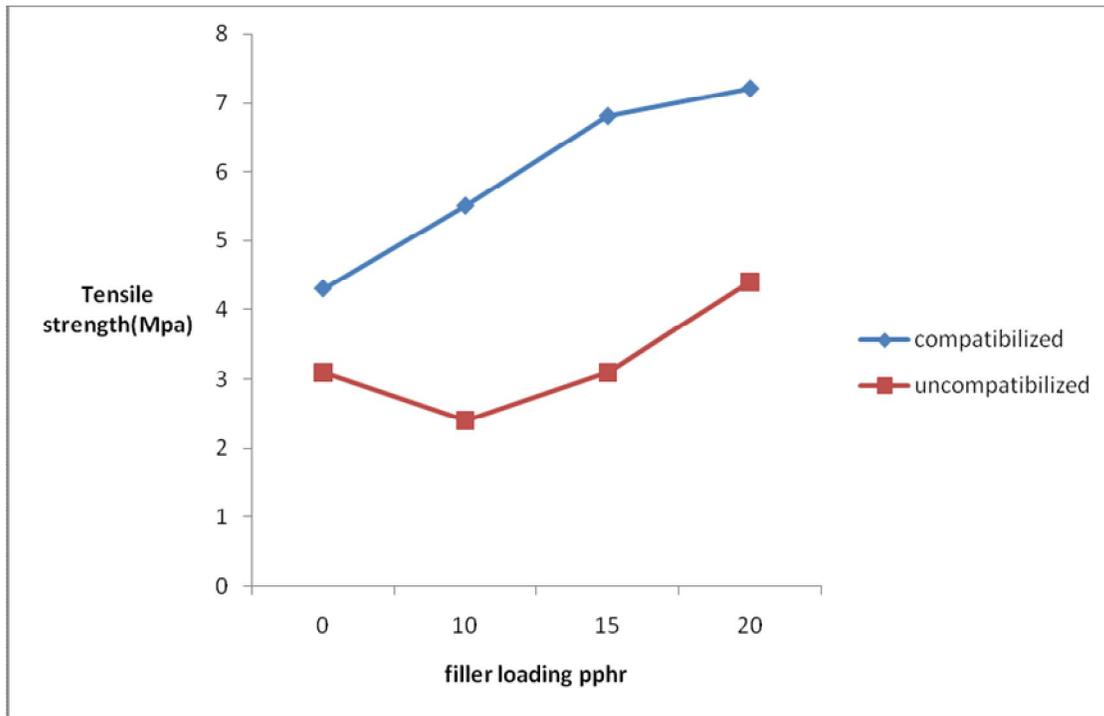


Figure 4.1: Plot of tensile strength versus filler loading for NR/PET/DNS composite.

The results in Table 4.2 and Figure 4.1 show the tensile strength of blend composition for both compatibilized and uncompatibilized NR/PET/DNS composites.

Figure 4.1 indicates that tensile strength of blend increased with increasing filler loading for both compatibilized and uncompatibilized

composition. However, initial decrease was observed for the uncompatibilized blend composition. This is probably due to the absence of filler loading. There was no initial decrease in tensile strength for the compatibilized blend. This could be attributed to the presence of MAPI/HMDA (the compatibilizer), which introduced a strong PET-co-HMDA-co-MAPI copolymer interface. This observation is in agreement with the work of Kwanruethai et al;(2008) who showed 100% tensile strength, tear strength of the compatibilized blends over uncompatibilized blend.

4.3 PERCENTAGE ELONGATION(%)

Table 4.3: Changes in Percentage Elongation for Compatibilized and Uncompatibilized blend Composition

PERCENTAGE ELONGATION (%)

Compatibilized	Uncompatibilized	Filler loading (pphr)
158	170	0
143	153	10
136	141	15
128	130	20

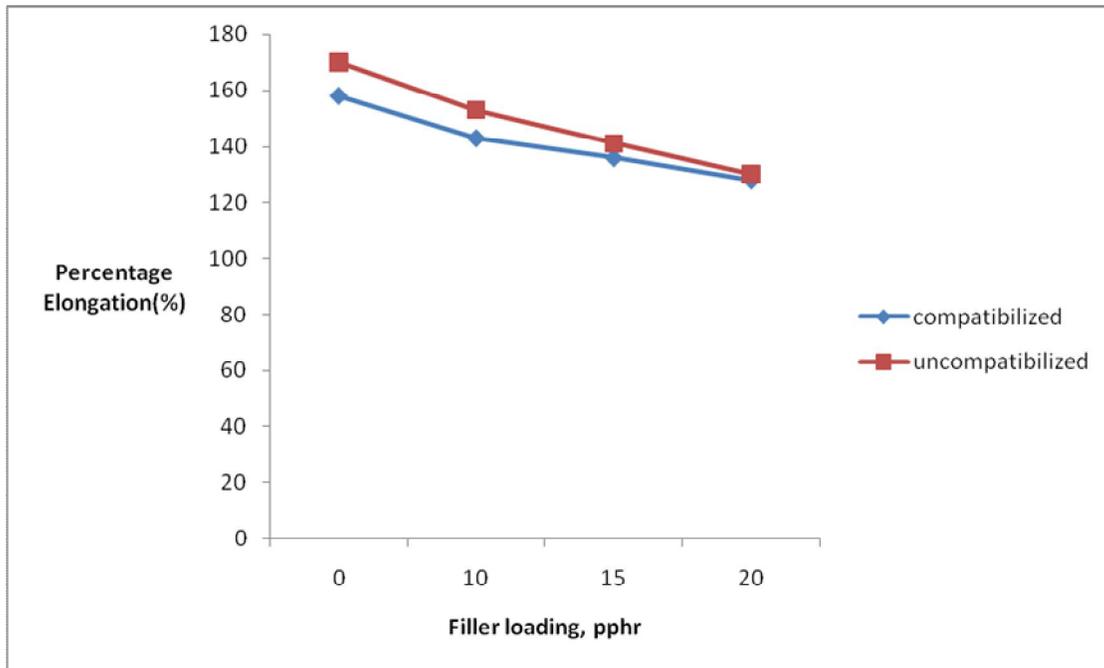


Figure 4.2: Plot of percentage elongation versus filler loading for NR/PET/DNS composite.

Percentage elongation is the measure of ductility of a material.

The Percentage elongation presented in figure 4.2 shows a decreasing behaviour with increase in filler loading for both compatibilized and uncompatibilized blend. This could be attributed to weak interfacial bonds due to poor filler/PET interaction facilitated by cracks. This is in line with the study of Nwanonyiet al.,(2013), who reported a decrease in percentage elongation of filled linear low density polyethylene with increase in the filler content.

4.4 MODULUS (Mpa)

Table 4.4: Modulus Properties for Compatibilized and Uncompatibilized blend compositions.

MODULUS (Mpa)		
Compatibilized	Uncompatibilized	Filler loading
2.7	1.8	0
3.8	1.6	10
5.0	2.2	15
5.6	3.4	20

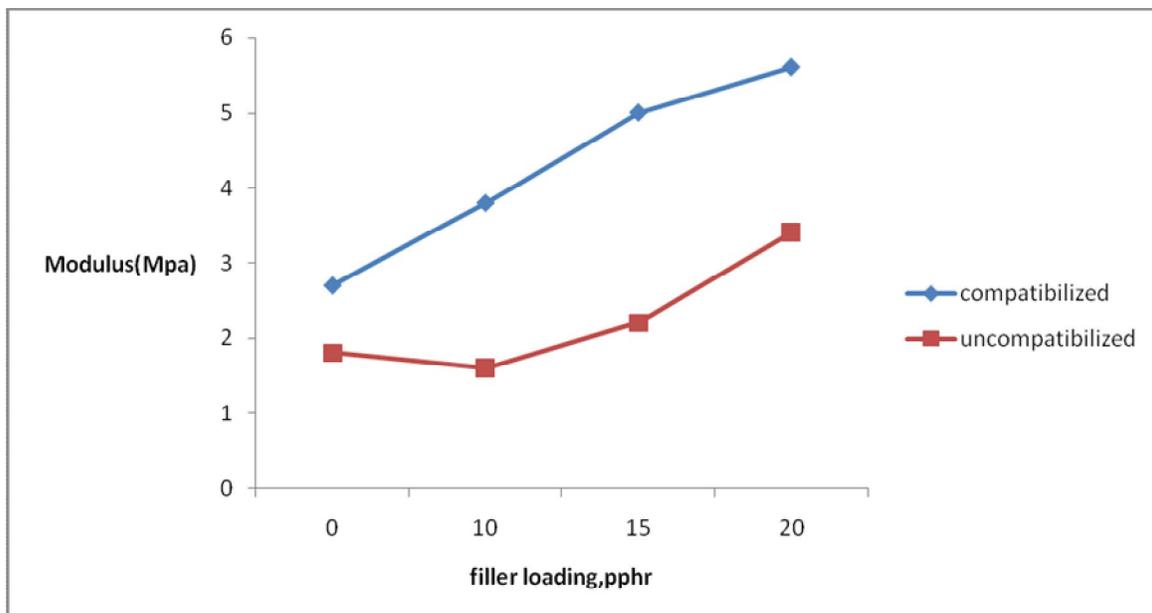


Figure 4.3: Plot of modulus versus filler loading for NR/PET/DNS composite

Figure 4.3 shows an increasing trend in modulus with increasing filler loading, but with an initial decrease in the compatibilized blend. This observation shows that polymer matrix-filler interaction is an important factor controlling the modulus.

It is evident also, from Figure 4.3 that the modulus of the compatibilized blend is higher than that of uncompatibilized blend. The surface activity is an important factor indicating the extent of polymer filler interaction, with polymer filler interaction there could be increases in modulus. The higher modulus in compatibilized blend could be attributed to the presence of compatibilizer, which enhanced polymer filler interaction and strong polymer interface. This is in agreement with the work reported by kwanruethai et al; (2008), compatibilization of natural rubber (NR) and chlorosulfonated polyethylene (CSM) blends with Zinc salts of sulfonated natural rubber. He reported that compatibilized blends showed higher levels of improvement in modulus than those not compatibilized.

4.5 COMPRESSION SET (%)

Table 4.5: Changes in Compression set with respect to blend Composition and filler loading.

Filler loading (pphr)	MAPI	HMDA	COMPRESSION SET(%)
0	0	0	39.6
10	0	0	43.1
15	0	0	46.8
20	0	0	50.8
0	2	0.5	30.0
10	2	0.5	30.5
15	2	0.5	32.6
20	2	0.5	35.2

10	2	0	32.4
10	2	0.3	31.7
10	2	0.5	30.5
10	2	0.7	23.4

Compression set measures the ability of a material to return to its original thickness.

Table 4.5.1: Changes in Compression Set property of compatibilized and uncompatibilized blend composition.

COMPRESSION SET (%)		
Compatibilized	Uncompatibilized	Filler loading (pphr)
30.0	39.6	0
30.5	43.1	10
32.6	46.8	15

35.2	50.8	20
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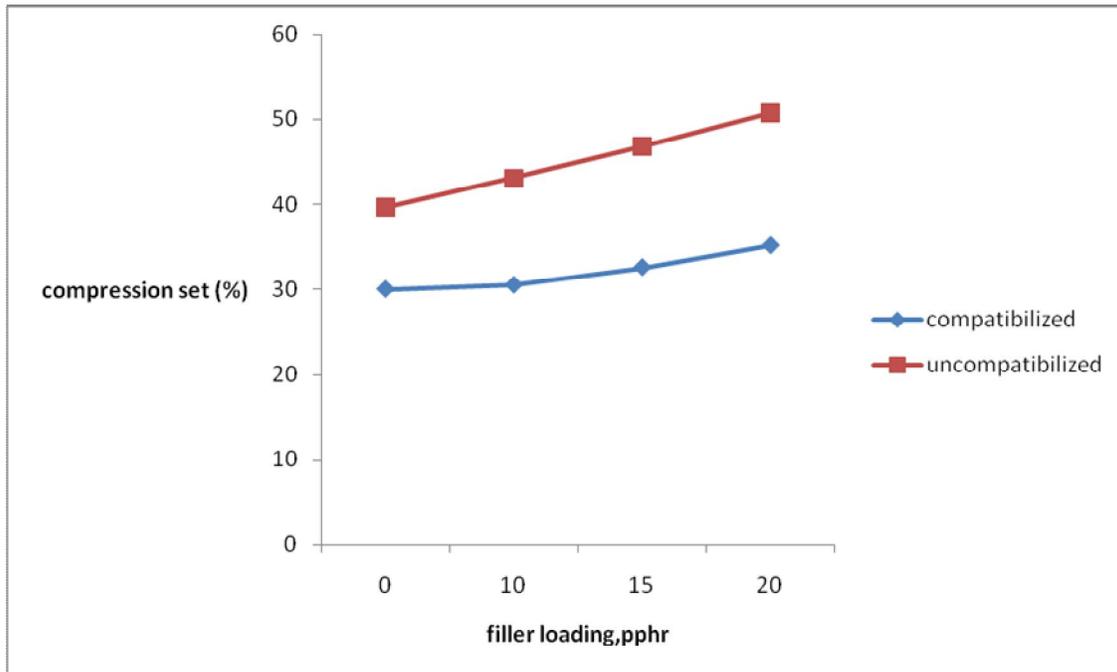


Figure 4.4: Plot of Compression Set versus filler loading for NR/PET/DNS composite

Figure 4.4 shows that compression set increased with increasing filler content. This could be attributed to increase in filler content which makes the blend more rigid and less susceptible to compression loading. The compatibilized blend exhibited a lower compression set property, when compared with the uncompatibilized blend. This could be due to the presence of the compatibilizers. Oboh, et al.,

(2015) in their studies reported that compression set showed an increase with increasing filler loading for all filled vulcanizate.

EFFECTS OF COMPATIBILIZER ON PHYSICO-MECHANICAL PROPERTIES OF NR/PET/DNS BIO-COMPOSITES AT CONSTANT FILLER CONTENT

Table 4.6: Changes in tensile strength with respect to compatibilizer content at constant filler loading.

FILLER LOADING (pphr)	MAPI/HMDA (pphr)	TENSILE STRENGTH (Mpa)
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10	2/0	5.1
10	2/0.3	5.3
10	2/0.5	5.5
10	2/0.7	7.1

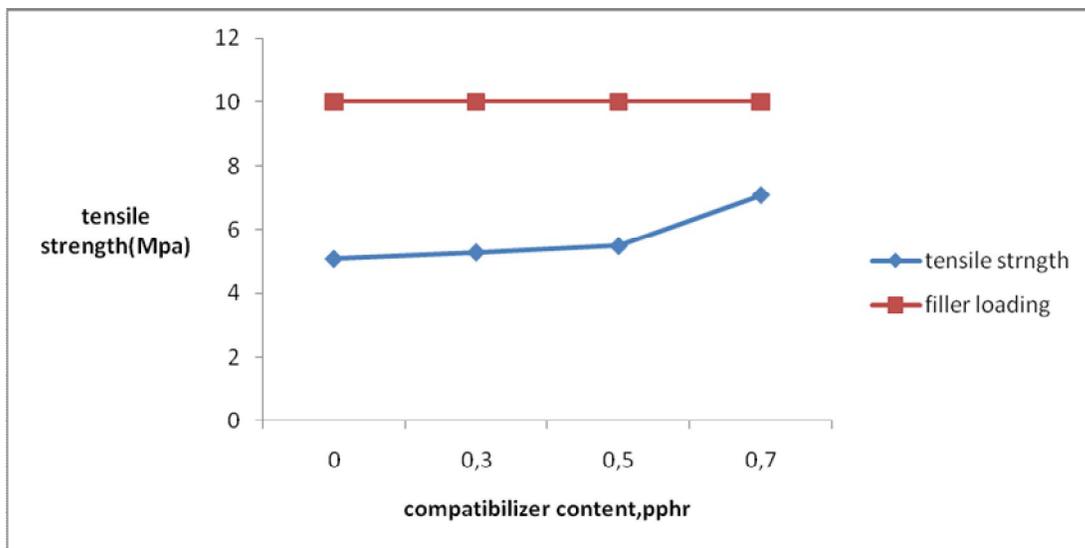


Figure 4.5: Plot of tensile strength versus compatibilizer content for NR/PET/DNS composite.

Table 4.7: Changes in percentage elongation with respect to compatibilizer content at constant filler loading.

FILLER LOADING (pphr)	MAPI/HMDA (pphr)	PERCENTAGE ELONGATION (%)
----------------------------------------	-----------------------------------	--------------------------------------------

10	2/0	147
10	2/0.3	145
10	2/0.5	143
10	2/0.7	140

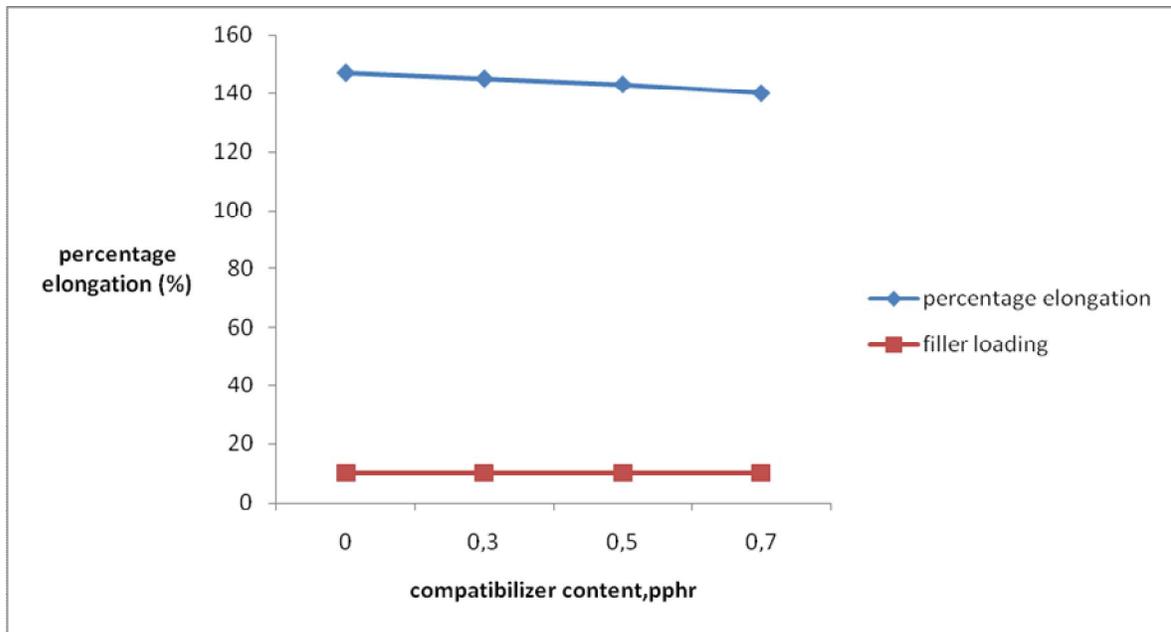


Figure 4.6:Plot ofpercentage elongationversus compatibilizer content for NR/PET/DNS composite

Figure 4.5 shows a further increase in tensile strength with increasing compatibilizer content. This could be attributed to the increasing

content of the compatibilizer interacting with DNS to achieve appropriate interfacial adhesion between the phases. (silvia, et al., 2013), reported a noticeable increase in tensile strength with increasing PP-g-MA (compatibilizer) content in the composite.

Figure 4.6 indicates a decreasing trend in percentage elongation with increasing compatibilizer content. Such a reduction in ductility of the composite with increase in compatibilizer content, could be attributed to increase in the deformation of a rigid interfacial interaction between fillers and matrix. This indicates that the composite is tending towards brittle nature. This is in agreement with (Nwanonyeni et al., 2013), who reported a decrease in percentage elongation of filled Linear low density polyethylene with increase in the filler and compatibilizer contents.

Table 4.8: Changes in modulus with respect to compatibilizer content at constant filler loading.

FILLER LOADING (pphr)	MAPI/HMDA (pphr)	MODULUS (Mpa)
10	2/0	3.5
10	2/0.3	3.7
10	2/0.5	3.8
10	2/0.7	5.1

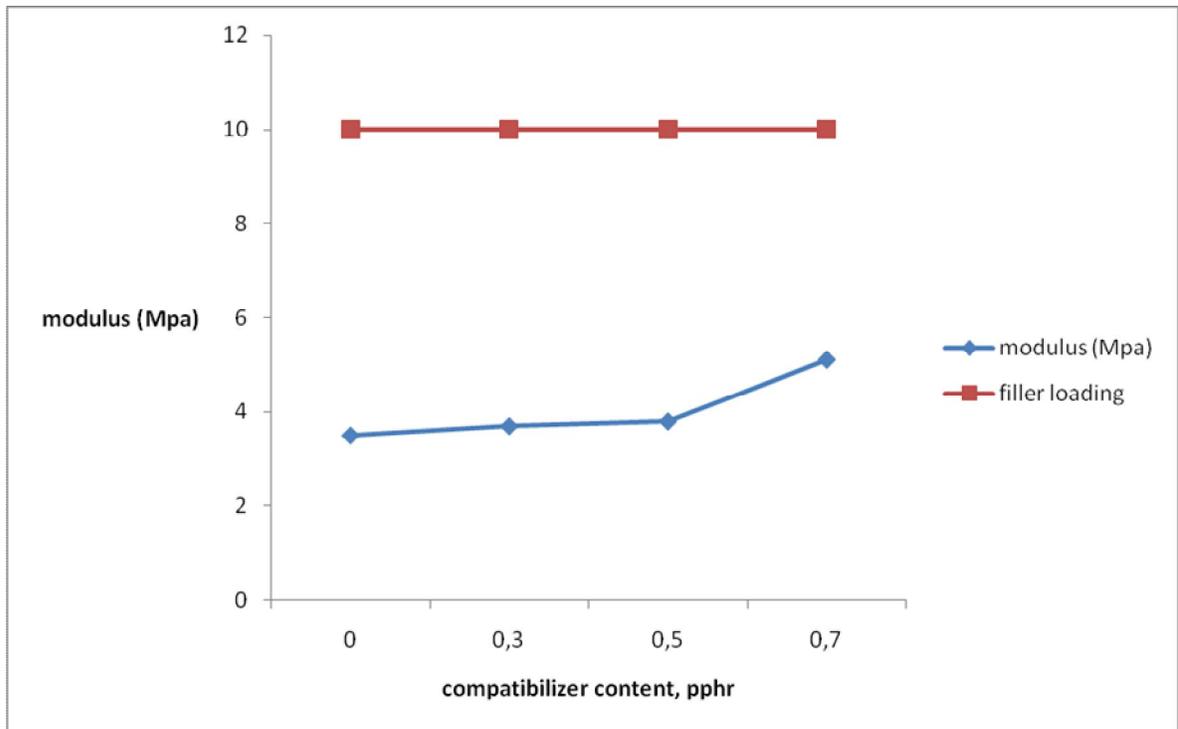


Figure 4.7Plot of modulus versus compatibilizer content for NR/PET/DNS composite.

Figure 4.7 shows that modulus increased progressively with increasing compatibilizer content. This could be attributed to the compatibilizer which gave better compatibility blend through interfacial chemical response, lowering the hydrophobicity of polymer matrix (PET), imparting polarity which makes it more compatible with hydrophilic DNS. This is in agreement with the findings of Khalil, (2015), who reported an increase in modulus with increase in chloroprene (compatibilizer) content.

Figure 4.8 below shows a progressive decrease in compression set, with increase in compatibilizer. This could be attributed to the compatibilizer which gave a better and improved resistance to permanent deformation of the blend.

Ramesan, et al.,(2001) in their studies reported that compression set decreased with increase in SBR (compatibilizer) content of the blend.

Table 4.9: Changes in compression set with respect to compatibilizer content at constant filler loading.

Filler loading (pphr)	MAPI/HMDA (pphr)	COMPRESSION SET (%)
10	2/0	32.4
10	2/0.3	31.7
10	2/0.5	30.5
10	2/0.7	23.4

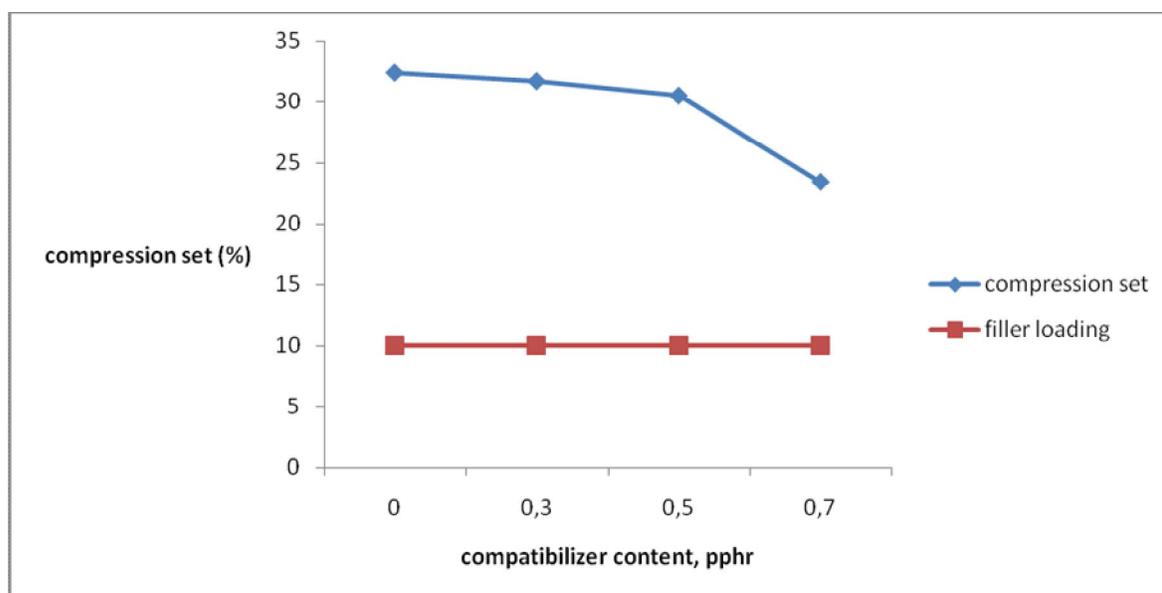


Figure 4.8 Plot of compression set versus compatibilizer content for NR/PET/DNS composite

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The following conclusions are drawn from this study:

NR/PET/DNS composites with compatibilizers have better and improved physico-mechanical properties, over the uncompatibilized NR/PET/DNS composites. Tensile strength and modulus were found to increase with increasing dianut shell powder (DNS) loading, for both compatibilized and uncompatibilized blends. This was due to the filler reinforcing ability. However, tensile strength and modulus exhibited further increase with increasing dianut shell powder (DNS) loading for compatibilized blend over the uncompatibilized blend. This is an indication that the presence of compatibilizer enhanced filler-matrix interface, resulting to better tensile and modulus properties. The same result was obtained for compression set, but compression set decreased with increasing compatibilizer content, due to improved resistance to permanent deformation by the compatibilizer.

Meanwhile, percentage elongation decreased with increasing (filler) dikanut shell powder (DNS) loading for both compatibilized and uncompatibilized blends. This indicates the presence of weak interfacial bonds due to poor filler/PET interaction facilitated by cracks.

Dikanut shell powder (DNS) appears to be a potential substitute filler in the rubber industry especially in the production of low cost/high volume rubber products where strength is not critical.

5.2 Contribution to Knowledge

The following contribution has been made to knowledge through this research;

- 1) Results obtained show that a combination of hexamethylenediamine (HMDA) and maleic anhydride grafted polyisoprene (MAPI) is an excellent reactive compatibilizer for NR/PET/DNS composite.

5.3 RECOMMENDATION

Scanning Electron Microscopy (SEM) should be carried out on Dikanut shell filled Nigeria Standard Rubber/ recycled poly (ethylene terephthalate) composite. This will confirm the improvement in physico-mechanical properties reported in this work.

REFERENCES

- Ahmad, A. Mohd, D. H. and Abdullah, I. (2004), Mechanical Properties filled Natural Rubber/Linear Low Density Polyethylene Blends. *Iranian Polymer Journal*. 13(3): 173-178.
- Ahmad, M.H. Jamil, A.A. Ahmad, H. Piah, M.A.M. Darus, A., Arief Y., Bashi, Z. N. (2012), Oil Palm Empty Fruit Bunch as a New Organic Filler for Electrical Tree Inhibition. *World Academy of Science, Engineering and Technology*.62: 335-340.
- Ahmenda, M., Johnson, M., Clarke, S.J., Marshal, W.E and Rao, R.M., (1997), Potential of Agricultural By-Products Based Activated Carbon for Use in Raw Sugar Decolourization. *Journal of Science Food Agriculture*, No 75, PP: 117-124.
- Arayapraneel W. and Rempel G. L. (2007), Properties of NR/EPDM Blends with or without Methylmethacrylate-Butadiene-Styrene (MBS) as a Compatibilizer. *International Journal of Materials & Structural Reliability*.5(1): 1-12.
- Arroyo, M. L. Manchado, M. A. Herrero, B. (2003), Organo-montmorillonite as substitute of Carbon black in Natural

Rubber Compounds. Journal of Applied Polymer Science.44: 2447-2453.

ASTMD 1509 (2012): Standard Method of Testing Moisture Content.

ASTMD 1510-13 (2012): Standard method of testing Iodine adsorption number(surface area).

ASTMD 1512-05 (2012): Standard Method of Testing for pH.

ASTMD 3184-80 (2012): Standard Method for Compounding Rubber.

ASTMD 7348-13 (2012): Standard Method for Testing loss on Ignition.

Ayo D.; Okebafé, L. Chukwu, M and Madufor, I. (2011), Effects of Carbonization Temperatures on the Filler Properties of Groundnut Shell Powder in Natural Rubber. International Journal Chem.21(1): 55-58.

Barrer, R.M, Skirrow, G, Barboza, V.C, Joeke, I. and Atvars, T.D.Z. (2007), Mapping Phases of Poly (Vinyl alcohol) and Poly (Vinyl acetate) Blends by Ft-Ir Micro Spectroscopy and Optical Fluorescence Microscopy. Journal of Applied Polymer Science. 645-655.

Boh, J.W., Louca, L.A., Choo, Y.S., Mouring, S.E.,(2005), Damage modelling of SCRIMP woven roving laminate beams subjected to transverse shear. Composite part B: Engineering , National University of Singapore.

- Buthaina A. Ibrahim & Karrer M. (2010), Influence of Polymer Blending on Mechanical and Thermal Properties. *Modern Applied Science*. 4(9): 157-161.
- Cates, M.D. and White J. H. (1956), Preparation and Properties of Fibres containing Mixed Polymers, Polyacrylonitrile- Cellulose Acetate Fibres. *Journal of Polymer Science*. 20(94): 155-180.
- Chen, C.C and White, J.L,(1993), Compatibilizing agents in polymer blends: Interfacial tension, phase morphology and mechanical properties. *Polymer Engineering Science*. 33(14):923.
- Chih-R and Chang R, (2006), Polymer Blends of Polyamide-6 and Poly (Phenylene oxide) Compatibilized by Styrene-co-Glycidyl Methacrylate. *Journal of applied Polymer Science*. 61: 2411-2421.
- Correia,N.C., Robitaille, F., Andrew,L., Christopher D.R., Suresh G.A.,(2004), Use of resin transfer molding simulation to predict flow, saturation and compaction in the VARTM process. *Journal of Fluids Engineering*. 126(2).
- Crank, J. Park, G.S. (2002), Preparation and Properties of Fibres containing Mixed Polymers ,Polyacrylonitrile-silk Fibres. *Journal of polymer Science*. 21 (97) : 125-138.
- Datta , S., and Lohse, D.,(1993), Graft copolymer compatibilizers for blends of isotactic polypropylene and ethane-propene copolymers. *Journal of Macro-molecules*. 26(8): 2064

- Deepa,B., Abraham, E., Cherian, B.M., Bismarck, A., Blaker, J.J., Pothan,L.A., Leao, A.L., de Souza, S.F., and Kottaisamy, M. (2011). Structure, morphology and thermal characteristics of banana nanofibres obtained by steam explosion: *Bioresource Technology* 102(2): 1988-1997. DOI: 10.1016/J.biortech.2010.09.030.
- Egwaikhide, P.A, Akporhonor, E. E and Okieimen, F.E (2007(b)), Effects of Coconut Fibre Filler on the Cure Characteristics Physico-Mechanical and Swelling Properties of Natural Rubber Vulcanizates. *Journal of Physical Science*. 2(2): 039-046.
- Egwaikhide, P.A., Akporhonor, E.E and Okiemien F.E. (2007(a)). An Investigation on the Potential of Palm Kernal Husk as Fillers in Rubber Reinforcement. *Middle-East Journal of Scientific Research* 2 (1): 28-32.121
- Favis, B.D., Chalifoux,J.P.,(1988). Influence of Composition on the Morphology of Polypropylene/Polycarbonate Blends. *Polymer*. 29(10):1761.
- Findik, F; Yilnuz, R; andKoksal, T, (2004), Investigation of Mechanical and Physical Properties of Several Industrial Rubbers. *Materials & Design*. 25: 269 – 276
- Frantis, K., Josef, B. Vesna, Ivan, F. Zdenek (2008), Compatibilization Efficiency of Styrene-Butadiene Block Copolymers as a Function of their Block Number. *Journal of Applied Polymer Science*. 108: 466-472.

- Frollini A. E, Leao L.H.C, Math o. (2003), Natural Polymer and Agro-fiber Composites. 1st Edition. San Carlos, Brasil. 1-6.
- Gaylord, N.G.(1976). Polymer Blends. Chemtech. 392, 186.
- George, K, (1993), In blends and alloys. Chapman and Hall, London, UK, 1st edition, 34 – 46
- Goren, A, Atas (2008), Manufacturing of Polymer Matrix Composites using Vacuum Assisted Resin Infusion Moulding. Archives of Mater Sci. and Eng; 117-119.
- Guo C.J, Kee D.D, Harrison B.J (2005), Vulcanization and Vulcanizing Agents. Maclarenandsons Ltd. London. 3
- Hanafi,I., andHairunezam, H.M., (2001), The effect of a compatibilizer on curing characteristics, mechanical properties and oil resistance of styrene butadiene rubber/epoxidized natural rubber. European Polymer Journal. 37:39-44.
- Ichazo, M. N., Hernandez, M. N, Albano, C., Gonzalez, J. (2005), Natural Rubber Filled with Wood flour; Influence of Particle size. Proceeding of the 8th Polymers for Advanced Technologies International Symposium Budapest, Hungary. 13-16.
- Igwe, I. O and Ejim, A. M (2011), The effects of Incorporating Snail shell powder as filler on the Properties of Natural Rubber. Material Science and Application. 2: 801-809.

- Ismail, H. Arjulizan, R. and Azura A. R. (2007), Utilization of Limestone Dust waste as Filler in Natural Rubber. *Journal of Polymer and the Environment*. 15: 67-74.
- Ismail, H. Hairunezam, H.M. (2001), The effects of a Compatibilizer on Curing Characteristics, Mechanical Properties and Oil Resistance of Styrene Butadiene Rubber/ Epoxidized Natural Rubber Blends. *European Polymer Journal* .37: 4817-4823.
- Ismail. H., Santiago R., Kamarudin H. (2010). The effects of Recycled Acrylonitrile Butadiene Rubber Content and Maleic Anhydride Modified Polypropylene(PPMAH) on the Mixing, Tensile Properties Swelling Percentage and Morphology of polypropylene/recycled acrylonitrile butadiene rubber/ rice husk powder (PP/NBRr/RHP) Composites. *Polymer-Plastics Technology and Engineering*. 49(13): 1323-1328.
- Johnson T., Thomas S. (2000), Effect of Epoxidation on the Transport and Mechanical Properties of Natural Rubber. *European Polymer Journal*. 41(20): 7511-7522.
- Jun, C.L.,(2000), Reactive blending of biodegradable polymers:PLA and starch. *Journal of polymer and environment*. 8(1):33-37
- Kamble, A. (2011), Effectiveness of Compatibilizers and Filler on the Performance of the Blends of Thermoplastic Polyurethane/Polyolefins. *Chemical Sciences Journal*. 34.
- Kang M.K., Lee W.I., Hahn H. T. (2001), Analysis of Vacuum Bag Resin Transfer Molding Process, *Composites*. 1553-1560.

- Kasama, J. and Sukunya, C. (2006), Compatibilization of recycled high density polyethylene (HDPE)/ polyethylene terephthalate (PET) blends. *Suranaree J. Science Technology*.14(1): 1-8.
- Kaushik Pal. (2010), Effects of Fillers on Natural Rubber/ Styrene Rubber Blends with Nano silica: Morphology and Wear *Journal of Materials & Design*.31(2):677-686.
- Khalil, A (2015), An Investigation on Chloroprene-Compatibilized Acrylonitrile Butadiene Rubber/High Density Polyethylene Blends, *Journal of Advanced Research*. 6(6): 811-817.
- Khattag, A.H. (2005), Exploratory Development of VARIM process for manufacturing high temperature polymer matrix composites. Ph.D. Thesis, University of Missouri.
- Kiaw G. (2000), Strategies for Compatibilization of Polymer Blends. *Journal of Polymer Science*.23: 707-757.
- Kim, D., Caruthers, J.M., Peppas, N.A, Meerwall, E. V. (2003), Reactive Compatibilization of SAN/EPDM Blend and Study of the Parameters affecting its Properties. *Iranian Polymer Journal*. 15(12).
- Koefoed M.S.(2003), Modelling and simulation of the VARTM process for wind turbine blades. Ph.D. Dissertation, Aalborg University.
- Koshy, A., Kuriakose, B. and Thomas, S.(1992), Studies on the effect of blend ratio and cure system on the degradation of natural rubber/ethylene-vinyl acetate rubber blends. *Polymer degradation and stabilization*.36(2):137-147.

- Koshy,A., Kuriakose, B.,Thomas, S. and Varghese, S. (1993), Studies on the effect of blend ratio and crosslinking system on thermal, X-ray and dynamic mechanical properties of blends of natural rubber and ethylene vinyl acetate copolymer.Polymer. 34(16):3428-3436
- krehula, G. (2012), Influence of Calcium Carbonate Filler and Mixing type Process on Structure and Properties of Styrene-Acrylonitrile/Ethylene-Propylene-diene Polymer Blends. Journal of Applied Polymer Science.126: 1257-1266.
- Kumnuantip C. and Sombatsornpop x. (2003), Dynamic Mechanical Properties and Swelling Behaviour of NR/Reclaimed Rubber Blends, Materials Letters.57(21):3167-3147.
- Kwanruethai, B., Manus S. and Natinee, L. (2008), Compatibilization of Natural Rubber (NR) and Chlorosulfonated Polyethylene (CSM) Blends with Zinc Salts of Sulfonated Natural Rubber. Songklanakarin J. Sci. Technol.30(4): 431-499.
- Lawandy, S.N and Botros, S.H. (1991), Effect of Type and Amount of Carbon black on the Interaction between Polychloroprene Rubber and Motor oil. Journal of Applied Polymer Science. 42(1):137-141.
- Leszek, A. (2009). Polymer Alloys Blends Thermodynamics, Rheology. Hanser Publisher S. New York.
- Lui,N.C and Baker, W.E.,(1992),Reactive Polymers for Blend Compatibilization .Advances in Polymer Technology. 11(4):249

- Madani, M., and Aly,R.,(2010), Monitoring of the physical aging of radiation crosslinked conductive rubber blends containing clay nano filler. *Materials and design*,31: 1444-1449.
- Madani, M., andBadawy, M.M., (2005), Influence of electron beam irradiation and step-crosslinking process on solvent penetration and thermal properties of natural rubber vulcanizates. *Polymers and Polymer Composites*(13):93-103.
- Masoud.F., Mahmood M., and Reza G., (1997), Studies on Recycling of Poly(ethylene terephthalate), Beverage Bottles. *Iranian Polymer Journal*.6(4):269-272.
- Meister,J.J.(2000), *Polymer modification: Principle, Techniques and Applications*. 1st edition, Marcel Dekker. New York.
- Naskar, A.K., Bhowmick, A.K and De, S.K (2001). Thermoplastic Elastomeric Composition Based on Ground Rubber Tire. *Polymer Engineering Science*.41(6):1087.
- Naskar, N., Debnath, S. C., and Basu, D. K. (2004). Polymer Blend: A Novel Method for the Preparation of Carboxylated Nitrile Rubber-Natural Rubber Blends using Bis (di isopropyl) thiophosphoryl polysulfide. *Journal of Applied Polymer science*. 80: 1725-1736.
- Nasrul, A. and Nairul H. (2008), Mechanical properties of Polystyrene/Polypropylene Reinforced Coconut and Jute Fibres. *CUSTE International Conference*. CRC Press.

- Ning, Y. Hesheng, X. Jinkui, W., Yanhu, Z., Guoxia, F., Chen, C. (2012), Compatibilization of Natural Rubber/High Density Polyethylene Thermoplastic Vulcanizate with Phyleneoxide through Ultrasonically Assisted Latex Mixing. *Journal of Applied Polymer Science*. 52:1007-1014.
- Nwanonenyi, S.C, Obidiegwu, M.U., and Onuegbu, G.C, (2013), Effect of Particle sizes, Filler Content and Compatibilization on the Properties of Linear Low Density Polyethylene filled Periwinkle Shell Powder. *The International Journal of Engineering and Science*. Vol.(2):1-8.
- Oboh, J.O., Agbajelola, D.O., and Okafor, J.O (2015), Effect of Delignified Coir Fibre Particulate Filler on Physical Properties of Natural Rubber Vulcanizate. *International Engineering Conference*. 458-464.
- Okieimen F.E, Akinlabi A. K, Aigbodion A. L, Bakare I, Oladoja N. A (2003), Effect of Epoxidized Natural Rubber on the Processability and Vulcanizate Properties of Natural Rubber. *Nigeria Journal of Polymer Science Technology*. vol 3(1): 2334-2351.
- Olabisi ,O., Robeson, L.M., and Shaw, M.T(1979), *Polymer-Polymer miscibility*, Academic Press, New York.
- Onyeagoro, G.N(2012). *Cure Characteristics and Physico-Mechanical Properties of Carbonized Bamboo Fibre filled Natural Rubber*

vulcanizate. International Journal of Modern Engineering Research(IJMER). 2: 4683-4690.

Onyeagoro, G.N., (2012), Influence of Carbonized Dikanut Shell Powder on the Vulcanizate Properties of Natural Rubber/Acrylonitril-butadiene Rubber Blend. Academic Research International. 2(3): 3321-3325.

Onyeagoro, G.N., Ewulonu C.M., and Ayo, M.D. (2013), Properties of Reactive Compatibilized Dikanut Shell Powder filled Recycled Polypropylene/poly(ethylene terephthalate) bio-composites using Maleated Polypropylene and Epoxy Resin Dual Compatibilizers. American Journal of Engineering Research. 2:158-169.

Onyeagoro, G.N., Ohaeri, E.G., Arukalam, I.O., Uko, M.J., Enwerem, U.O., and Uzoigwe, C.O., (2014). Effect of MAPI/HMDA dual compatibilizer and fillre loading on physico-mechanical and water sorption properties of natural rubber/polyethylene terephthalate/dikanut shell powder composites. British journal of applied science and technology. 4: 3383-3401.

Paul, D.R., and Newman, S. (1978), Polymer Blends. Academic Press, New York. 1(2).

Ramesan, M.T., Kuriakose, B., Pradeep, R., Alex and Varghese. (2001), Compatibilization of SBR/NBR Blends using Chemically Modified Styrene Butadiene Rubber. International Polymer Processing. 16 (2): 183-191.

- Robert, M., Golok, B.N., Vijayn k., and Ncelakanthan, N.R., (2009), Mechanical dynamic mechanical properties of miscible blends of epoxidized natural rubber and poly(ethylene-co-acrylic acid). *J.Polymer science*. 37(24): 5387-5394.
- Sa-Adriyajan, S.C., Siton, C and Supayang, P.V.,(2012), Mechanical properties and cure test of a Natural rubber/Poly(Vinyl alcohol) blend. *Rubber Chemistry and Technology*. 85(1):147-156.
- Sathe, S; Devi, S and Rao, K, (1996), Relationship between Morphology and Compatibilized Ternary Blends of Polypropylene and Nylon 6. *Journal of Applied Polymer Science*.61 (1): 97 – 107.
- Shailendra M., Lorcan L and Mary A.K., (2013), Study on an Increased Mechanical Recycling Target for Plastics. *Bio-Intelligence*. plastic Recyclers Europe.
- Silvia, H.P., Maria P.M., Luiz, H. C., (2013), Effect of Lubricant on Mechanical and Rheological Properties of Compatibilized PP/Sawdust Composites. *Science Direct*.94(2):800-806.
- Sirilux, P. Yuko, I., Yota, k. and Takeshi, S. (2008), Cattle Bone as Reinforcing Filler for Natural Rubber. *European Polymer Journal*. 44: 4157-4164.
- Sirisinha, C., Baulek-Limcharoen, S.andThunyarittikorn, J. (2003), Relationships among Blending Conditions, Size of Dispersed Phase, and Oil Resistance in Natural Rubber and Nitrile Rubber Blends. *Journal of Applied Polymer Science*. 82:1232-1237.

- Sirisinha, C., Saeoui, P and Guaysomboon, J. (2004), Oil and thermal aging resistance in compatibilized and thermally stabilized chlorinated polyethylene/natural rubber blends. *Journal of Applied Polymer*. 45:4909-4916.
- Sirqueira, A.S., and Soares B.G. (2003), The effect of mercapto and thioacetate-modified EPDM on the curing parameters and mechanical properties of natural rubber/EPDM blends. *European polymer journal*.(39):2283-2290.
- Stephen, R., Jose, S., Joseph, K., Thomas, S and Ommen, Z. (2006), Thermal Stability and Ageing Properties of Sulphur and Gamma Radiation Vulcanized Natural Rubber(NR) and Carboxylated Styrene Butadiene Rubber (XSBR) Lattices and their Blends. *Polym. Degrad. Stab.*91(8):1717-1725.
- Tillekeratne, I., and Scott, G., (2006), Studies on the use of solar energy for preparation of liquid rubber. *Journal of rubber research Institute, Srilanka*. 54: 501-507.
- Tzetzis, D.(2008), Experimental and finite element analysis on the performance of vacuum-assisted resin infused single scarf repairs. *Materials and Design*. 29(2): 436-449
- Utracki, A.L.,(1999), *Polymer alloys and blends*. New York. Hanser.
- Utracki, A.L.,(2002), *Introduction to Polymer Blends*. *Polymer Blends Handbook*. 1, Kluwer Academic Publishers, Dordrecht (2002). 12-24.

- Valsamis, L; Kearney, M; Dagli, S; Merhta, D and Polchocki, A, (1988), Phase Morphology of a Model Polyblend Fabricated in Industrial mixers: Time and Melt flow Dependent Supradomain Structures, *Advances in Polymer Technology*. 8(2): 115 – 130.
- Wolf, S; Wang, Mand Tan, E, (1994). Surface energy of fillers and its effects on rubber reinforcement. Part 1. *Kautsch.GummiKunstst*, 47:780-798.
- Xanthos, M., Daghi, S.S., (1991), Compatibilization of polymer blends by reactive processing. *Polymer Engineering Science*. 31(13):929.
- Yan, N. Xia, H., Wu, J., Zhan, Y., Fei, G and Chen, C. (2012), Compatibilization of natural rubber/high density polyethylene thermoplastic vulcanizate with graphene oxide through ultrasonically assisted latex mixing. *Journal of applied polymer science*. 37861-37872.
- Zhang L., Deng X and Huang, Z, (1997), Miscibility, Thermal behaviour and morphological structure of poly(3-hydroxybutyrate) and Ethyl cellulose binary blends. *Polymer Journal*. 38: 5379-5387.



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