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Thermoplastic/Ground tyre rubber blends for potential application in automotive Components

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List of Abbreviations

ABS- Acrylonitrile-butadiene-styrene

BFD- Buffing dust

CR – Crumb rubber

DSC - Differential Scanning Calorimetry

DMA- Dynamic Mechanical Analysis

ELT - End-of-Life-Tyres

EPDM– Ethylene-propylene-diene-monomer

EP– Ethylene propylene rubber

EPR– Ethylene propylene rubber

FFKM- Perflouroelastomers

FKM- Flouroelastomer

GTR- Ground tyre rubber

HDPE – High density polyethylene

l.w.t – Length, width, thickness

MFI - Melt Flow Index

Mt- Million tons

M_w – Molecular weight

MWD - Molecular weight distribution

NAAMSA- National Association of Automobile Manufactures of South Africa

NR- Natural rubber

OECD- Organization for Economic Cooperation and Development

OEM- Original Equipment Manufacturers

PA– Polyamide

PBT- polybutylene terephthalate

PC-Polycarbonate

PE – Polyethylene

PMMA- Poly(methyl methacrylate)

PP – Polypropylene

PPE-polyphenylene ether

PS- Polystyrene

PTFE- Polytetrafluoroethylene

PUR– Polyurethane

PVC – Poly vinyl chloride

SBR- Styrene butadiene rubber

SDT- Simultaneous DSC-TGA (SDT)

SEM- Scanning Electron Microscope

SWT- sidewall and tread

Tg- Glass transition temperature

TGA – Thermogravimetric Analysis

TPE– Thermoplastic elastomers

TPO– Thermoplastic olefins

TPV– Thermoplastic vulcanizates

TT- Truck Treads

UV- Ultraviolet

V – Vistamaxx^{TM} 6202

VW- Volkswagen

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ABSTRACT

The development of thermoplastic elastomers (TPE) based on the utilization of Ground Tyre Rubber (GTR) generated from waste tyres is a promising alternative strategy to deal with environmental burden caused by the accumulation of waste tyres in landfill sites. The market for TPE blends is at a rapid increase owing to the material having an improved balance of properties than those obtained from a single polymer such as impact strength while being easier to process and recycle.

This study utilized PP-T20 and GTR material for waste tyres to prepare a low-cost waste based TPE which will have properties of both PP and GTR components for the potential utilization in automotive parts. GTR and PP are incompatible therefore an EPR (ethylene-propylene monomer) was incorporated in the formulations at a ratio of 80%GTR: 20% EPR to overcome the lack of adhesion between the materials. The morphology of the blends studied by SEM indicated that the encapsulation of GTR by the EPR can be an adequate technique to formulate TPE blends based on recycled materials.

The results highlighted the importance of control of factors such as particle size and distribution, rubber composition etc. Impact tests for homogenous particle distribution and smaller particles showed more improvement. The 3-point bend test indicated the formation of elastomeric stress-strain curves upon addition of the GTR.

Tan delta (Tg) values decreased with the addition of GTR however the intensity of the peak increased, and this increase was higher in the GTR that contained butadiene rubber. This GTR also has the lowest onset temperature characteristic of butadiene rubber. Additionally, morphology analysis showed that blends with great deformation to the surface and a discontinuous matrix caused by inadequate adhesion of the thermoplastic with the GTR had poor mechanical properties.

1. INTRODUCTION

Automobiles have been around since 1886 invented by Karl Benz and Henry Ford the brands known today as Mercedes-Benz and Ford [1]. However, the utility of automobiles at the time was for leisure to the aristocrats and the wealthy, where larger population did not have access to automobiles. Over the years various automobile brands immerged in Europe and America, resulting in different types of vehicles being made. This variants of automobiles are trucks, buses, tractors, and passenger vehicles, which are utilized for convenient transportation of passengers, goods, and services both domestically and globally [2]. As it stands automobiles have become one part of daily lifestyle needs across various population classes all over the world. Currently, South Africa is on the top 25 automobiles producers in the world, and the largest in Africa [3]. According to the National Association of Automobile Manufactures of South Africa (NAAMSA)'s flash report, South Africa manufactures and assembles approximately half a million automobiles per year and 31 455 passenger vehicles were reported to be sold locally as of the first half of this year [1, 3]. There are over 55 vehicle brands made in South Africa selling more than 3000 model derivatives and 26 bakkie brands with more than 700 bakkie models [3]. Furthermore, South Africa manufactures over 200 automobile components, ranging from tyres, seats, spare parts, and other materials [3]. As a result, the automobile industry at large presently employs 110 000 people to manufacture and assemble vehicles and parts and is responsible for approximately 457 000 jobs in the formal sector of the South African economy [3, 4].

1.1. Automobiles

a. Parts and Components of Automobiles:

A typical automobile is made up of approximately 30 000 parts/components; these components differ in their nature and material type category [5, 6]. The commonly utilized materials are ferrous metals and alloys (steel and/or aluminum etc), rubber, upholstery glass, and plastics. Factors such as ease of processing, thermal stability, UV and chemical resistance together with mechanical strength and durability are an important consideration when making the selection of the material to use when manufacturing a part [7, 8]. Different types of steel have been utilized in varying levels of rigidity to construct the body and chassis of the automobile. On average 900 kilograms of steel is utilized in a single automobile [ref]. This demand is mainly due to its high modulus elasticity, high strength and weldability when compared to the alternative materials used in the automotive industry. It is such properties that make steel ideal for the construction of the body and chassis of a vehicle [7, 8].

Metal accounts for 68% of the weight of a vehicle, while rubbers and elastomers account for 5% of the weight [8]. However, the 5% can be summed up as tyres contributing about a third of the weight, while the rest is from V-belts, trimming profiles, hoses, seals, and gaskets [6-8].

Plastics are the second most common class of automotive material by weight after ferrous metals and alloys [7, 8]. A typical passenger vehicle is made up of 110-150 kilograms of plastics and composite materials accounting for approximately 8-10% of the total weight of the automobile [6]. There are about 10 000 parts in an automobile that are made out of plastics. Depending on the make and the model range of the vehicle, plastics parts offer a wide range of applications with about 50% of the plastic content being utilized in interior components such as seat assemblies, dashboards and safety subsystems and doors [5, 8]. Figure 1.1 details the breakdown of the materials utilized in a vehicle by weight [9].

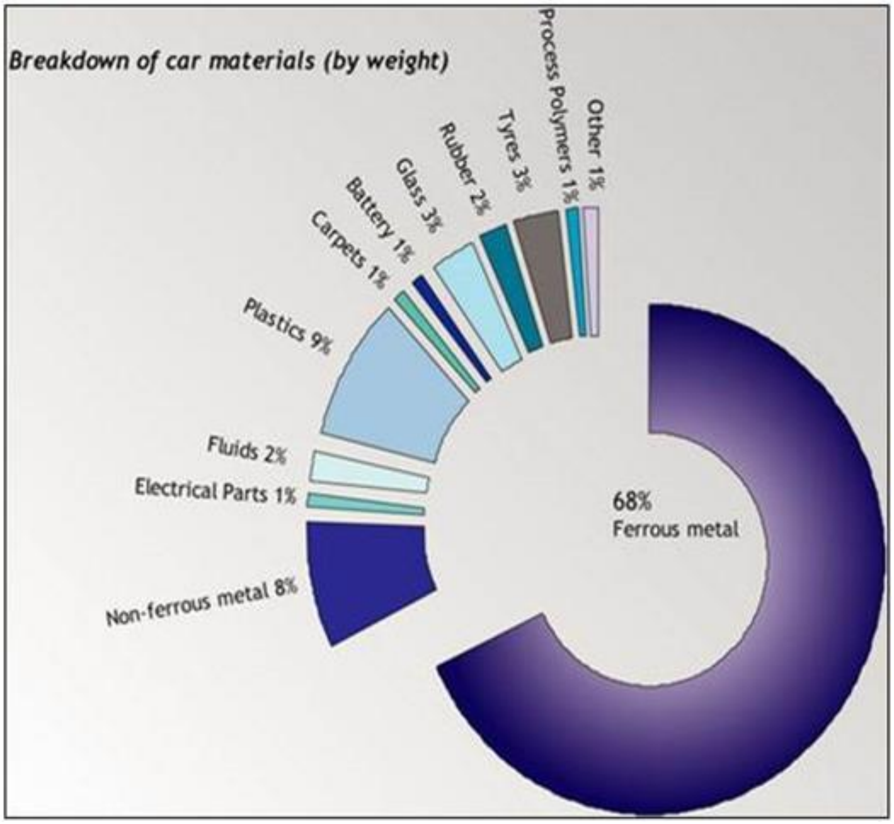


Figure 1.1: The breakdown of materials used in a vehicle by weight [9].

During field performance automobiles are subjected to abrasion and high impacts, therefore the material used in their production must be safe and offer overall vehicle stability. There is an increasing requirement for materials used in a vehicle to have high melt viscosities and thin wall moulding to reduce the weight of the vehicle [10]. Due to the high output demand, injection moulding is the typical plastic manufacturing technology for the automotive components since total automation is possible and different mold sizes and shapes can be utilized ensuring that the end-product has the desired specifications at all times it is also the cheapest process for standard mass-distributed parts [11, 12].Thermoplastics are increasingly being utilization for both interior and exterior automotive applications as seen in Table 1.1 [7] as they are easy to mold and compatible with various processing methods.

Table 1.1: Thermoplastics utilized in a vehicle [7].

Component	Types of Plastics	Weight Contribution(kg)
Exterior Components	ABS, PA, PBT, PP	4
Lighting	PC, PBT, ABS, PMMA	5
Body (including panels)	PP, PPE	6
Upholstery	PVC, PUR, PP, PE	8
Under-bonnet components	PA, PP, PBT	9
Bumpers	PS, ABS, PC/PBT	10
Seating	PUR, PP, PVC, ABS, PA	13
Interior Trim	PP, ABS, PET, PVC	20
Dashboard	PP, ABS, PC/PBT	7
Fuel systems	HDPE, PA, PP, PBT	6
Electrical components	PP, PE, PBT, PA, PVC	7
Liquid reservoirs	PP, HDPE, PA	1
Total		**96**

b. Plastic Parts:

According to the OECD, the global plastic production for the year 2019 was 460 million tons, of which 5-13% is consumed by the automotive and transportation industry [13] According to Gupta and Singhal [refs], there are approximately 13 different thermoplastics that may be used in one model of a passenger vehicle. Thermoplastics such as Polypropylene (PP), Polyamide (PA; nylon 6 and nylon 6,6), High Density Polyethylene (HDPE) Polyurethane (PUR), Polycarbonate (PC), and Acrylonitrile Butadiene Styrene (ABS) are the most common plastics to be utilized in automotive parts (Figure 1.2). However, PP is the most dominant plastic and accounts for 32% and is typically found in interior trims all the way to chemical/fluid tanks/reservoirs and in under the hood applications of the vehicle [7]. Utilization of PP and PP-based material in automotives is substantial due to PP having relatively better chemical resistance, durability, ease of processability amongst other things and most importantly relatively cheaper than other competing materials [14]. Furthermore, its properties can be improved when compounded with several fillers which can either be synthetic or natural [10].

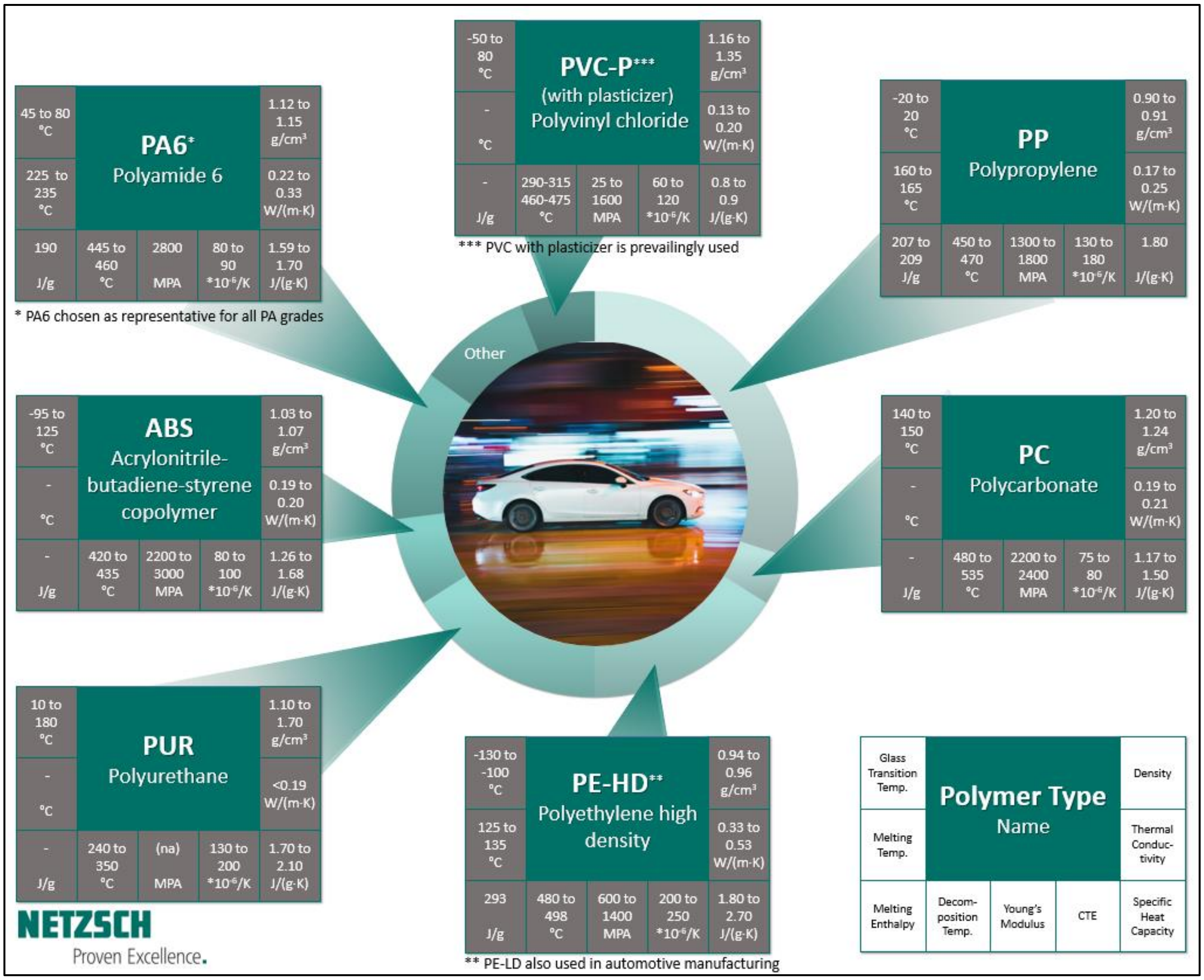


Figure 1.2: The illustration of the thermoplastic demand in a vehicle [14].

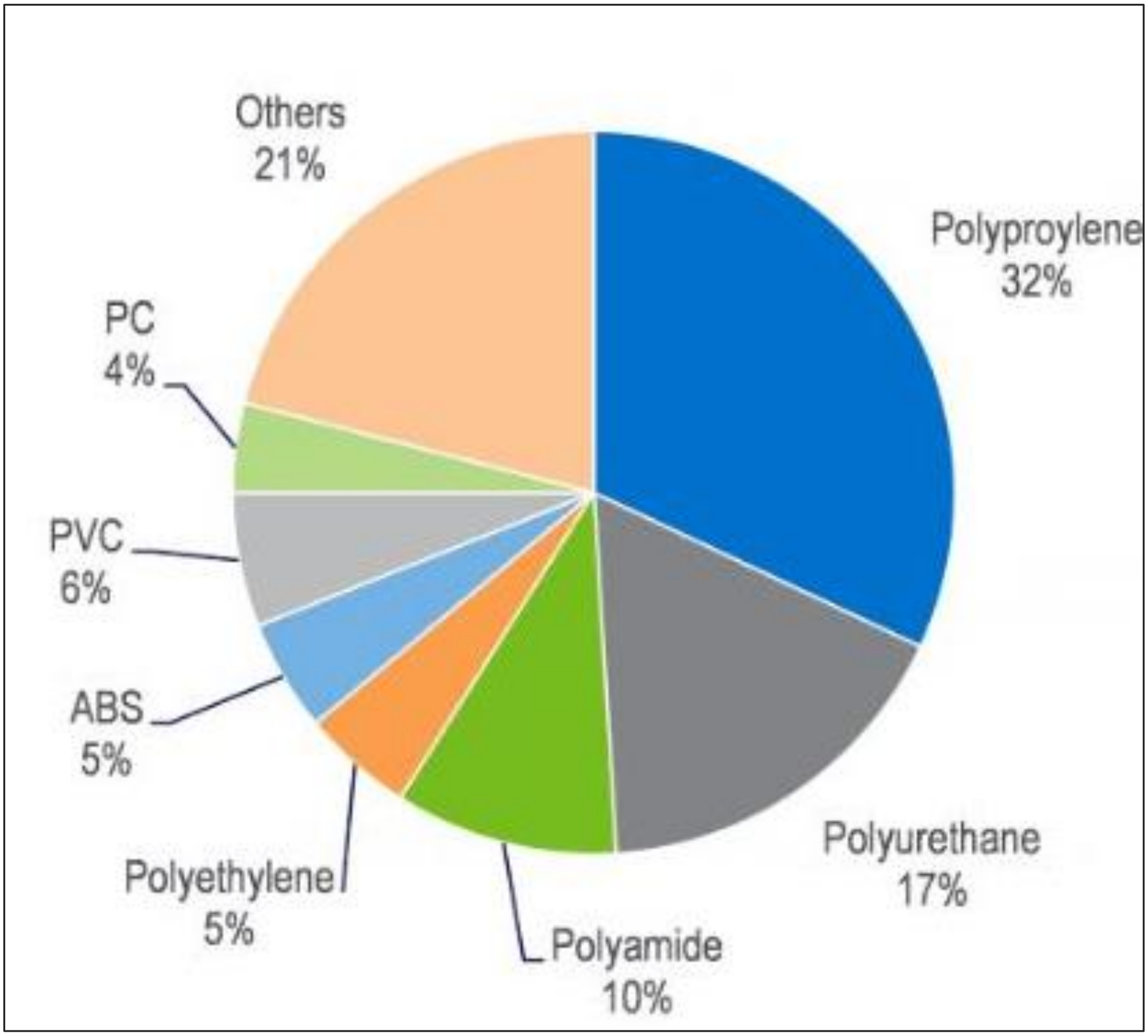


Figure 1.3 : North America plastics consumption in automotive sector in 2017 [15]

1.2. Polypropylene

According to Maier and Calafut [16], polypropylene is one of the extensively used commodity thermoplastics with a market share growth of 6-7% annually. Figure 1.4 illustrates that it is behind low density polyethylenes (LDPE/LLDPE) as the most used thermoplastic. The increase in the utilization of PP is due to its adaptability, and having good combination of properties at a relatively low price [16]. This thermoplastic is compatible with an array of processing techniques due to the contribution of the stereochemistry of the material [15].

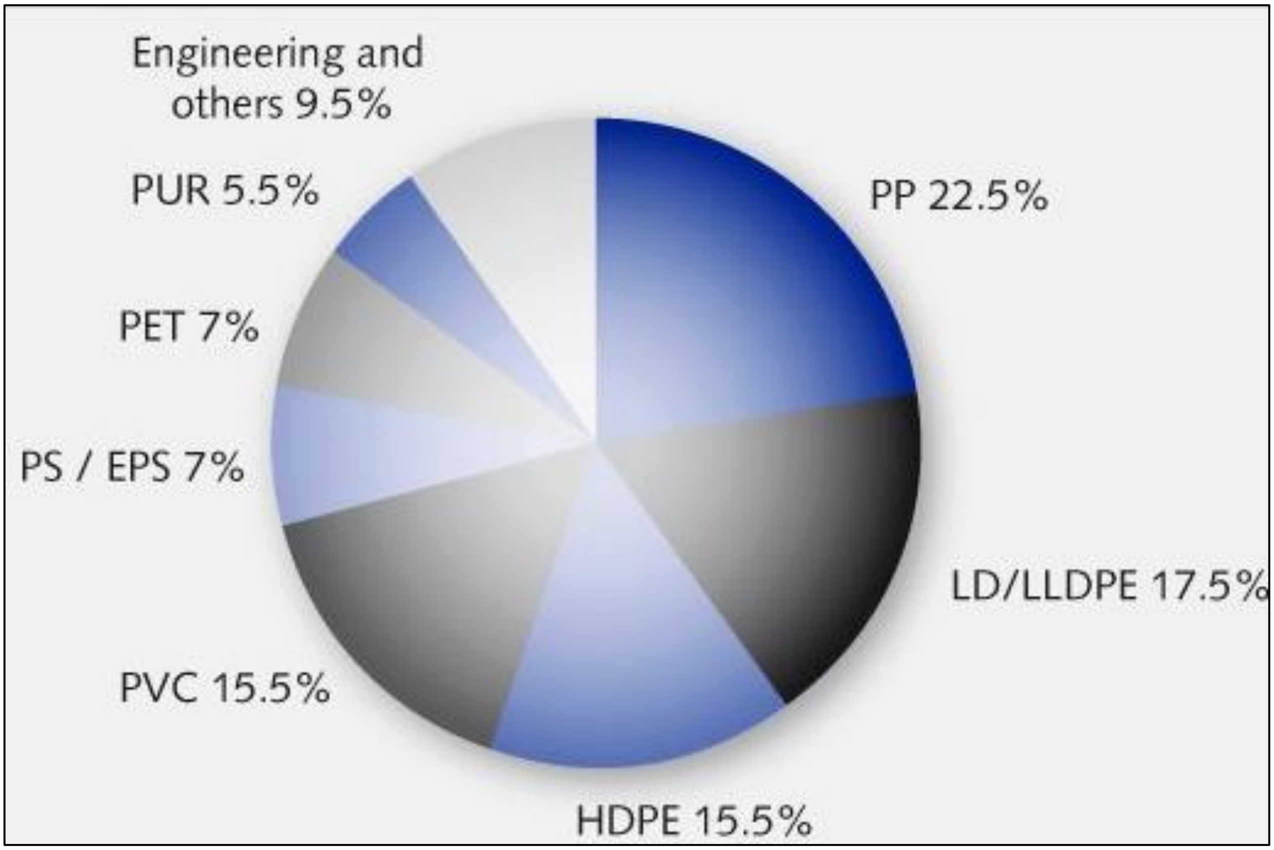


Figure 1.4: Polypropylene share of world thermoplastic consumption [17].

Polypropylene has three different forms available commercially namely, homopolymer, random copolymer and block copolymer. Homopolymers contain a propylene monomer in a semi-crystalline solid form and are the widely used general purpose grade. The copolymers contain propene and ethane monomers, random copolymers feature a random insertion of about 6% ethene in the PP chains. In block copolymers the co-monomers are arranged in a regular pattern making them less brittle and they contain a higher ethene content than the random copolymers which is between 5-15% [18-20]

Impact copolymer is another type of PP which is a homopolymer containing a random copolymer phase with propylene and ethylene; 45-65% ethylene content is mainly used in the automotive industry [10, 19].

The three physical configurations are isotactic PP (iPP), syndiotactic PP (sPP) and atactic PP (aPP). PP is prepared by polymerizing propylene monomer in a gas phase which is subjected to an organometallic (Ziegler-Natta) and transition metal catalyst [19]. Propylene adds to the polymer chain in a particular orientation depending on the chemical and crystal structure of the used catalyst this addition leads to an increase in the chain length. The propylene molecules are added head-to-tail in the polymer chain this results in the formation of polypropylene [18, 19]. Isotactic PP is the most common configuration commercially where the pendant methyl groups are attached on the same side to every other carbon atom on the linear polymer chain; they therefore have the same configuration. The regular and repeating arrangement in iPP leads to a high degree of crystallinity. In syndiotactic PP the pendant methyl groups are on opposite sides of the chain and of opposite configurations while for atactic PP the pendant methyl groups are randomly arranged [19, 21].These ensure the possibility to modify PP to suit a wide range of applications this possibility is also enhanced by the ability of PP to be compounded with fillers and reinforcements [18].

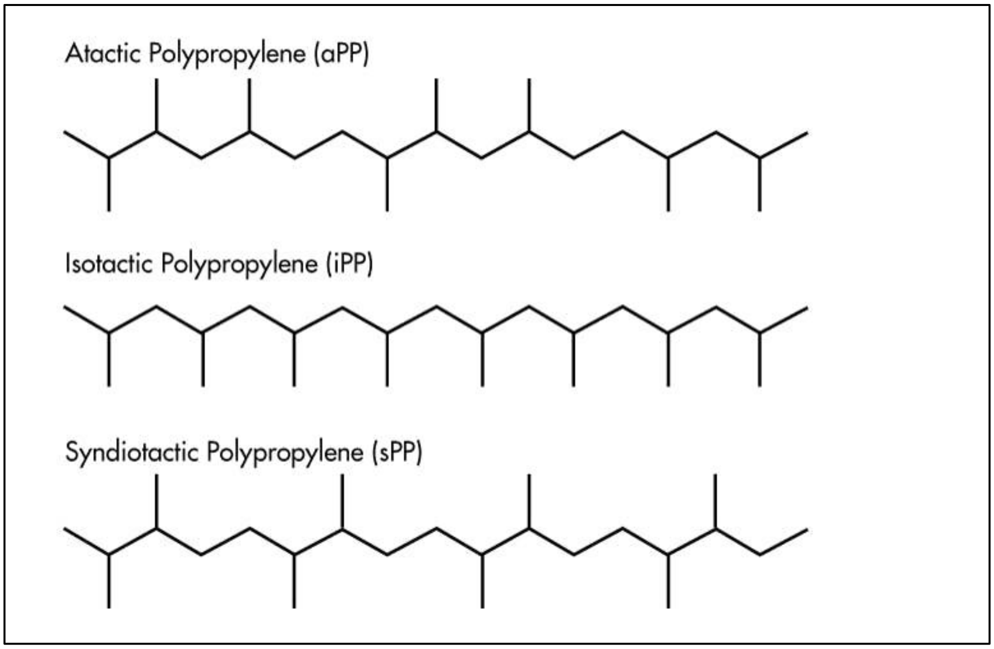


Figure 1.5: Chemical structure and orientations of PP [19].

The commercial form of PP is a semicrystalline thermoplastic with a melting point around 165 ℃. Varying degrees of crystallinity and different types of crystal structures are possible depending on the stereochemical structure, the presence of additives and the crystallization conditions. The melting point temperature of 165 ℃ is higher than some commodity thermoplastics such as polyethylene and polyvinyl chloride; hence PP has better heat resistance. However, unmodified PP is brittle at sub-ambient temperatures [18, 19].

1.2.1 Characteristics and Properties of PP

The performance and utilization of materials is vastly dependent on the characteristics and properties exhibited by materials. For polymers in particular, characteristics such as Molecular weight and molecular distribution accompanied by the stereochemistry, set as an equation which leads chemical, mechanical, and physical properties of polymers [11, 19]. From such properties one can derive the processing conditions, chemical exposure medium, mechanical performance, storage, and weathering exposure conditions just to mention a few. Knowing the chemical resistance of the polymer aids the determination of which applications are suited to avoid exposure to solvents or anything that may lead to loss of functional ability. Oxidative degradation leads to chemical structure changes therefore affecting the crystallinity of the polymer an example is photooxidation which causes a polymer to lose toughness and become brittle thus affecting mechanical performance.

I. Stereochemistry

Polypropylene is produced in three stereo configurations; Atactic, Isotactic, and syndiotactic which all vary in properties [16, 19]. The isotactic form of polypropylene has the highest crystallinity amongst the three, resulting in relatively higher stiffness and tensile strength while syndiotactic polypropylene has lesser stiffness than isotactic. However, increasing crystallinity results in more opaque materials with lesser transparency and clarity, also reduced impact resistance due to the induced stiffness [19]. Nevertheless, atactic PP has the lowest crystallinity due to its irregular configuration resulting in much higher impact resistance than the two configurations of PP. In addition, atactic PP is clearer and more transparent than the other two PP forms making It ideal for films and wraps [16, 19]. It should be noted that commercially available PP is rarely acquired as one form of configuration, where a mix of two sometimes all three configurations can be found [19]. This is due to several reasons, one being the selectivity of the process during polymerization, another being a balance of properties since each configuration brings about different properties [16, 19, 20]. Additionally, PP can exist as homopolymer, block copolymer and random copolymer. These also influence mechanical properties. For example, the homopolymer has high tensile strength than the copolymer while the copolymer is more flexible than the homopolymer. Table 1.2 lists the properties of polypropylene and the effects of different stereoisomers [19].

Table 1.2: Effect of different stereoisomers on Polypropylene properties [19]

Properties	**Atactic**	**Isotactic**
Stiffness	Decreases	Increases
Moduli	Decreases	Increases
Room temperature: Impact resistance	Increases	Decreases
Strength	Decreases	Increases
Elongation	Increases	Decreases
Melting temperature	Decreases	Increases
Solubility	Increases	Decreases
Smoke and fume generation	Increases	Decreases

II. Molecular weight

An increase in molecular weight results from longer chains. The molecular weight for PP generally ranges from 220 000-700 000 g/mol with melt flow indices ranging from 0.3 g/10 min to over 1000 g/ 10 min [19]. The melt flow index (MFI) is the ease of flow of the melt and provides an estimate of the average molecular weight of the polymer. It is related to molecular weight in that higher MFI values translates to lower molecular weight. Furthermore, the MFI can indicate which processing technique is best suited for a material [19]. Materials with a low MFI are used in processes that require increased melt strength such as sheet and blow moulding while those with MFI from 8 g/10 min are suited for extrusion coating and injection moulding of thin-walled part that require rapid filling of the mold [9, 19]

Molecular weight is also related to molecular weight distribution (MWD) which indicates the variation in chain lengths in a polymer and it is the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). It is narrow when most molecular chains are the same length [16, 19]. MWD also influences processability; PP with broad MWD is shear sensitive and can be processed by injection moulding.

The physical properties of PP are affected by its crystallinity thus the structural arrangement of the polymer networks. An increase in crystallinity is seen in shorter chains with broader MWD and lower molecular weights and it is characterized by a decrease in properties such as impact resistance, and flow rate due to the increase in the rigid sites in the PP matrix [19, 20]. Therefore, to improve impact strength and tensile elongation it is ideal for PP utilized to have a higher molecular weight, narrow molecular weight distribution and increased mobile sites in its matrix according Kontopoulou and Ho [22] to this can be done by adding elastomeric materials. These materials will increase the mobility, impact strength, and elongation while maintaining the crystallinity of the material; thus ensuring minimal decrease in tensile strength and hardness [18, 19]. Table 1.3 lists the general effects of increasing molecular weight on PP properties.

Table1.3: The effect of increasing Molecular weight on PP properties [19]

Properties	Increasing Molecular weight
Moduli	Decreases
Impact resistance	Increases
Strength	Decreases
Elongation	Increases
Solubility	Increases
Melting temperature	Decreases

III. Chemical resistance

PP is nonpolar as such PP is resistant to attack by polar chemicals such as alcohols, soaps, and wetting agents; however, the plastic does soften or undergo surface crazing when exposed to liquid hydrocarbons, chlorinated solvents, and strong oxidizing agents [15]. Exposing PP to certain chemicals can cause blistering, swelling on the surface leading to an inhomogeneous surface, thus loss of functional ability [19]. Factors that affect chemical resistance include molecular weight where PP with a lower molecular weight tends to be more crystalline and therefore more chemically resistant. Other factors include mechanical load, type of fillers used and the temperature and duration of the exposure

IV. Oxidation

Polymer oxidation occurs through a free radical chain reaction. Heat, mechanical stress or the presence of oxygen and metal catalyst residues cause homolytic cleavage of either the carbon-carbon or the carbon-hydrogen bonds in the PP chain. The initiation of this reaction results in the formation of two radicals with an unpaired electron, propagated through the formation of a hydroperoxide and another free radical. Finally, the presence of a tertiary hydrogen on the carbon atom bonded to the pendant methyl group results in PP being highly susceptible to oxidation since the PP radical is formed form the abstraction of the tertiary hydrogen [21]. During oxidation, polypropylene undergoes oxidative chain scission which reduces the molecular weight this process occurs through a disintegration of an alkoxy radical in the polymer chain under normal processing conditions such as injection moulding. The decrease in molecular weight leads to PP becoming more brittle and to the development of fine cracks which further decreases the materials toughness characterized by loss of impact strength among other mechanical failures [19]. Additionally, oxidation produces carboxylic acids, aldehydes etc., as by products and this results in chemical modifications such as yellowing.

1.2.2 Applications of PP in automobiles

The automotive industry is the second largest consumer of PP following the packaging industry (Figure 1.5) [15]. Polypropylene is used throughout the automobiles in interiors, exteriors, and under-the-hood parts of the vehicle. Mineral filled and glass reinforced PP, PP foams, PP homopolymers and copolymers as well as thermoplastic vulcanizates are used in application ranging from structural components and energy absorbing media to interior trim, carpeting and fluid containers [16, 19].

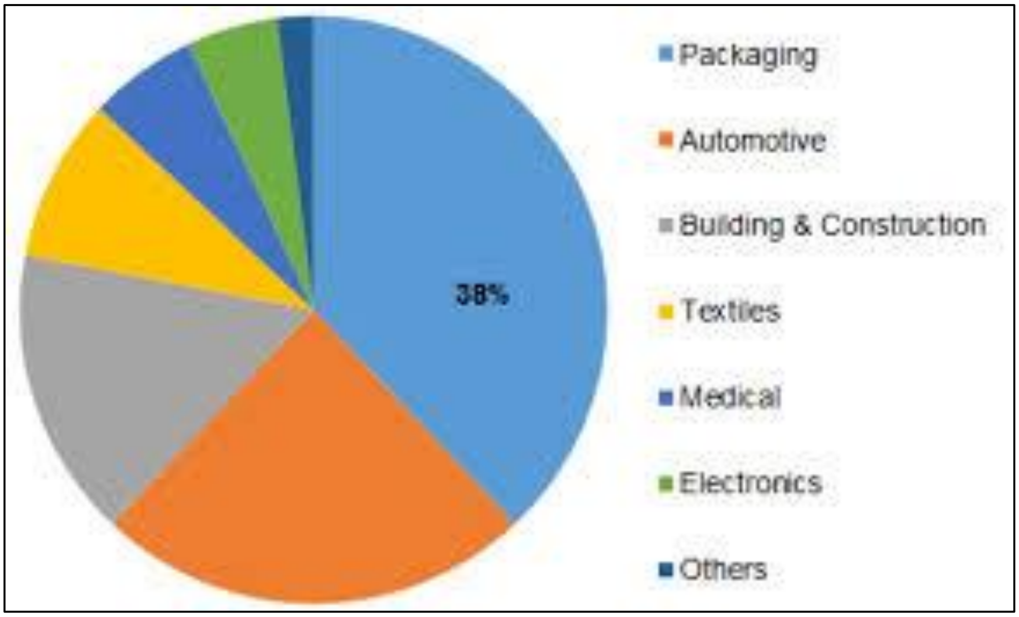


Figure 1.5: Consumption of Polypropylene in different applications [15]

Most exterior and interior automotive parts require good impact resistance and rigidity as such PP block copolymer are often utilized for their manufacture [19, 22]. Blends of PP/EPDM/talc are also often utilized, since PP has poor impact resistance when compared to other thermoplastics used in automobiles such as polycarbonate and ABS to mention a few; there is a need to incorporate an elastomer modifier such as EPDM which improves impact. The addition of fillers such as talc provides reinforcement to PP, increases rigidity and gives UV stabilization for parts that are exposed to the sun [19].

I. *Exterior automotive applications*

Exterior parts must comply with high performance quality. These parts often function as protective shields for other parts of the car and include but are not limited to bumpers, mirror housing and underbody covers to name a few. Therefore, they must be able to absorb impacts in minor collisions; those that are exposed to sunlight must be UV stabilized and have excellent weathering and chemical resistant properties. Automobile manufacturers such as Opel, Ford (Orion, Escort) and Volvo utilize PP for their bumpers and Volkswagen (Polo Vivo) utilizes PP/EPDM blends for their underbody covers [19].

II. *Interior automotive applications*

The requirement for these components is abrasion resistance, color fastness, those within a specific radius of the driver cannot break into pieces with jagged and sharp surfaces on impact. These components must also be aesthetically pleasing and during operation they must not rattle and squeak [ref]. An impact modified and talc filled grade of PP is often utilized; its applications include door post cladding and pockets, fascia panels and door panels [10, 19]. Volkswagen uses PP reinforced with 20% talc for pillar trims of the Polo and the material retains toughness even at low temperatures but has poor scratch resistance. In the BMW 3 series PP is used for door handles and provides good rigidity/toughness ratio, scratch resistance, sound-deadening properties, and low thermal expansion [19].

III. *Under the hood automotive applications*

According to Maier and Calafut [19] the engine compartment has the most severe conditions in the automobile with temperatures that vary from extremely cold to hot; the parts in here are exposed to chemical attacks by lubricants, fuel and vibration. Since the engine compartment is prone to higher temperatures, a property of interest is heat resistance for under the hood applications. PP is utilized largely in battery cases, the material property requirements for battery cases includes good rigidity and impact resistance even at low temperatures [19]. Fluid reservoirs and cable ducts are some of the other applications that use PP. Ventilation grilles that use PP show good weathering resistance and retain their visual appearance even after use over several years [19].

1.2.3 Recycling of PP

Production of plastic waste is rapid due to population growth and development of a report by the OECD (the Organization for Economic Cooperation and Development) states that only 9% of plastic waste is recycled while the bulk either ends up in landfills or leaking back into the environment, causing pollution [23, 24].There are environmental safety legislation rules that have been established by governments and local authorities to guide proper disposal of plastic waste after use. Various plastic waste management strategies include pyrolysis, landfills, incineration, bioremediation, and recycling (Table 1.5), these methods ensure good plastic waste disposal and by extension a clean environment.

Table 1.5: Various techniques of handling plastic waste [25, 26]

Type of recycling/reclaiming	**Mechanism**	**Ultimate usage**
Pyrolysis	Waste plastic is subjected to high temperatures under in inert atmosphere, where the produces hydrocarbon oil and pyrolytic char	Energy generation
Incineration	Waste plastic is burned in oxygen, where enough heat and steam are produced to turn turbines for electricity generation	Energy recovery
Landfills	Plastic waste is disposed of by being buried in one area and left to degrade	Energy source (production of methane gas and carbon dioxide)
Recycling	Collecting waste material and converting into secondary raw materials.	Furniture production, Lower demand for new virgin raw materials

Recycling of PP requires material separation due to its diverse applications even with extensive sorting the degradation of PP is substantial and this is another limitation for PP recycling [24, 25]. The quality of recycled PP is often reduced when compared to the virgin material due to the decrease in molecular weight and increase molecular weight distribution [23], as a result of repeated extrusion processes and thermal treatments. The mechanical properties such as tensile strength, elongation at break, crystallinity, viscosity, and impact strength of recycled PP are therefore negatively affected [24]. Nevertheless, Ragaert *et.al* suggests that closed loop recycling for PP may be possible through dilution with virgin plastic [25, 27].

This has been done by Hoechst where during mechanical recycling the recycled resins or regrinds are combined with virgin materials to produce parts with performance properties that match the pure virgin material [23].

PP recovered from battery casings and automobile bumpers was combined with virgin PP, fillers, and other additives to form high-quality PP granules which are used in wheel arches of the VW Polo, footrests in the Honda and in thrust rod covers in the Mercedes [23].

1.2.4 Impact thermoplastics

Polypropylene homopolymer contains only a propylene monomer which provides stiffness, rigidity and toughness but has low impact strength at low temperatures [12]. For automotive applications the requirement is high impact strengths even at low temperatures; hence the use of impact copolymers, thermoplastic olefins, and thermoplastic vulcanization which provide improvement of properties [12, 28]. This is what can be referred to as impact modification of the plastic where the impact copolymers of PP are formed by mechanically blending homopolymers or random copolymers with poly(ethylene-propylene) rubber (EPR), ethylene-propylene-diene monomer (EPDM), polyethylene or plastomers [29, 30]. The copolymer levels in impact copolymers range from 5-25% [20, 31]; thus the copolymer will not be miscible in a homopolymer but rather forms an amorphous rubber phase that is evenly distributed throughout the semicrystalline PP matrix resulting in phase separation. The phase separation leads to the formation of elastomeric nodules which provide impact resistance by absorbing energy that results in local deformation, instead of allowing crack propagation through the material [31].The higher the impact strength of the impact copolymer the resultant stiffness of the material will be reduced since this is determined by the polypropylene matrix [32, 33]. It has been noted that impact copolymers which contain fillers such as glass fiber and talc can withstand higher temperatures without significant distortion, and this is attributed to the fillers such as talc having reinforcing properties and being nucleating agents and thus enhancing the crystallization capacity of the thermoplastic therefore increasing the temperature of melting [28, 31].

EPM or EPR are blends of two polymer systems such as PP as the crystalline matrix and ethylene propylene rubber (EP) or EPDM as the elastomeric phase. Optimum particle dispersion and cold temperature impact resistance are obtained with particle sized of ≤ 1 μm, uniform particle dispersion leads to more consistent properties. The TPO are replacing engineering plastics in the automotive industry due their low cost, formulation flexibility and properties [34].

Thermoplastic vulcanizates (TPV) are also a blend of PP and rubber. They are similar to EPM, except that the rubber is crosslinked or vulcanized. The commonly used rubber is EPDM, EPR, butyl rubber and natural rubber [32, 34]. Typically, the elastomeric phase consists of 1 – 2 μm particles dispersed in the PP matrix. TPV properties, which include hardness, low compression, excellent fatigue resistance and good energy dampening, are determined by the crosslinking of the elastomeric phase while PP phase provides melt processability. Crosslinking provides chemical resistance Increasing the rubber particle size with a lower degree of crosslinking lowers the tensile strength and elastic recovery [32, 35].

Most industrially used thermoplastics are easily recyclable such as PP, PET, and PE's etc. However, as mentioned above, recycling of these materials result in significant reduction of physical and mechanical properties due to the chain scission, resulting in reduced molecular weight and broadened molecular weight distribution [36].

However, companies such as ExxonMobil, Dow, and BASF have developed what is known as thermoplastic elastomers (TPE's), which are a class of materials that have the best of both thermoplastics and elastomers.

1.3.TPE (Thermoplastic elastomers)

TPEs are materials that combine polyolefin hard thermoplastic and the soft elastomeric components [32, 35, 36]. These materials have elastomeric characteristics and can be processed as melts by extrusion and injection molding. Several distinct types of polyolefin-based thermoplastics exist which include [12, 28, 36]:

- dynamically vulcanized blends of ethylene propylene random copolymer
- random block copolymers
- block copolymers
- graft copolymers
- stereo-block polymers.

Synthesis of these elastomers is either by step-growth or chain-growth polymerization. An example of synthesis by chain growth is Polystyrene-*block*-poly(ethylene-*ran*-butylene)-block-polystyrene (SEBS) where two polystyrene blocks at the end of the polymer chain confer partial rigidity to the backbone chains and crystallinity to the bulk. The central block of ethylene-ran-butylene confers flexibility to backbone chain and the amorphous parts of the bulk [35, 36]. TPEs formed by step growth polymerization are composed of short altering polydispersed blocks of soft and hard segments [29, 36].

Thermoplastic elastomers are of considerable commercial importance due to the combination of processability and unique properties, they are considered to be superior to thermoplastics and elastomer due to their functionality [36].They can be used in many applications such as consumer products, electronics, medical devices and automotive.

Table 4 lists some of the commercially used thermoplastics and their applications [37-39].

Table 1.4: Summary of commercially available TPE’s [37, 39]

TPE/TPV	**Manufacturer**	**Type**	**Base**
Santoprene	ExxonMobil	EPR	Ethylene-Propylene
Desmopan	BAYER	TPU	Urethane
Engage	DOW	TPO	Ethylene-Octene Ethylene-Butene
Elastollan	BASF	TPU	Ether-Urethane Ester-Urethane
HYTREL	DuPont	TPC-ET	Ether-Ester
TRPlast	TRP	FFKM	PTFE-FKM

Due to their expensive nature and difficulty of recyclability, TPE’s are becoming less popular and cheaper alternatives are now in demand [29]. Adopting the concept of impact modification where PP is blended with EPDM, waste tyres have been considered as the impact modification materials of choice. Tyres are known to be very durable, elastic and mechanically strong not forgetting inexpensive to purchase upon reaching end of life. This makes waste tyres to be very attractive to utilize in the modification of PP and other thermoplastics to produce what is termed as “Alternative TPE”. Similar to products such as Exxon’s Santoprene and BASF’s Engage, these alternative TPE’s should bare similar properties and processability, where tyre crumbs will provide the elastic part and PP provides the thermoplastic properties. Due to the surface chemistry of these materials compatibility is a challenge since tyres are already vulcanized [22].

1.4. Alternative TPEs

According to the Global Rubber Market about 80% of the rubber consumption is from natural and synthetic rubber materials which are utilized in tyre production with China noted to be the largest consumer of natural rubber for the sole purpose of tyre manufacturing [17]. The increased demand in automotive production is directly accelerated by globalization. This increased demand also translates to the increase in tyre production for a typical passenger car four wheels are produced and 18 wheels are produced for trucks. The formulation of a tyre consists of NR; SBR; BR and about 33% of carbon black and additives such as sulfur for rubber curing [35, 40]. This robust nature of aids in the inability to degrade and contributes to difficulty in recycling [33]. Other factors that contribute to challenges in recycling tyres include consumption of space due to the bulky and heavy nature, high risk of leaching toxins to the soil and contamination of ground water and in most cases being poor sources of rubber [33, 35, 40].

Nevertheless, eventually these tyres reach their end of life and several methods to manage end-of-life are listed in Table 1.5.

Table 1.5: Management of End-of-Life tyres [40, 41]

Type	**Processing**	**End Product/Use**
Pyrolysis	Thermal conversion of waste tyres in inert atmosphere	Fuel gas and oil. Recovered carbon black
Devulcanization	The breakdown of C-S and S-S cross-linking bonds.	Second generation “green” rubber
Crumbing and Granulation	Generation of grounded rubber particles, through mechanical shredding producing materials between the sizes of 100 mesh to 3 mesh	Mats, artificial playgrounds, road paving and development of thermoplastic elastomer
Re-treading and Remoulding	Removal and shredding off the old layer of the tread and sidewall, leaving the carcass exposed. Which is then recoated with a new layer of the tread or both tread and sidewall l	Buffing dust Thermoplastic elastomer development

The use of GTR originating from crumbing and retreading-remolding have been of interest in studies involving the development of thermoplastic elastomer by incorporation of GTR (crumb rubber and buffing dust) in thermoplastic matrices [35]. This is due to these GTRs being a cheaper alternative to be used as impact modifier in thermoplastic blends. The study conducted by Egodage *et.al* [31] reveal the potential the GTR has as an impact modifier and a filler for thermoplastic-GTR blends to be used in automotive application. It involved the investigation of the influence of increasing GTR content in the recycled PP from 0% to complete replacement. The results of the study indicated that lower loading of GTR kept the mechanical properties such as impact failure strength, tensile strength, and modulus constant. At GTR content above 30% difficulty in processability of the blends was apparent. Notable agglomeration of the particles was also apparent at GTR content of 70% [31].

Sadhan *et.al* [42] studied the morphology and specific area of the GTR and their subsequent blends using electron microscopy. The authors determined that the surface of the crumb rubber from the cryogenic processing was smooth, angular, and showed striated lines where fracture had occurred [35, 43, 44]. For the ambient crumb rubbers and those the surface of the particles was rough and convoluted. Furthermore, according to Sadhan *et.al* [42] characterization of the GTRs is important since factors such as composition, particle size and distribution, shape, surface topography and surface functionalities affect performance properties [40].

The replacement of EPDM by GTR promises to be an effective method to reduce tyre waste accumulation while producing TPEs which are easier to recycle and can be processed by extrusion and injection moulding [35]. As mentioned previously GTR is a cost-effective replacement for impact modification, however it does not only provide impact modification because its source is waste tyres which contain elastomers such as SBR and BR that have abrasion resistance properties. BR is also resistant to low temperatures, whilst the presence of carbon black in the GTR provides reinforcement to the blends [34, 35, 45].

The purpose of this study is to screen the 6 GTR which differed in particle size, shape and distribution and cost which is attributed to the technique involved for their production for the potential replacement of EPDM as impact modifiers. This study also seeks to develop cost-reduced alternative which can be potentially utilized in automotive parts manufacturing. The GTR was in the form of crumbs with mesh sizes from 30 mesh to 60 mesh and the buffing dusts from truck re-treads (BFD TT) and passenger tyre remolds (BFD SWT). PP-T20 is used as the benchmark as per original equipment manufacturer to test against the blends from formulations containing different amounts of GTR content and PP-T20 content.

The material properties to be investigated are thermal, mechanical, and morphological which will be carried out for PP-T20, GTR as well as the formulated blends to examine both chemical and physical attributes of the blends. Evaluation of thermal stability and glass transition behaviour will be done using Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) respectively. Mechanical properties and Flexural properties will be assessed in the form of impact strength and 3-point bend and dual cantilever. Morphology studies will be conducted to understand blend and GTR composition and structure. The study of morphology will highlight the possibility of optimizing mechanical properties of polymer blends by selection suitable blend compositions and processing conditions.

The objectives of the study are:

1. Characterize the raw materials (GTR and PP-T20)
2. Prepare blends of PP/GTR and study the interaction
3. To study the physical, morphological, and thermal properties of the blends
4. Develop optimum TPE blends from PP-T20/GTR formulations

2. EXPERIMENTAL

Summarized in this section are the materials, the instruments used for the experiments. This section also details the formulations, the sample preparation, experimental setup, and the procedure followed.

2.1. Materials

2.1.1. Polymers

Automotive copolymer grade polypropylene-20% Talc Masterbatch (Hostacom TRC352 C12507) from Lyondell Basell with a melt flow rate of 18g/10 min was used as the base polymer component. The impact modifier elastomeric material utilized for the study was Ground Tyre Rubber (GTR) obtained from both truck and passenger tyres treads and sidewalls, in a form of crumb rubber and buffing dust. The buffing dust was sourced from retreading truck tyres and passenger tyres re-moulding; while the crumb rubber was sourced in four variants of two types, three of the same type which differ in particle size produced and a single variant produced cryogenically. Table 2.1 gives a detailed summary of the utilized GTR for the study.

Table 2.1: Summary of sourced Ground Tyre Rubber Materials

GTR	Type		Supplier
30# CR	Crumb Rubber	Dry crumbing	Mathe Group
40# CR			
60# CR			
60#C CR		Cryogenic Crumbing	Patco Technologies
BFD-TT	Buffing Dust	Re-treading	TrenTyre
BFD-SWT		Re-moulding	Safari Tyres

The binding material utilized was Vistamaxx^{TM} 6202, an EPR from ExxonMobil which contain 15% ethylene with a melt flow of 20 g/10min.

2.2. Processing method

The investigation to the size, shape and form of ground tyre rubber as an impact modifier was carried out by preparing ternary blends of PP-GTR with an EPR(Vistmaxx) as binder. The ratio between GTR and the binding material was kept constant through the study as 80-20 (GTR-EPR), which was obtained from previous studied demonstrating this as an optimum ratio between GTR-EPR [46] The GRT-EPR package was varied from a minimum of 5% to 70%, from a thermoplastic dominant material to an elastomeric dominant material. Table 2.2 below gives a summary of the alternative TPE's blends investigated.

Table 2.2 : Summary of alternative TPE blends

Sample	PP-T20 (%)	GTR (%)	EPR (%)
PP-T20/ 5%(GTR-EPR)	95	4	1
PP-T20/ 15%(GTR-EPR)	85	12	3
PP-T20/ 25%(GTR-EPR)	75	20	5
PP-T20/ 35%(GTR-EPR)	65	28	7
PP-T20/ 50%(GTR-EPR)	50	40	10
PP-T20/ 70%(GTR-EPR)	30	56	14

2.2.1 Injection moulding

The blends were prepared using a two step in-situ process, where a reciprocating screw injection moulder was utilized as a mixer and and injection moulding unit. The loose materials were subjected to screw rotation at 300 rpm, allowing the GTR to fuze and blend within the molten phase of PP and the EPR at a temperature 200 ℃. There after the blends were injected at a pressure of 30 bars through the sprue filling up the mould cavity at a speed of 50 ml/min, while the mould is stable at ambient temperature as the molten blend is allowed to cool for 30 sec and ejected. The processing of the blends was done on a Arburg 250 Ton family mould injection moulding machine with a moulding schedule summarized in Table 2.3 below.

Table 2.3: Injection moulding parameters

Rear	Centre	Front	Nozzle	Injection	Holding	Cooling
200 ℃	230 ℃	220 ℃	210 ℃	12 sec (30 bars)	8 sec (50 bars)	30 sec

15 specimens where attained from these samples and where used to test various properties of the blends. The Arburg 250 Ton injection moulding machine used in this study and an example of the specimen is shown in Figure 2.2.

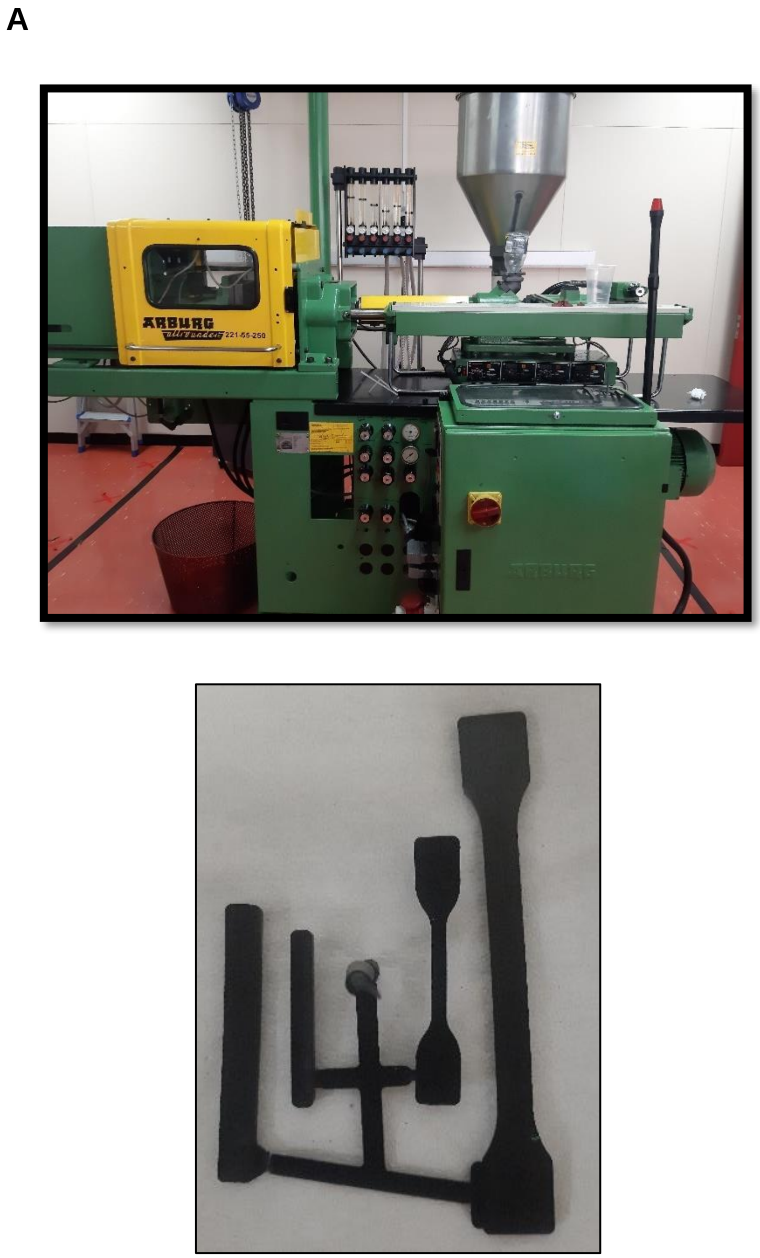


Figure 2.2: Injection moulding machine (A) and example of specimen formed (B).

2.3. Material Characterization

2.3.1 Composition Characterization

Simultaneous DSC-TGA (SDT)

The simultaneous DSC-TGA is a thermal analysis technique which measures heat flow and weight changes in a material in a controlled atmosphere as a function of temperature or time [41]. The information obtained for this technique allows differentiation between endothermic and exothermic events which are not associated with weight loss (e.g., crystallization and melting) and those which do involve weight loss (such as degradation). The instrument utilized for this technique is the Q600 SDT (Figure 2.3.1).

Figure 2.3.1: A photograph of the Q600 SDT machine.

Thermogravimetric analysis was performed for the different GTR material using the Q600 SDT(Figure 2.3) where the weight changes in relation to change in temperature were measured resulting in a weight loss curve which provided information to determine the composition of NR/SBR or BR in the material as well as the amount of carbon black present in each of the GTR material. The method of testing is as follows:

1. Furnace purge with nitrogen at 100 ml/min
2. Ramp 20.00 ºC/min to 550 ºC
3. Secondary purge with air at 200 ml/min

4. Isothermal for 10 min
5. Ramp 20.00 ºC/min to 800 ºC

In order to ascertain the degradation steps in TGA traces the derivative thermogravimetric (DTG) curves are also constructed; they are represented by the rate of change in mass in a selected temperature interval. These curves have well defined peaks that are superimposing the mass loss observed in a TGA curve [41].

2.3.2. Morphological and Structural Characterization

The structural characterization of the GTR's was done to understand the distinctions between in the shape and size of the various, where at very low magnification optical miscoscopy was utilized and at high mag scanning electron microscopy detailing the size distribution natural morphology of the GTR's prior to any blending.

2.3.2.1 Optical Microscopy

A Leica DM2700 was deployed to monitor the surface roughness and porous nature of the various sources GTR's. This characteristic would then be used to predict the surface tension and surface interactions between the molten phases and amorphous GTR. The samples were images at 10 times magification on glass slide.

2.3.2.2 Scanning Electron Microscopy (SEM)

High resolution imaging of the GTR's was done using a JOEL JSM-IT100 SEM, and was carried as two types of investigations. The first investigation was for characterization of the powderd rubber, while the second investigation was done as part of postmotem failure analysis for the various blends. The failure analysis specimens were obtained from Impact Resistance break samples, where the fractured surfaces of the specimen were cut and taken for imaging (Figure 2.3.2.2).

Figure 2.3.2.2 A: A photograph of an Impact Resistance break sample used for failure analysis using SEM.

The blends and powderd recycled end of life tyres were springles on a double sided tape followed by gold sputter coated under vaccum. The coated speciments were placed under vacuum conditions in the SEM machine where an electron gun fires beams of electrons onto the samples surface. These elecron beams scan the sample surface area in lines from side to side and top to bottom. The interaction of the electrons with the samples surface produces secondary, backscattered electrons and rays that are characteristic of the sample [32, 35, 41]. These signals are picked up by detectors in the microscope to create high-resolution images that are displayed on computer screen.

Figure 2.3.2.2 B: An image of the JOEL JSM-IT100 [47].

2.4 Mechanical Testing

Figure 2.4: A photograph of the Resil Impactor junior used in the study.

The impact test or as used in this instance the Izod impact test is one of the commonly utilized techniques to evaluate the relative toughness of a polymer material as its ability to resist shock under applied stress at high speed. In the Izod test a standardized hammer on a pendulum is raised then released to break through a specimen moulded into a flat rectangular shape (typical dimensions of l.w.t: 80mm×10 mm×4mm) and cantilevered on the tester [20, 41]. The flat plane of the specimen is also notched, this notch functions as a stress concentration and simulates factors that affect material performance such as scratches and in extreme case cracks and voids which make the material easier to break [20].

Therefore, the Izod test can be taken as a measure of the notch sensitivity by measuring the energy absorbed by a notched specimen while breaking under an impact load. The energy absorbed by the specimen is determined by measuring the decrease in the motion of the pendulum arm [20]. For this study the samples were tested for their impact strength using the Resil impactor junior (Figure 2.4) the swing energy was set at 7.5 J according to ASTM D6110 at room temperature. The digital display on the instrument showed the total energy absorbed during impact which is measured by an encoder at low friction. The test was repeated several times for each sample and then the average value was calculated. These values were reported in kJ/m^2 and represent the energy required to break the specimen.

2.5 Thermomechanical testing

Dynamic Mechanical Analysis

The DMA can be used as a method to characterize dynamic mechanical properties of polymers as a function of temperature, time, frequency, stress and atmosphere or a combination of the properties. In this technique a small deformation in the form of an oscillating manner is applied to the sample and its response to stress, temperature etc is studied. Thus, the DMA allows the relation of material behaviour to product properties, molecular structure, and processing conditions.

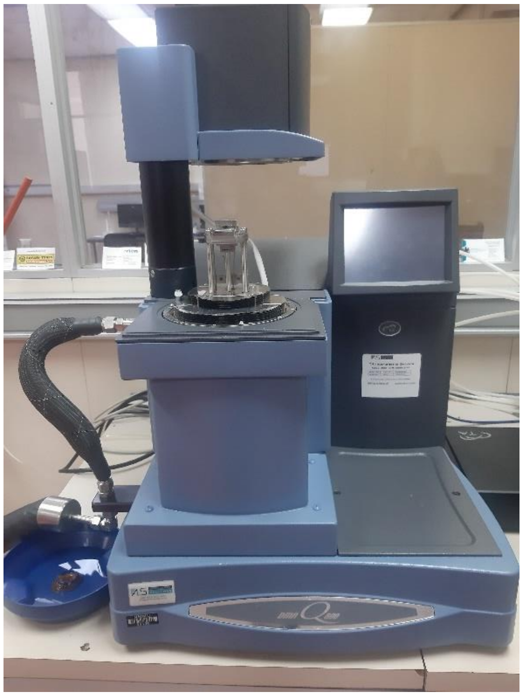


Figure 2.5: A photograph of a TA-Instruments DMA Q800.

An air bearing DMA Q800 form Ta-Instruments was used to monitor the flexural properties of the blends using the 3-point bend test. The test was run in both ambient and sub-ambient temperatures, In sub- ambient temperatures the blends where subjected to a nitrogen quench. Frequency was 1Hz with a force of 1N under 1% strain.

Testing procedure for blends at ambient temperatures

1. Ramp force 3N/min to 17.2 N

Testing procedure for blends at -20 ºC

1. Equilibrate at -20ºC
2. Go to next segment at -30ºC
3. Ramp force 3N/min to 17.2 N

To monitor the glass transition and storage modulus for the blends a dual cantilever clamp was used, and the test conducted was a temperature scan at frequency 1Hz with a force of 1N under 1% strain.

Testing procedure for the blends

1. Equilibrate at -100 ºC
2. Ramp 5 ºC/min to 70ºC

3. RESULTS AND DISCUSSION

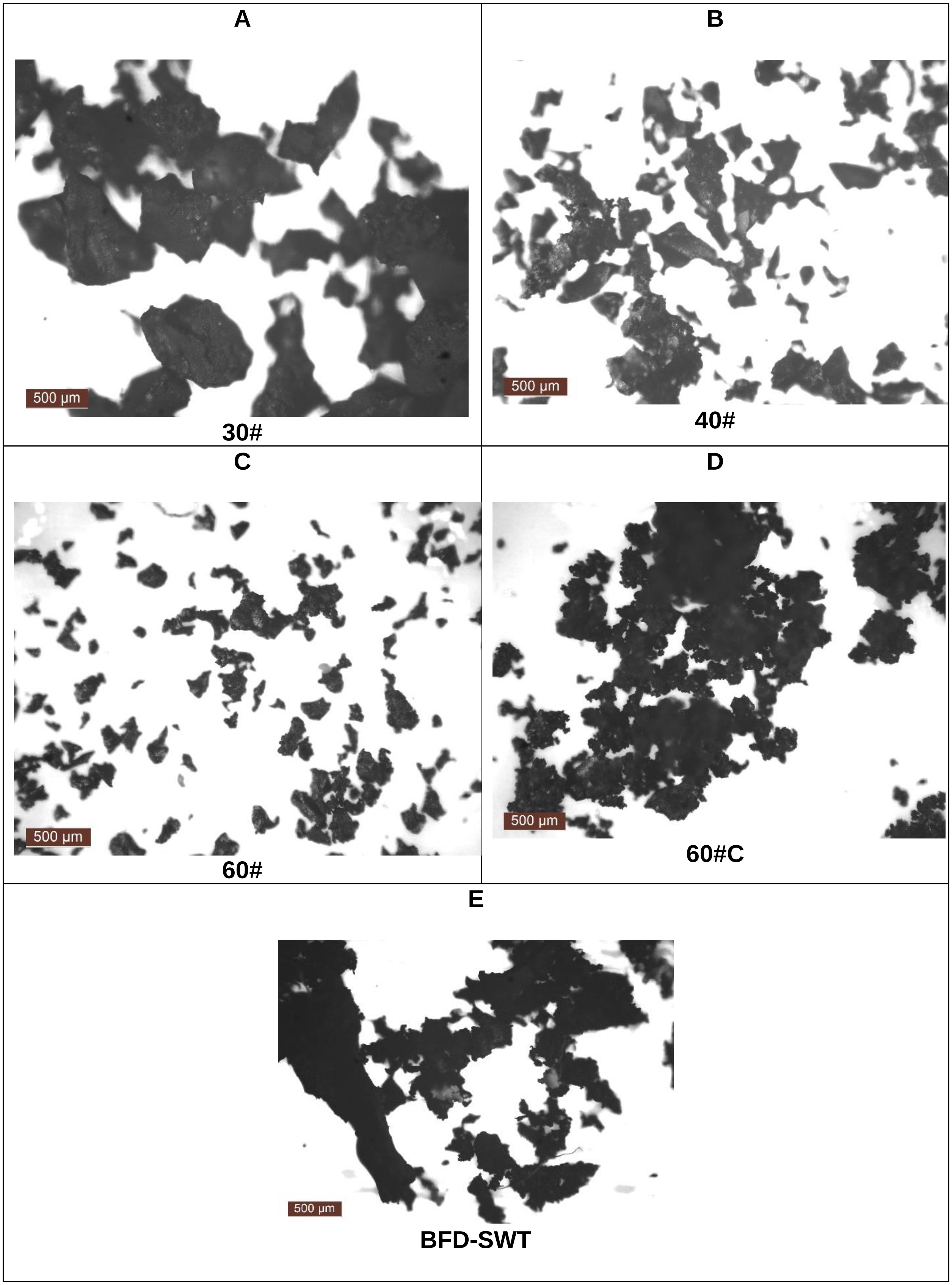
This section of the study details the experimental data collected from the characterization of the raw material and testing of the samples. The performance of the waste material derived TPEs is of significance in the analysis and discussion.

3.1 Raw material characterization

The utilization of various processing techniques to evolve waste tyres into GTR influences the properties of the GTR [32, 34, 35] Thus, it is necessary to characterize the GTR. The results obtained may aid in the understand these properties and provide guidance on which products the GTR may be suited for. Ambiently ground GTR differs from cryogenically ground GTR hence also yielding different properties upon blending with thermoplastic [34].

3.1.1 Optical Microscopy

Figure 3.1.1 shows the differences between GTR powders obtained by different grinding methods the micrographs were obtained at 4× and 10× magnifications. Ambient grinding processes produce narrow particle size distribution compared to cryogenic processes (Fig.3.1.1 d) and have a complex morphology thus a larger surface area [32]. According to Forrest [48] it had been denoted that the larger surface area and complex surface morphology leads to improved bonding being achieved with ambient ground GTR when combined with other materials to produce composites. Cracked and rough surfaces are seen for ambiently ground GTR (Fig 3.1.1 a-c & e) as the process involves shearing and tearing. Cryogenic grinding processes produces particles with broader width particle size distribution and exhibit smooth surfaces due to cooling before cutting (Fig 3.1.1 d) thus having a low surface area [33, 48] Smoothness can limit binding to other matrices particularly. Therefore, surface area influences the adherence of GTR to other matrices [34, 41]. Hoyer et.al determined that the inhomogeneity of the ambiently ground resulted in a fluctuation of material characteristics[41]. Tensile fatigue for the same particle size was investigated for cryogenic and ambient materials and the ambient material gave better tensile fatigue this was highlighted to be due to the higher surface area of the particles which led to better integration of the matrix [20, 41].



30#

40#

60#

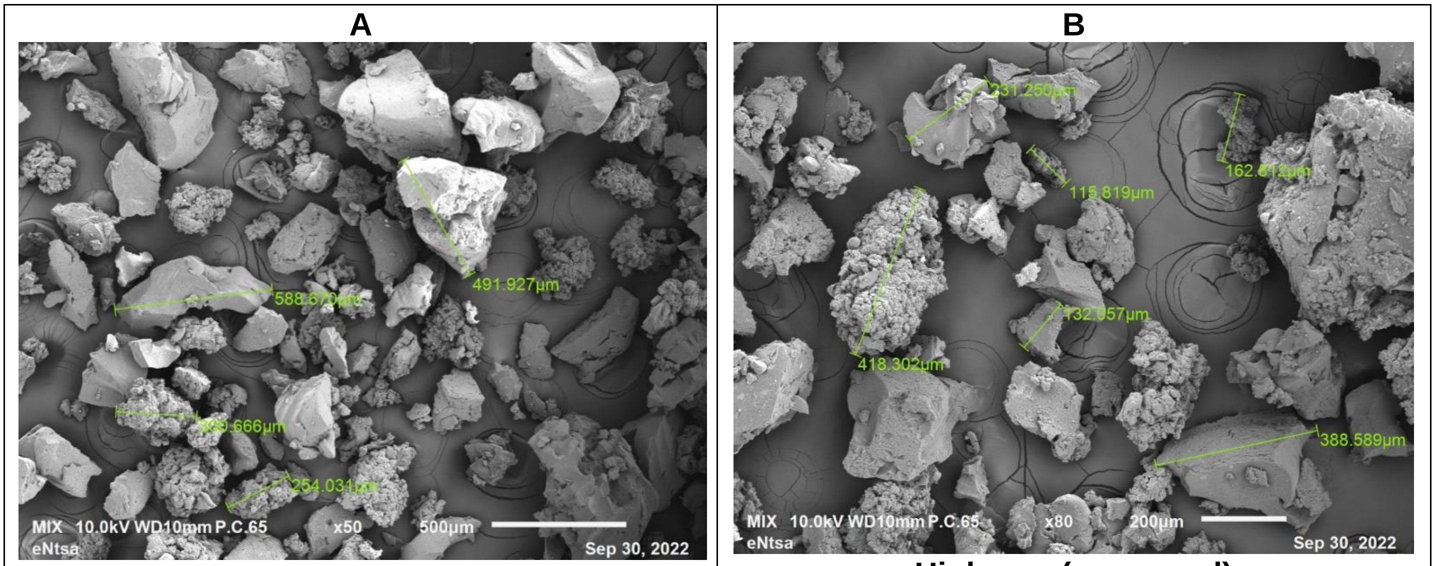
60#C

BFD-SWT

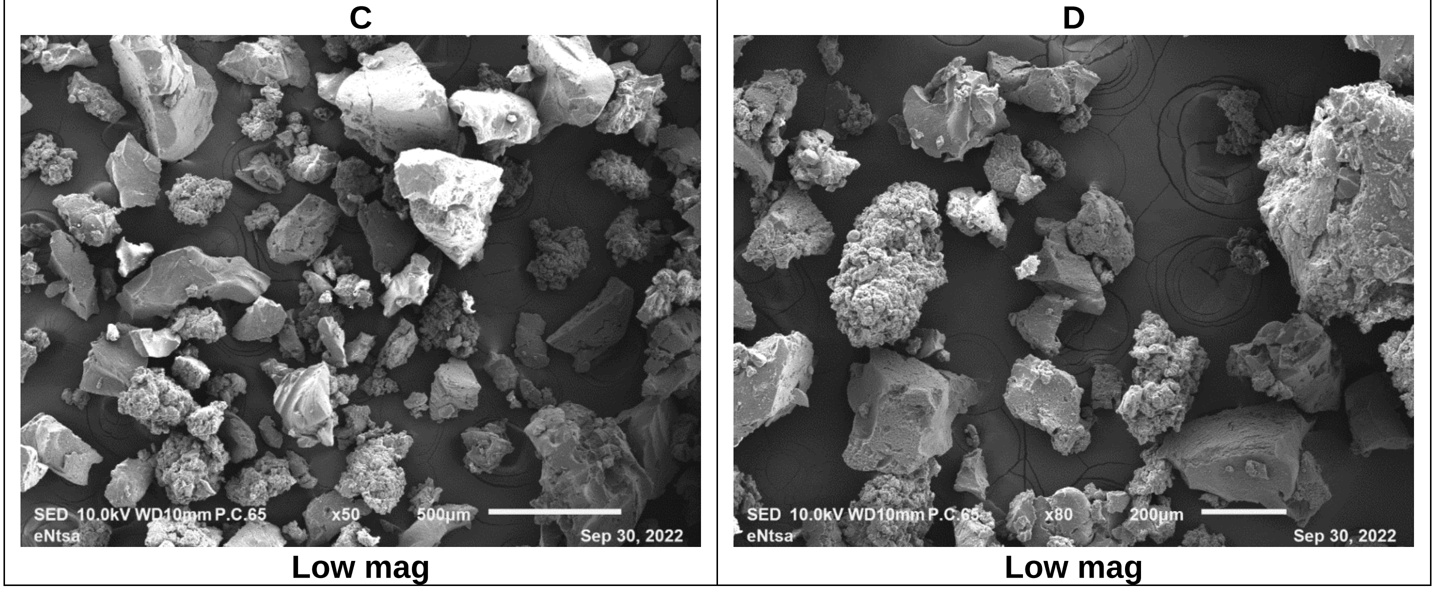
Figure 3.1.1: Optical Micrography imaging:

3.1.2 SEM micrography

The micrographs (Figs 3.1.2.1-3.1.2.6) were obtained at low (50×) and high (80× and 450×) magnifications. Among the procedures to produce these powders is sieving which is a simple cost-effective method to achieve separation. The mesh (#) size refers to the screen used to separate the GTRs to the desired particle size these sizes can range from 30# the larger particles to finer sizes for 60# as seen in Figs 3.1.2.1-3.1.2.4. While screening rubber powder at different mesh sizes it is possible for smaller particles to fall through the mesh and when this occurs it results in the non-uniform particle sizes being obtained in the rubber powders this is seen particularly for the ambiently ground CR (Fig 3.1.2.1). Cryogenic CR (Fig 3.1.2.4) is shown to have improved homogeneity. The buffing dusts (BFD TT & SWT) (Figs 3.1.2.5,3.1.2.6) consist of larger particles overall when compared to CR. The ambiently ground CR and buffing dusts TT (truck tread) and SWT (sidewall and tread) have irregular shapes and inconsistent appearance (Fig 3.1.2.1-3.1.2.3,3.1.2.5-3.1.2.6). For cryogenically grounded CR (Fig 3.1.2.4 B) the particle shapes appear to be more regular and more defined. Hoyer *et.al* also suggested that considering morphology only, the cryogenic particles bond better to new matrices [41]



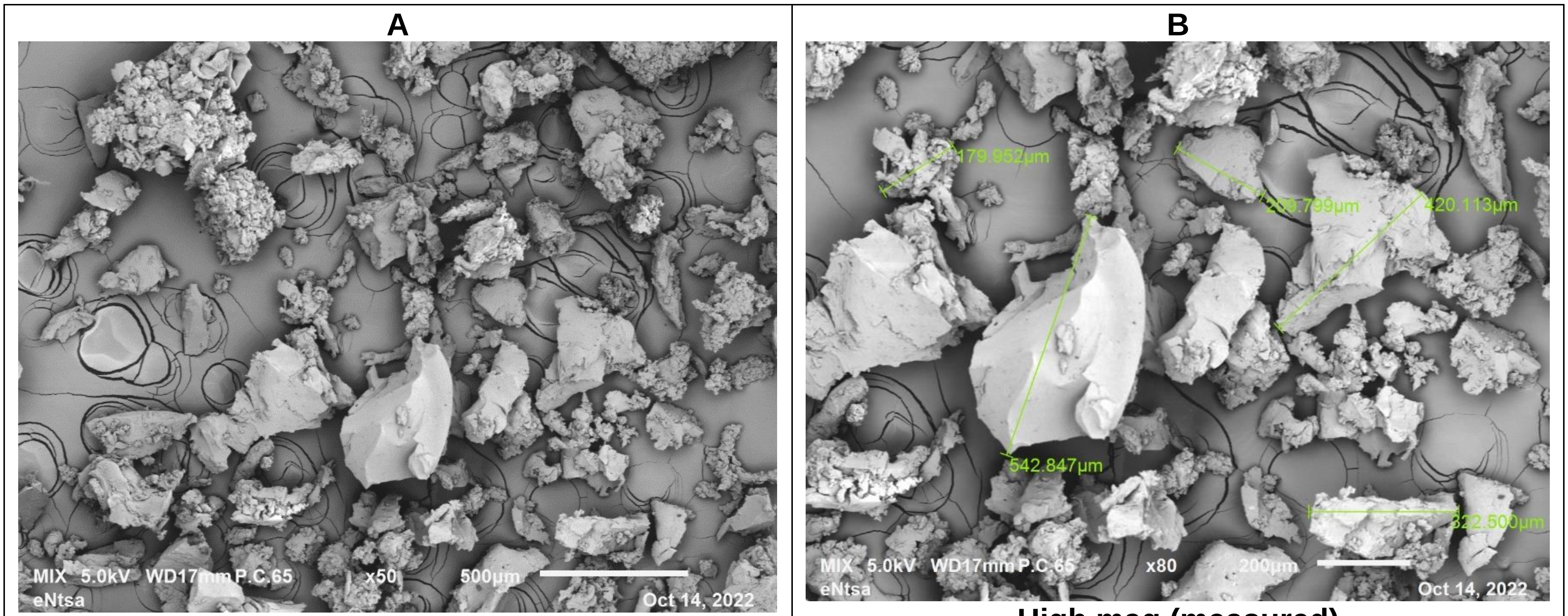
Low mag(measured) High mag(measured)



Low mag Low mag

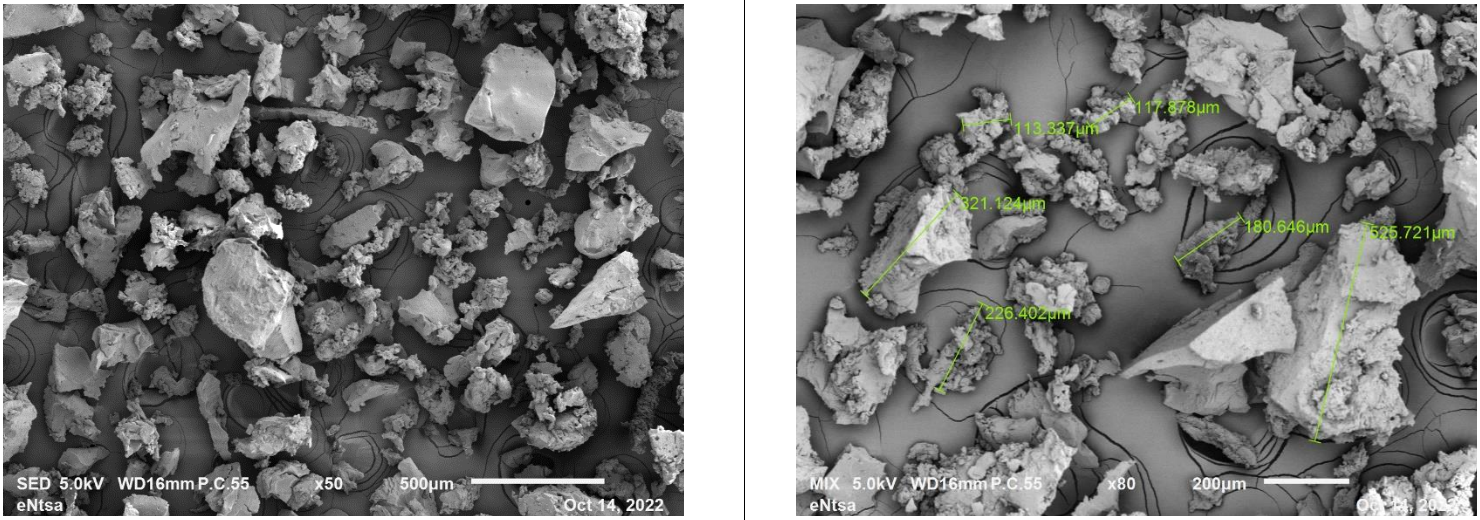
Figure 3.1.2.1: SEM Micrography of 30# CR

A B



Low mag High mag (measured)

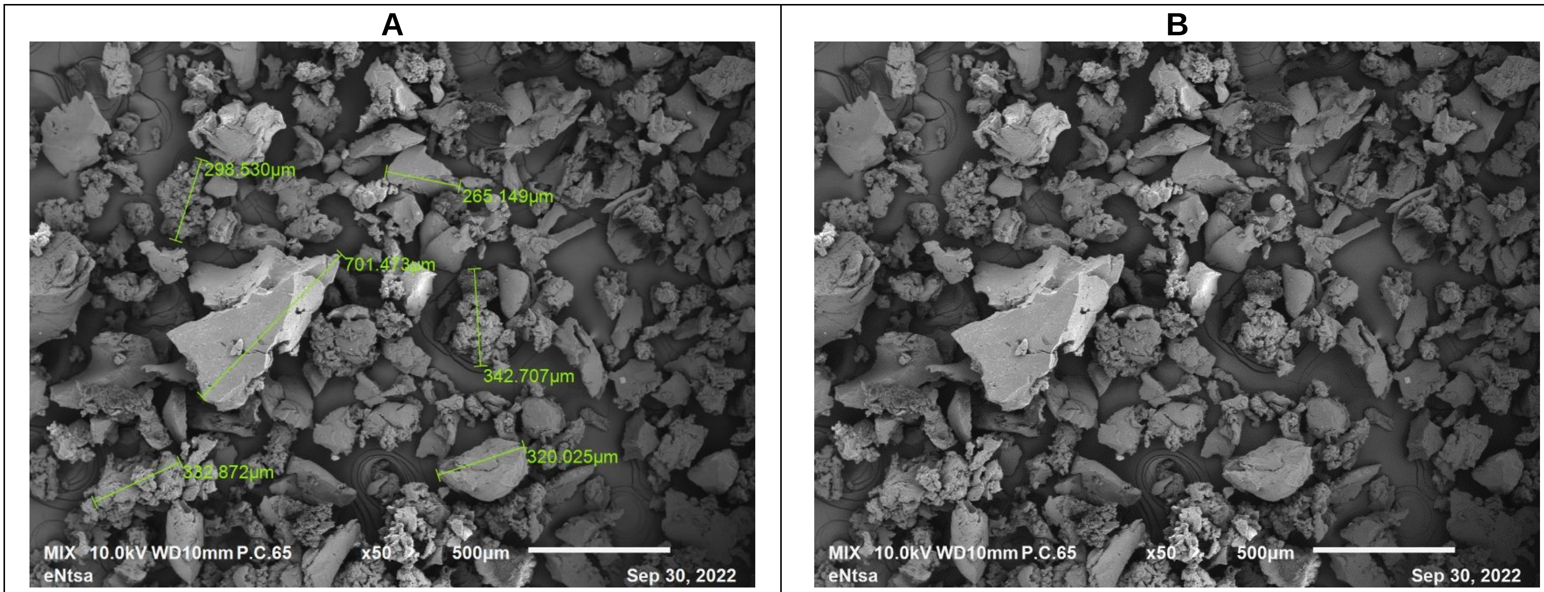
C D



Low mag High mag (measured)

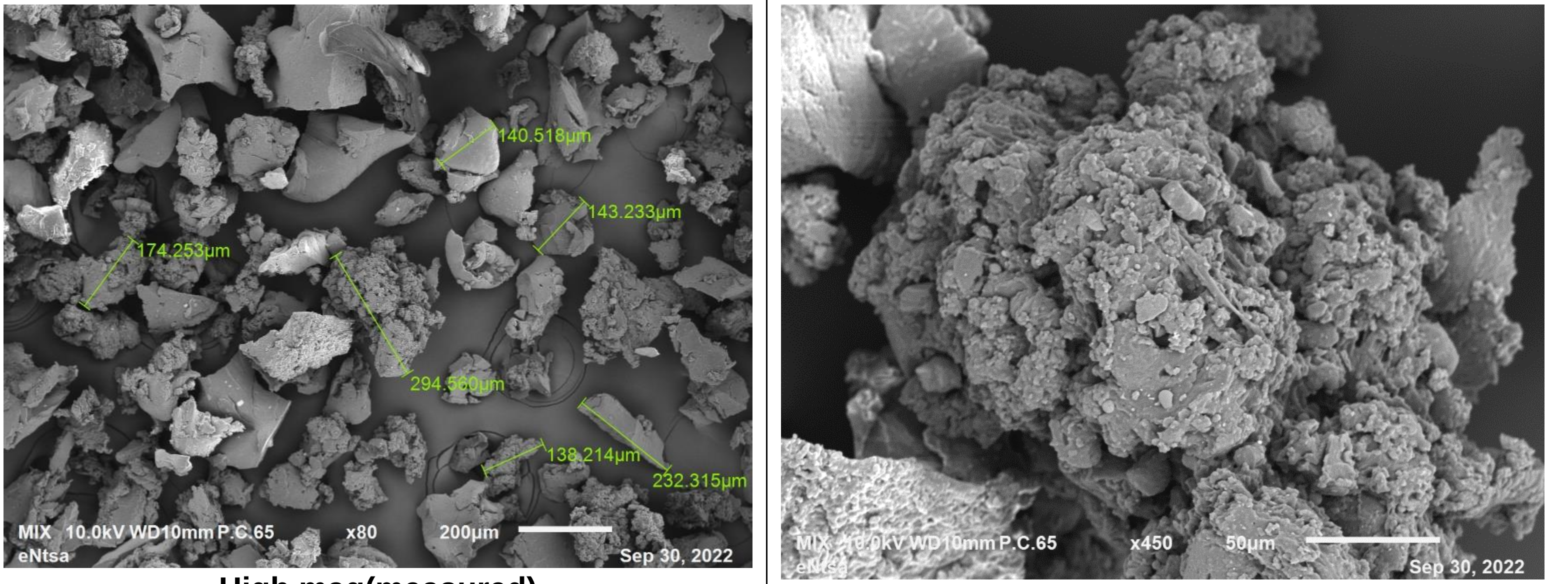
Figure 3.1.2.2: SEM Micrography of 40# CR

A **B**



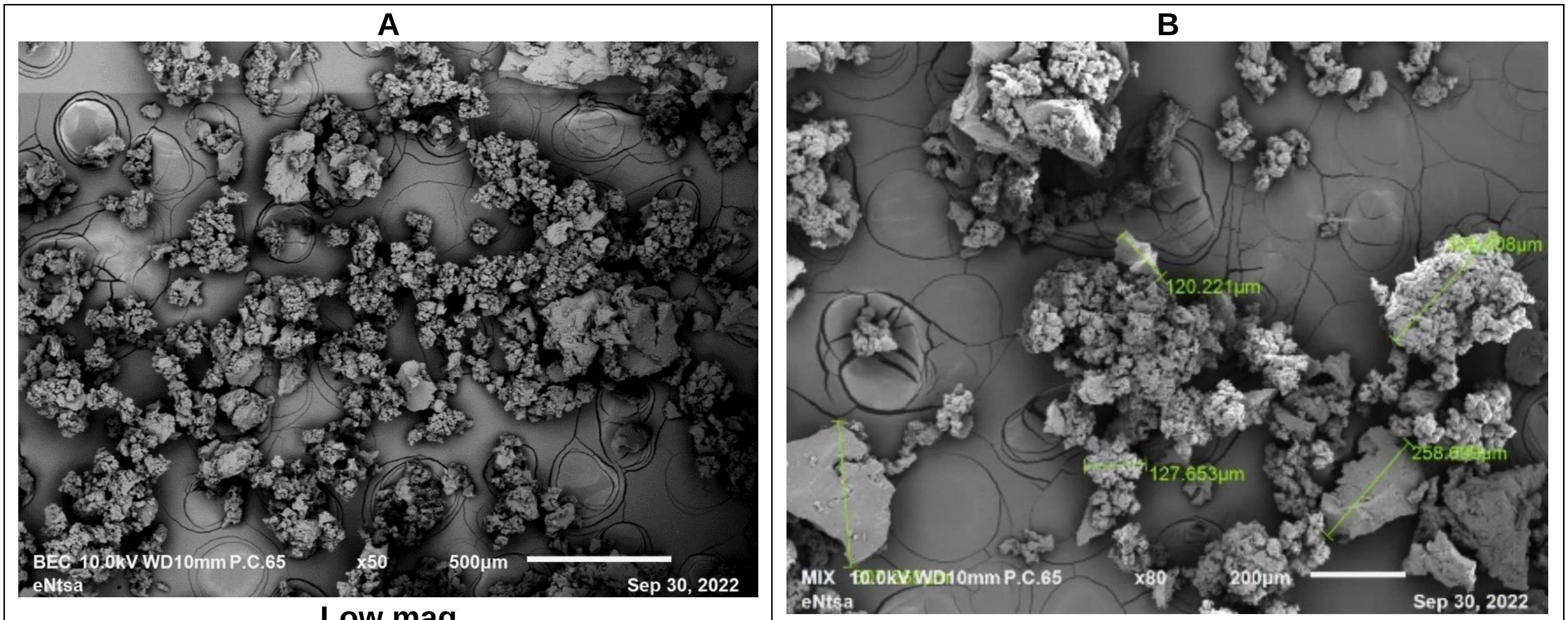
Low mag(measured) **Low mag**

C **D**



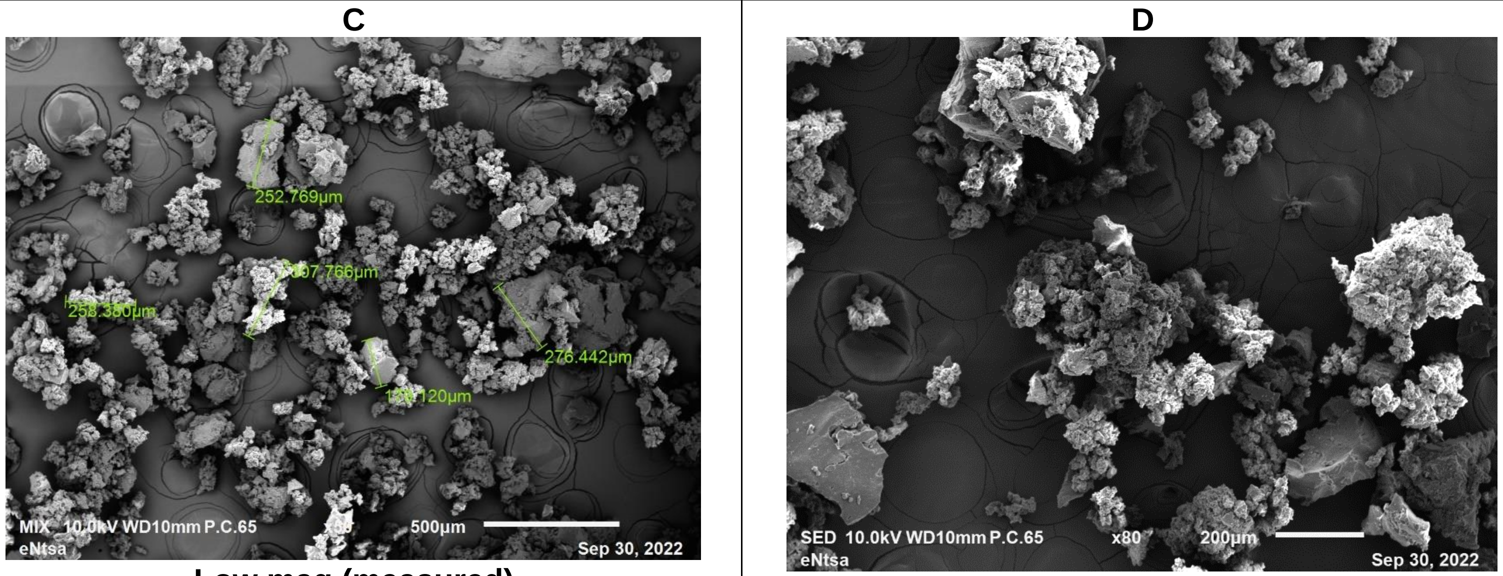
High mag(measured) **High mag**

Figure 3.1.2.3: SEM Micrography of 60# CR



Low mag

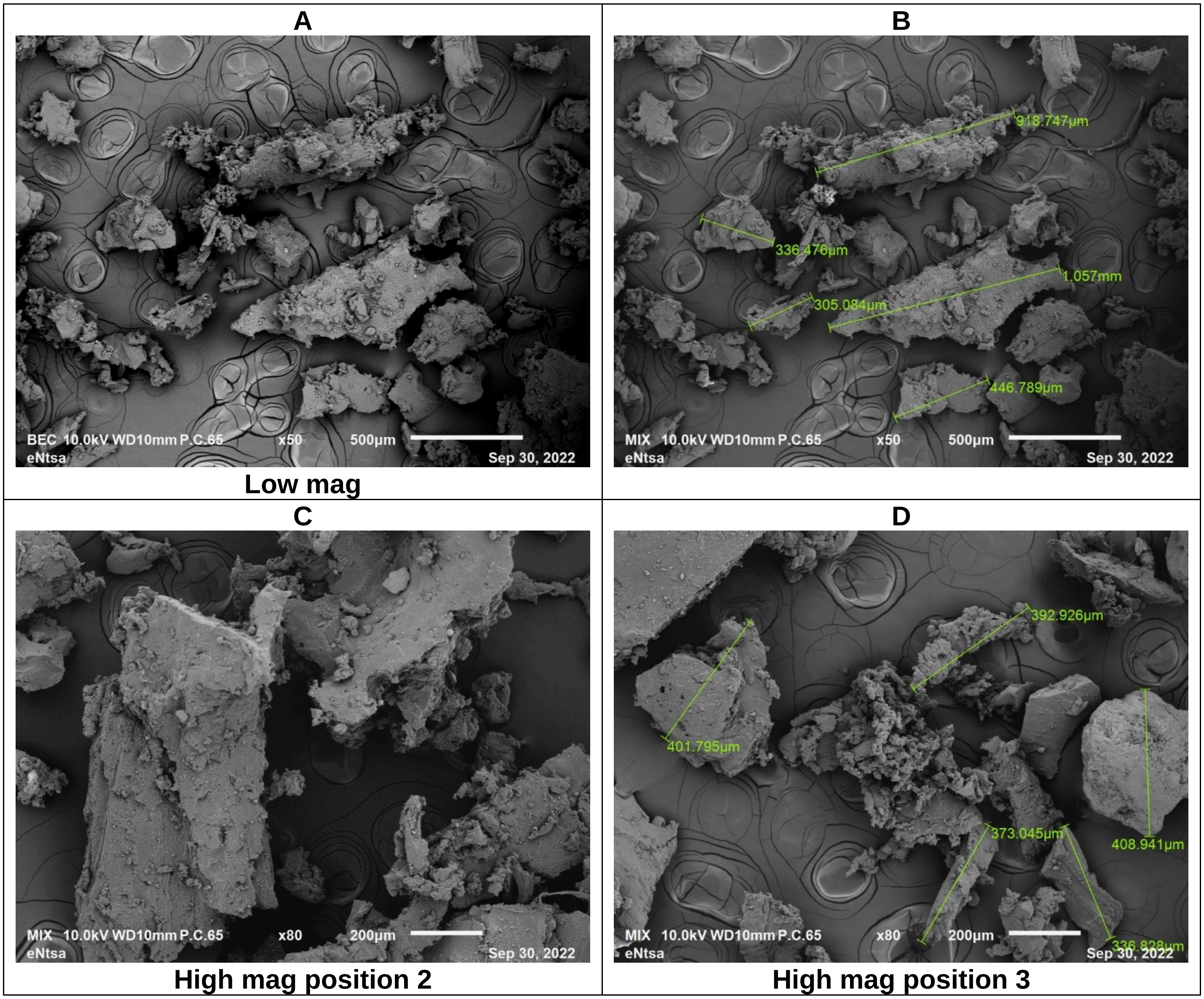
High mag(measured)



Low mag (measured)

High mag

Figure 3.1.2.4: SEM Micrography of 60# cryogenic CR

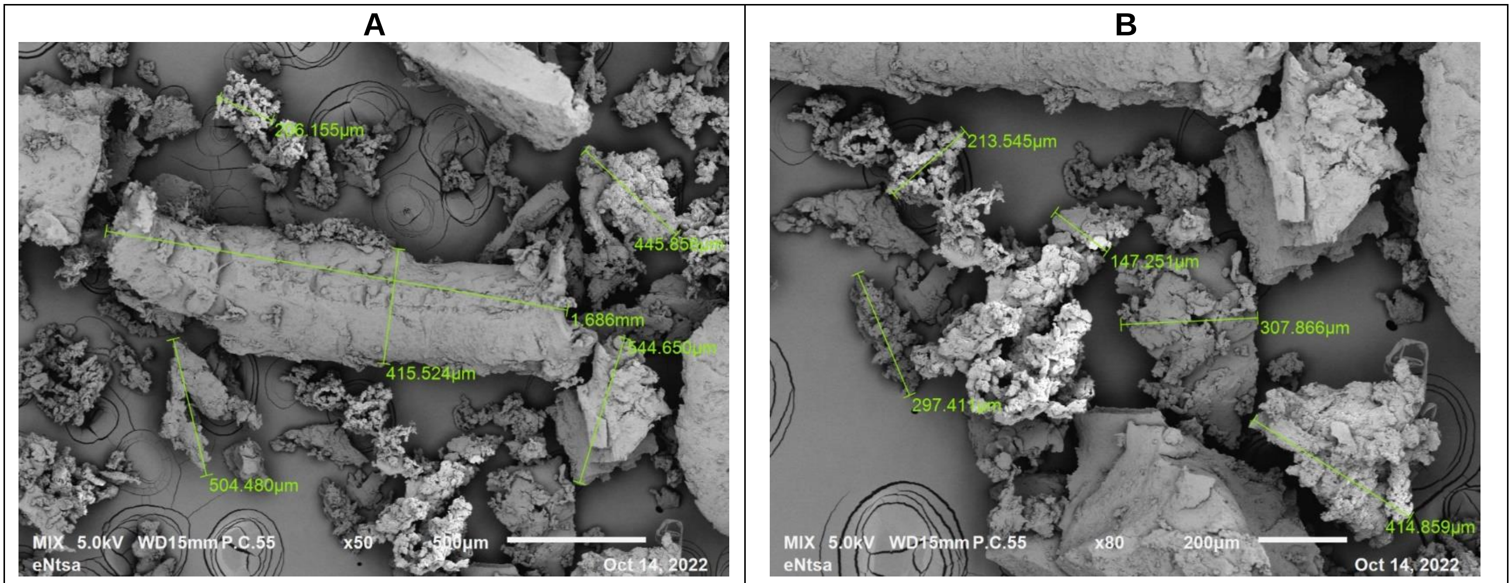


Low mag

High mag position 2

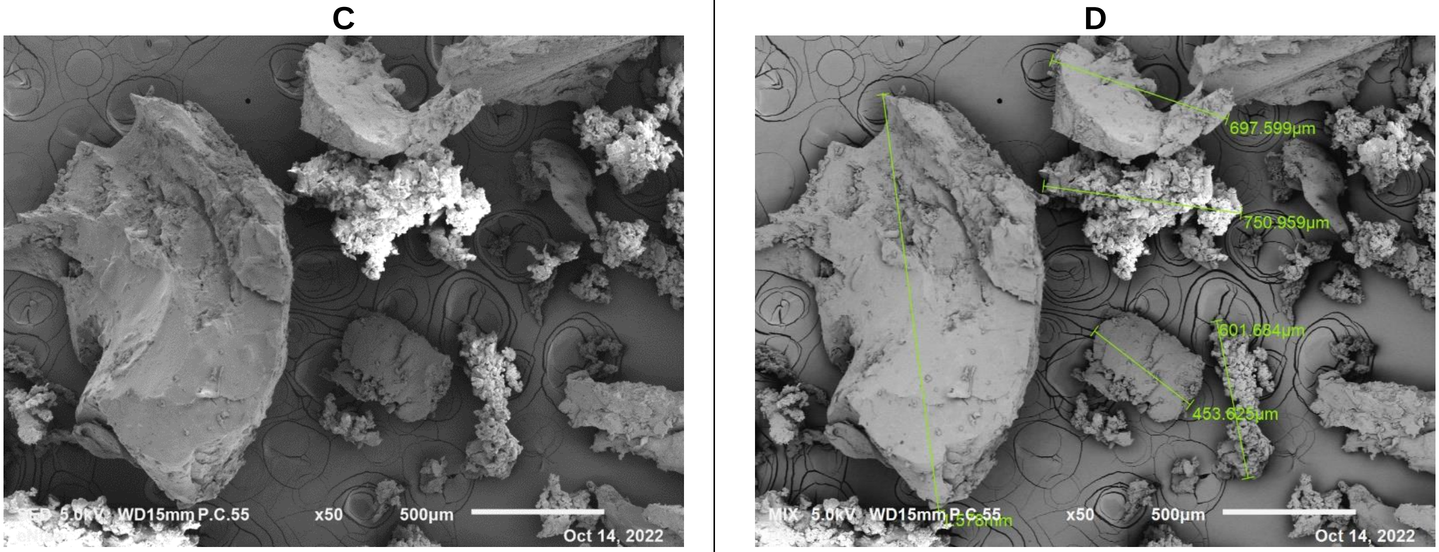
High mag position 3

Figure 3.1.2.5: SEM Micrography of BDT-TT



Low mag measured

High mag measured



Low mag position 2

Low mag position 2 measured

Figure 3.1.2.6: SEM Micrography of BFD-SWT

3.1.3 Composition

A typical tyre for both passenger vehicles and trucks consists of NR/BR/SBR; each of these elastomers has properties which aid in the functioning of a tyre. Thermal degradation patterns of these polymers can be seen in Fig 3.1.3.1. BR has excellent rebound properties and is excellent for abrasion resistance, thus it is commonly utilized in the sidewall of the tyre since this part is exposed to debris; its degradation appears as a single peak between 450-480 °C. NR provides grip performance and is used in the tread of the tyre. Its degradation occurs between 350-400 °C and appears as a single peak. SBR provides the tyre with abrasion resistance and its degradation appears as a double peak for the styrene and BR contents at 410-480 °C. Therefore, the same degradation patterns are expected for the GTR's.

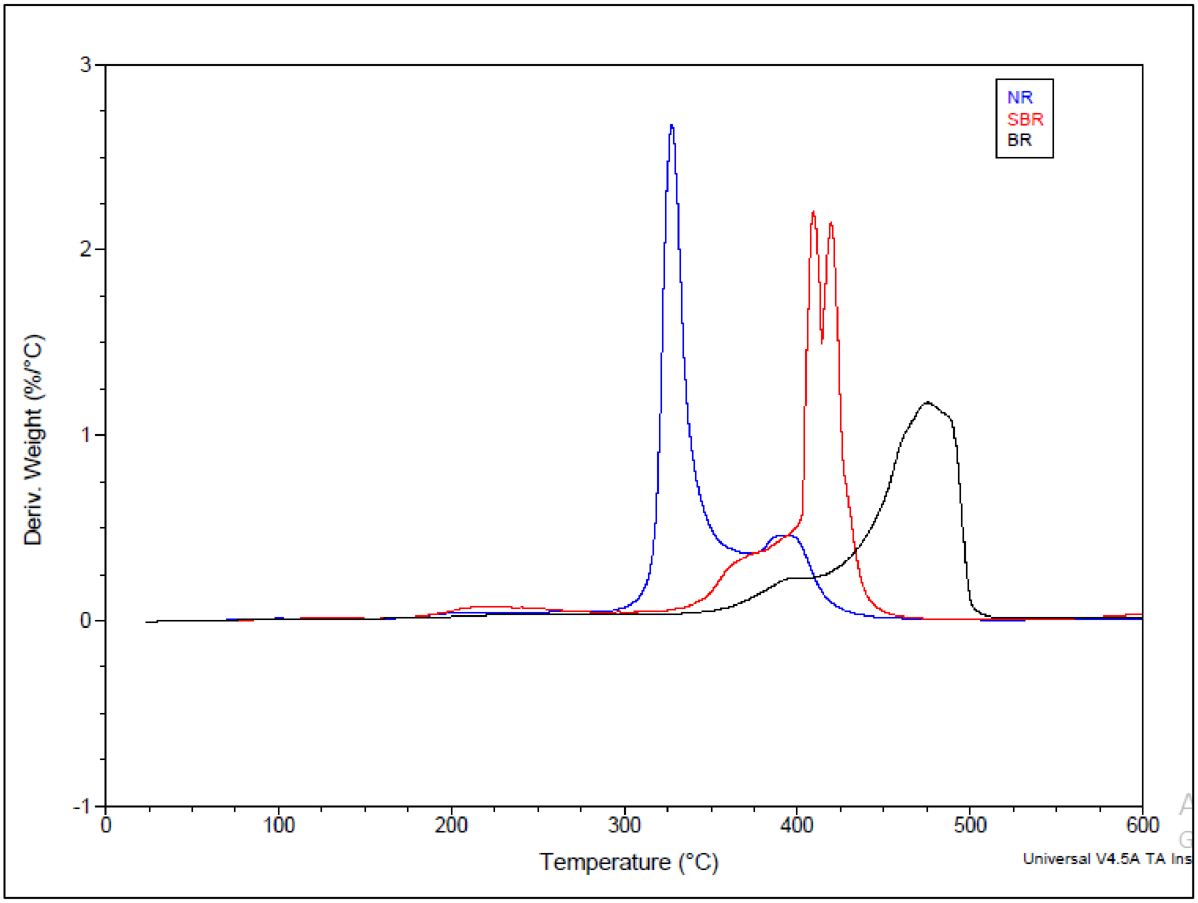


Figure 3.1.3.1: Derivative weight curves depicting the breakdown of tyre (passenger and truck) rubbers by TGA.

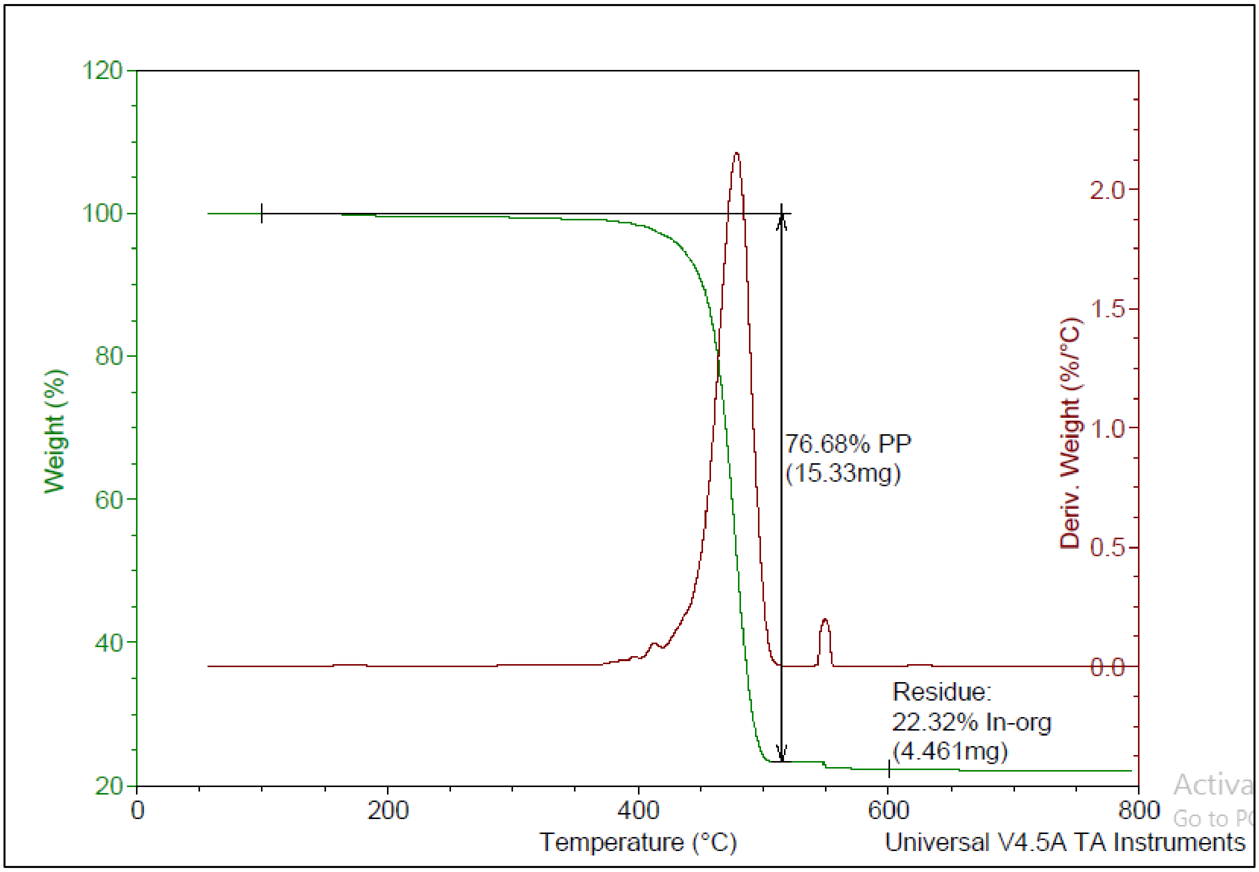


Figure 3.1.3.2 A: Composition breakdown of PP-T20 by TGA

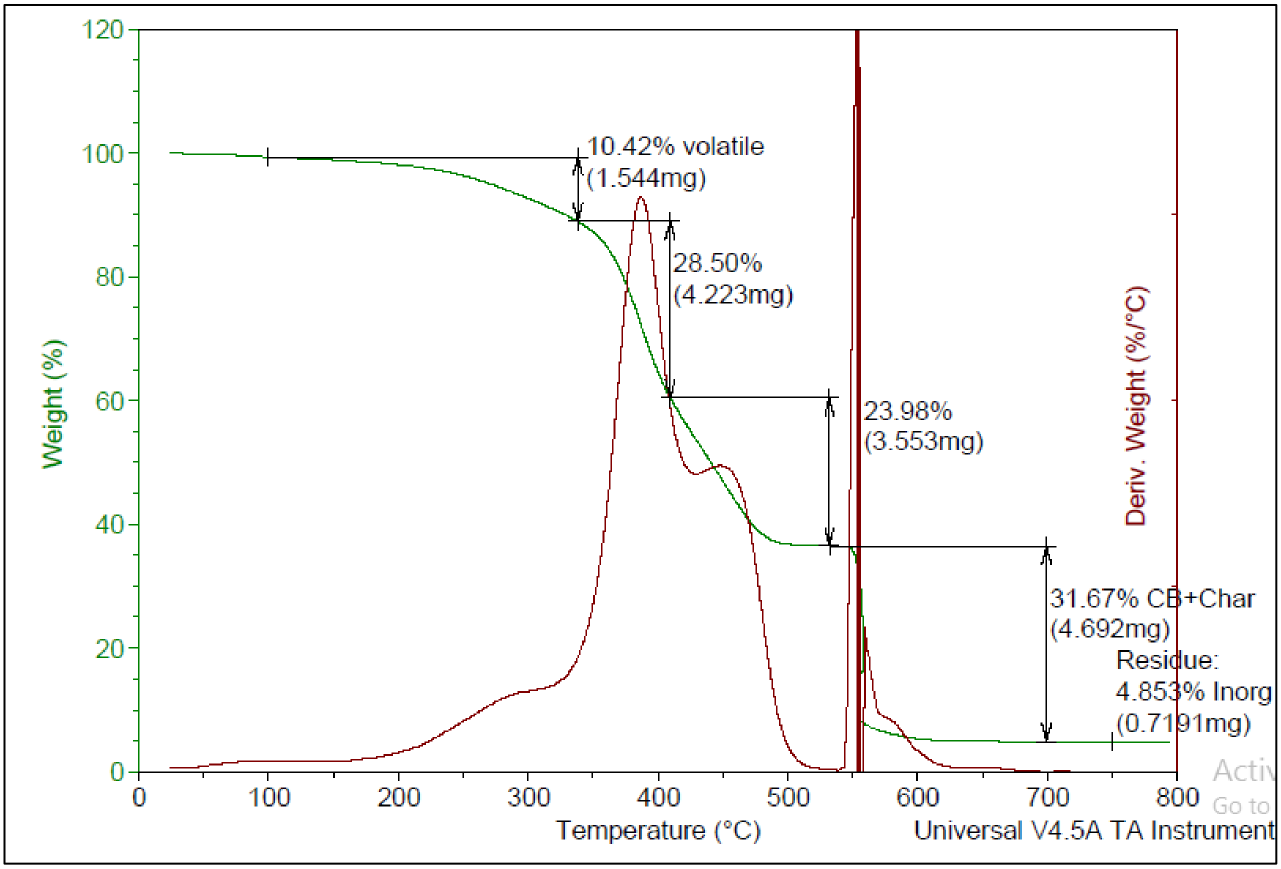


Figure 3.1.3.2 B: Composition breakdown of GTR by TGA

Table 3.1.3: Composition breakdown of materials by TGA

Material	PP (%)	NR (%)	SBR/BR (%)	Volatiles (%)	CB (%)	In-organic (%)
PP-T20	77	-	-	-	-	22
30#	-	36	23	5	29	7
40#	-	35	21	5	33	6
60#	-	34	22	6	31	7
60# cryogenic	-	36	23	5	28	8
BFD-TT	-	29	24	10	32	5
BFD-SWT	-	25	29	7	33	6

PP-T20 analysis determined that 77% of PP and 22% talc was present in the compound. Truck tyres contained higher amounts of natural rubber since there must be minimal heat buildup when experiencing shock and dynamic loads which trucks are often subjected to. Truck treads also contain SBR which provides abrasion resistance and excellent traction properties. The crumb rubbers and BFD TT contain NR at relatively high amount and SBR (Table 3.1.3); they are then confirmed to originate from truck treads. SBR content decreases in larger tyre treads due to the requirement to reduce hysteresis and consequent heat accumulation during service. BFD SWT has a lower amount of NR (Table 3.1.3); this is characteristic of the passenger vehicle sidewall compound, which also contains BR since it originates from the sidewall which provides resistance to low temperatures and cracking, while also improving rebound properties of the tyre it also contains SBR, the actual relative amounts of these rubber could not be determined [30, 42]. Furthermore, it is important to note that when comparing all-season passenger tyres to high performance passenger tyres the composition of BR and SBR will differ this is due to the tyres having different tread depths. High performance tyres have improved grip and thus contain more tread than sidewall and will subsequently contain more SBR than BR when compared to all-season passenger car tyres [49].

Carbon black incorporation in tyre formulations aid in the conduction of heat away from the tread and belt areas to reduce thermal damage [30, 42].

3.2 Mechanical Evaluation

In the blends the elastomeric phase has a toughening effect also the inclusion an elastomer the PP matrix results in shear yielding [33, 40]. Lima *et.al* states that these inclusions of rubber induce regions of stress concentrations leading to a shear band effect in the material which prevents the growth process of surface cracks on the blends [40]. The composition of PP/GTR thus the resultant morphology particularly at certain GTR content thresholds (discussed in detail in failure analysis) influences the energy absorbing process of the blend [33]. Adequate GTR particle dispersion has been shown to increase the ductility of the material by prevention of the formation of surface cracks [33, 40] Interfacial adhesion also influences the toughening behaviour of the blends. If there is separation of the PP phase and the GTR phase during deformation, there is a relief in the stress field which leads to the formation of voids which lead to the deterioration of impact strength [33]

3.2.1 Impact resistance

Impact is considered as one of the criteria utilized in the specification of the mechanical usefulness of any material therefore providing a method for quality control particularly for external automotive parts such as the underbody cover which is subjected to impacts at high and low speeds while driving. It is the ability of the material to resist the fracture under stress applied at high velocity [33, 41], hence impact properties are often directly related to the overall toughness of the material.

PP does not have great molecular flexibility and therefore is brittle due to this it has low impact resistance as it cannot respond rapidly to mechanical stress. Subjecting PP to impact leads to brittle failure. Impact strength of PPT20 in this study was determined to be 35 kJ/m^2, therefore the addition of GTR was expected to improve this strength according to studies by Lima *et.al* and Fazil [33, 40]. The addition of GTR in PP at smaller loadings of 4% to 28% GTR content indicated significant deterioration of the impact strength for all the crumb rubbers and the buffing dust TT (Fig 3.2.1.1-3.2.1.4 & 3.2.1.5). The buffing dust SWT showed an increase in the impact strength even at small GTR loading it was the only one to exhibit this behaviour (Table 3.2.1.6). Addition of 20% GTR showed a great deterioration in the % improvement factor for the blends (Fig 3.2.1.7) while 40 % GTR showed significant increase in % improvement factor particularly for the 60# cryogenic and 40# CR which were improved by 54% and 47% respectively. For the SWT buffing dust an improvement of 40% was seen at 20% GTR content this can be said to be due to matrix inversion which seems occur earlier for this GTR when compared to the others which reach the threshold at 40 % GTR content. The occurrence of the early matrix inversion is due to the SWT buffing dust containing larger fiber like particles (Fig 3.1.2.6 A) which become embedded at the center on the PP matrix during melt processing providing a cushioning effect, thus the ability to absorb energy during impact. Overall, the reduction and increase of the impact strength can be described by the nature of GTR particles and the interaction with the PP matrix resulting in encapsulation or the lack thereof (detailed in failure analysis).

Table 3.2.1.1: Summary of Impact Data for 30#

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	1.3	33
PP-T20/ 15%(GTR-EPR)	1.3	33
PP-T20/ 25%(GTR-EPR)	1.2	30
PP-T20/ 35%(GTR-EPR)	1.3	33
PP-T20/ 50%(GTR-EPR)	1.7	43
PP-T20/ 70%(GTR-EPR)	1.14	29

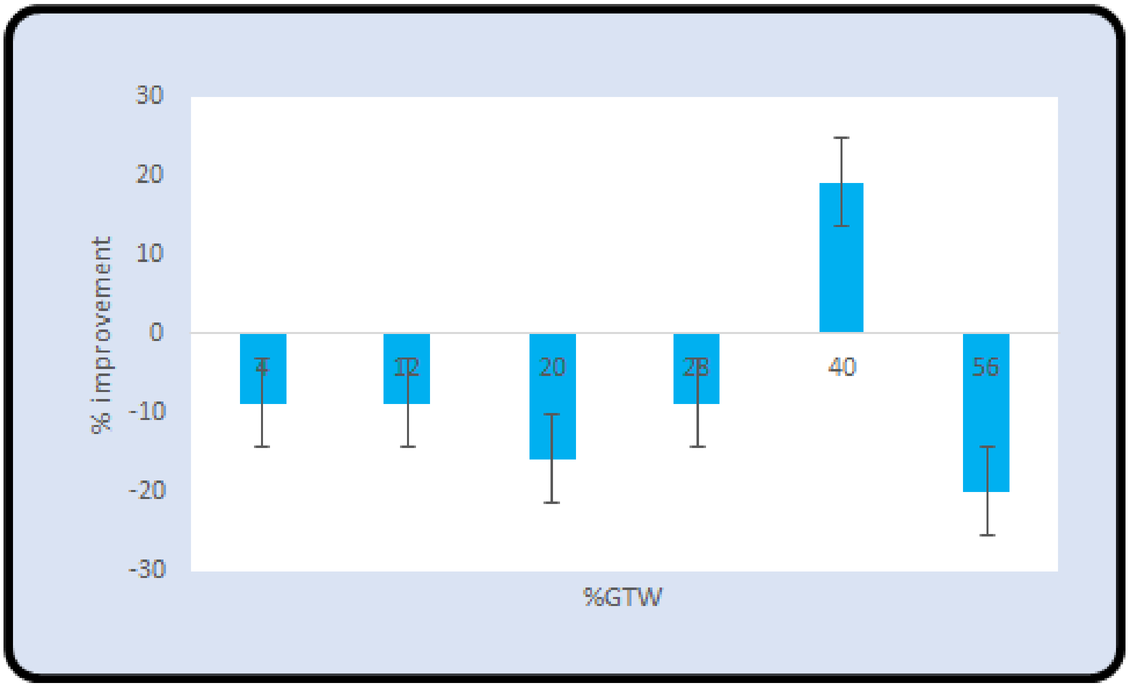


Figure 3.2.1.1: Impact percentage improvement 30 #

Table 3.2.1.2: Summary of Impact Data for 40#

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	0.88	22
PP-T20/ 15%(GTR-EPR)	0.77	19
PP-T20/ 25%(GTR-EPR)	0.92	23
PP-T20/ 35%(GTR-EPR)	0.96	24
PP-T20/ 50%(GTR-EPR)	2.1	53
PP-T20/ 70%(GTR-EPR)	1.26	32

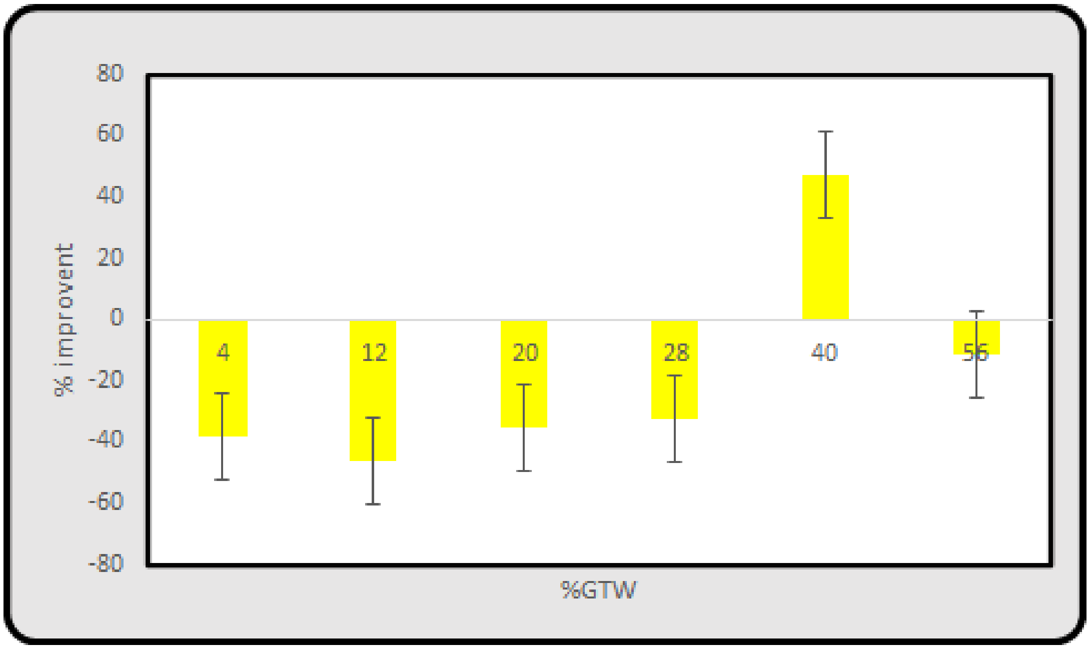


Figure 3.2.1.2: Impact percentage improvement 40#

Table 3.2.1.3: Summary of Impact Data for 60#

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	1.7	43
PP-T20/ 15%(GTR-EPR)	1.3	33
PP-T20/ 25%(GTR-EPR)	1.2	30
PP-T20/ 35%(GTR-EPR)	1.7	43
PP-T20/ 50%(GTR-EPR)	1.8	45
PP-T20/ 70%(GTR-EPR)	1.26	32

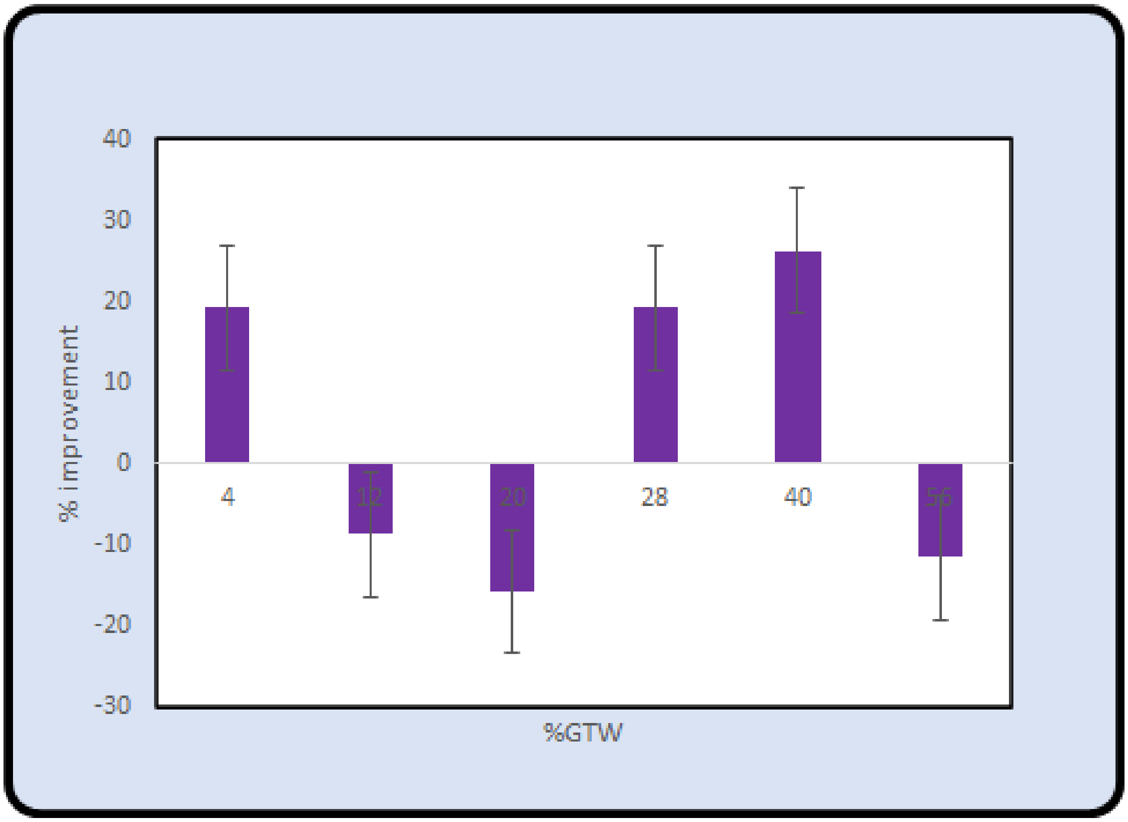


Figure 3.2.1.1: Impact percentage improvement 60 #

Table 3.2.1.4: Summary of Impact Data for 60# cryogenic

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	1.02	26
PP-T20/ 15%(GTR-EPR)	0.7	18
PP-T20/ 25%(GTR-EPR)	0.84	21
PP-T20/ 35%(GTR-EPR)	0.8	20
PP-T20/ 50%(GTR-EPR)	2.2	55
PP-T20/ 70%(GTR-EPR)	1.041	26

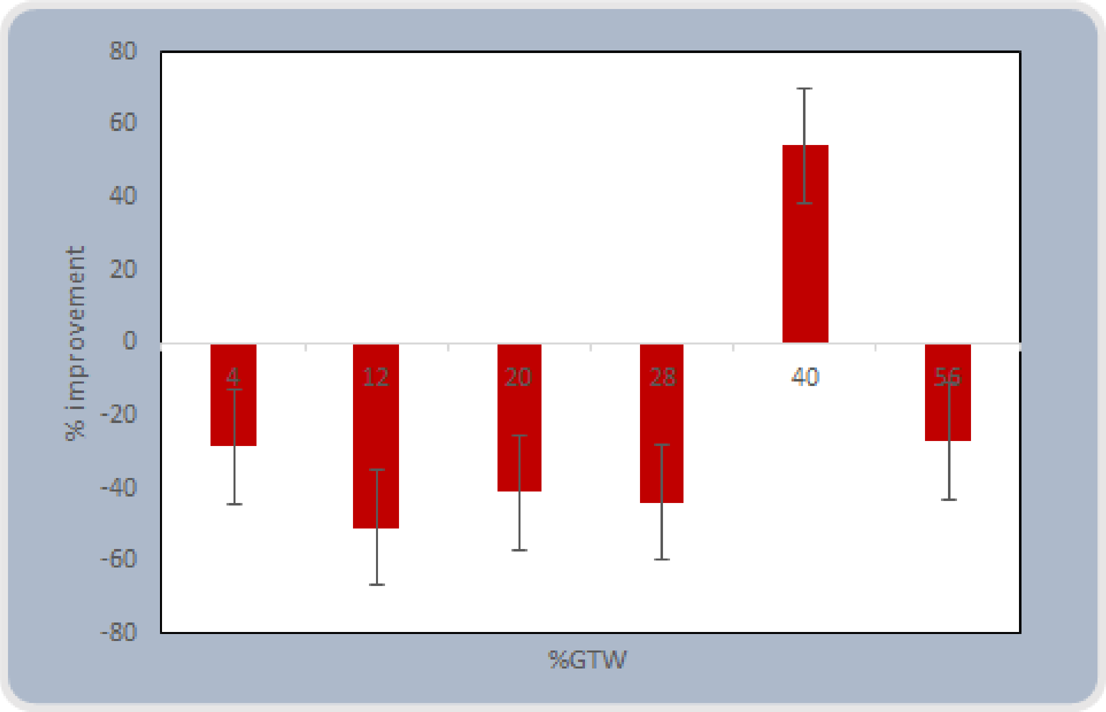


Figure 3.2.1.4: Impact percentage improvement 60# cryogenic.

Table 3.2.1.5: Summary of Impact Data for BFD TT

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	1.11	28
PP-T20/ 15%(GTR-EPR)	1.06	27
PP-T20/ 25%(GTR-EPR)	0.6	15
PP-T20/ 35%(GTR-EPR)	0.8	20
PP-T20/ 50%(GTR-EPR)	1.31	33
PP-T20/ 70%(GTR-EPR)	1.30	33

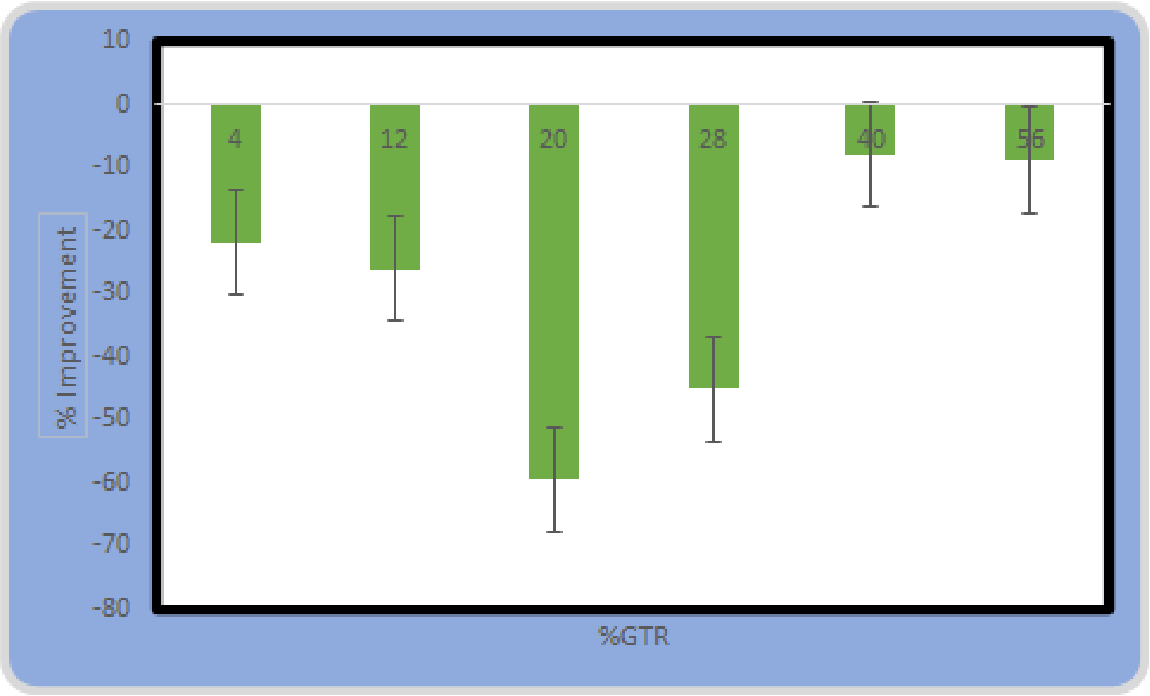


Figure 3.2.1.5: Impact percentage improvement BFD TT

Table 3.2.1.6: Summary of Impact Data for BFD SWT

Sample	Energy (J)	kJ/m^2
PP-T20/ 5%(GTR-EPR)	1.7	43
PP-T20/ 15%(GTR-EPR)	1.8	45
PP-T20/ 25%(GTR-EPR)	2	50
PP-T20/ 35%(GTR-EPR)	1.5	38
PP-T20/ 50%(GTR-EPR)	1.7	43
PP-T20/ 70%(GTR-EPR)	1.435	36

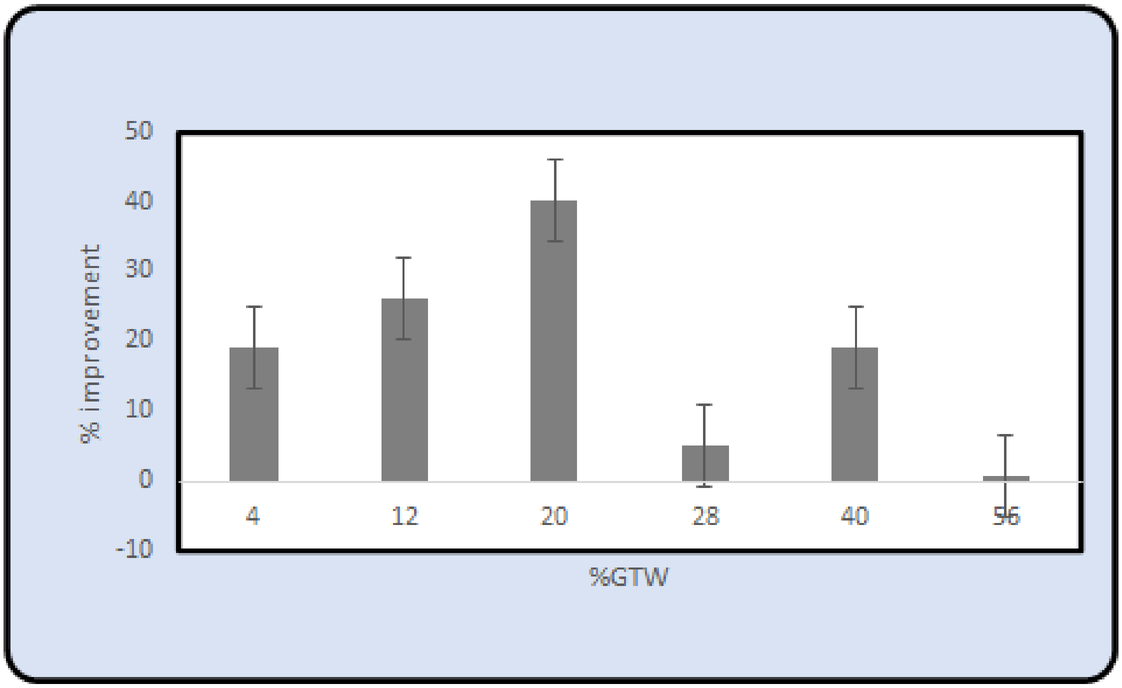


Figure 3.2.1.6: Impact percentage improvement BFD SWT

Table 3.2.1.7: Percentage improvement with the addition of GTR to PP/T20

GTR	4%	12%	20%	28%	40%	56%
BFD SWT	19	26	40	5	19	1
BFD TT	-22	-26	-59	-45	-8	-9
30 #	-9	-9	-16	-9	19	-20
40#	-38	-46	-35	-33	47	-12
60#	19	-9	-16	19	26	-12
60# cryogenic	-28	-9	-41	-44	54	-27

3.2.2 3-Point bend

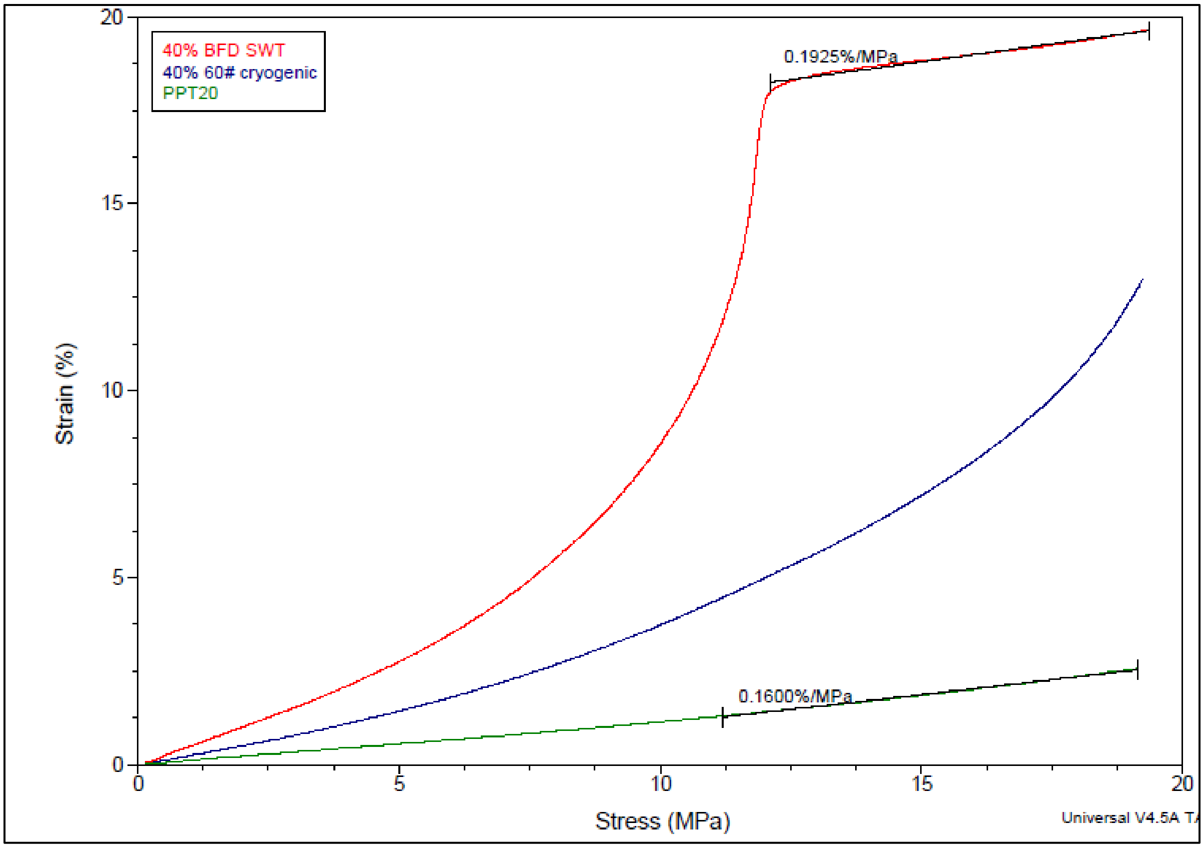
3-point bending is the simplest flexure fixture to test a materials response to a load measured as strain or stress it allows the monitoring of the region of linear behavior, the force needed to break a sample and the amount of force required to make the sample yield (shear yielding).

In Fig 3.2.2.1 A, PPT20 exhibits a plastic response which is a common characteristic for crystalline polymers by having a linear increase which is characteristic of the rigid nature of this material. It did not deform when stress was applied. The blend with 40% cryogenic rubber started to indicate elastomeric behavior at 10 MPa this is depicted by the exponential increase in strain (%) indicating the presence of both the rigid thermoplastic phase as well as the softer elastomer phase. Exponential increase occurs earlier for the SWT buffing dust at about 5Mpa this can be said to be an indication of the dominance of the elastomer phase which leads to a greater deformation of the material indicated by a large increase in strain (%) a maximum influence for the elastomer region is reached at 12 Mpa thereafter thermoplastic behaviour is observed. This phenomenon can be explained by failure analysis as it suggests that there may be a greater cluster of the elastomer at the center of the PP matrix which causing phase inversion.

In Fig 3.2.2.1 B, the PP-T20 and the 40% cryogenic rubber blend show similar behavior at sub-ambient temperatures when cooling rubber it tends to become more rigid and brittle as the molecules become immobile this is indicated by significant decrease in strain (%). The SWT also indicates a decreased elastomeric behaviour its slight decrease in comparison to the cryogenic rubber is due to having BR which is resistant to low temperatures [30].

In Fig 3.2.2.2 A and B, the 3-point bend percentage improvement for blends containing 40% GTR content at ambient and sub-ambient temperature is represented in a graphical form. The addition of GTR content led to a deterioration which is characterized by an increase in strain (%); this can be related by low stiffness of the GTR phase as well as the presence of interfacial voids and defects inside the blends thus more bending is obtained leading to increased permanent deformation. According to Fazil [40], Interfacial interaction is controlled by both GTR particle size and content. Improvement in flexural properties being attributed to lower particle sizes which have higher specific surface area leading to better interfacial interaction with thermoplastic molecules leading to fewer structural defects.

Even so the increase in elasticity with increase in GTR blends indicates that these TPE blends may still be functional for the underbody cover which requires long lasting elasticity as opposed to the rigidity of the PPT20 alone. The test was conducted at -20 ˚C to monitor the functionality of the blend at low temperatures, the underbody cover is an external component and therefore may be exposed to extreme temperatures and a requirement is that it still maintains its function.



A

Figure 3.2.2.1 A: The stress-strain curve of PP-T20 and GTRs at ambient temperatures.

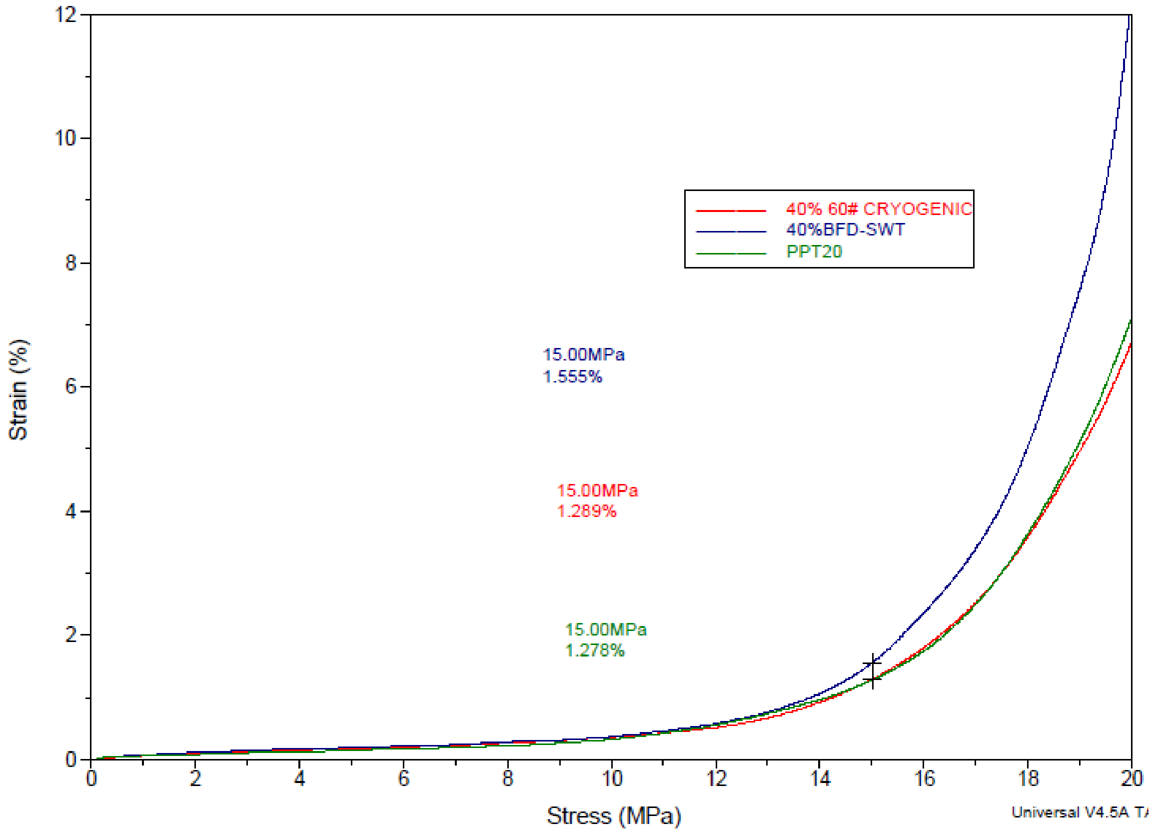


Figure 3.2.2.1 B: The stress-strain curve of PP-T20 and GTRs at -20 ˚C

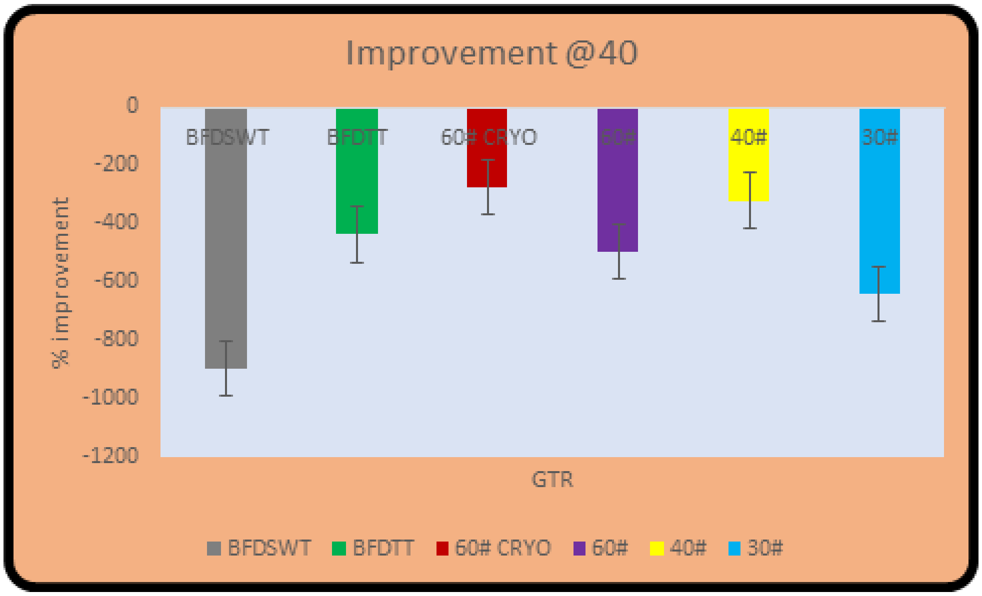


Figure 3.2.2.2 A: 3-point bend improvement at 40 % GTR contents at ambient temperatures.

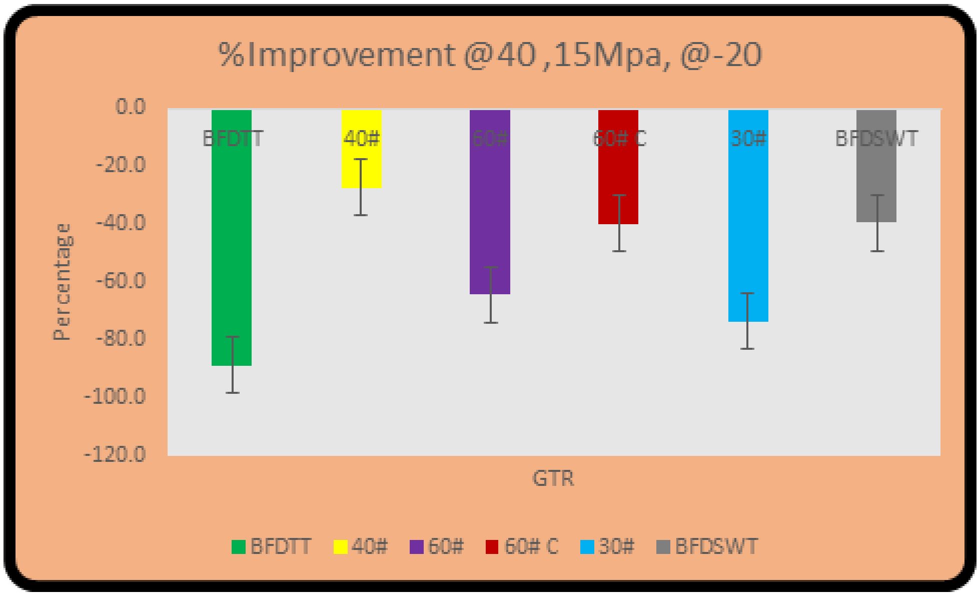


Figure 3.2.2.2 B: 3-point bend improvement at 40 % GTR contents -20 ˚C

3.2.3 Visco-Elastic behaviour

This test varies temperature at a set rate and scan across the transition regions of a materials behaviour. The difference in tan delta with temperature is illustrated in Table 3.2.3. Tan delta is influenced by the quality of the blend interface. Addition of GTR leads to an increase in tan delta due to the increase in elastic behavior, quantified by a great degree of molecular mobility this suggests that there is energy dissipated by GTR particles during stress transfer from the PP matrix to GTR and better damping properties of the material according to Fazil [40]. Lower tan delta peak is attributed to lower mobility as seen in Table 3.2.3 PP-T20 has a lower tan delta and is crystalline and more rigid [33, 40].

The tan delta peak (Fig 3.2.3) corresponds to the glass transition temperature, it is a more accurate measure of Tg as it considers the free volume of a polymer. This test was used to determine the operating range for the 40 wt% GTR blends which is the area before reaching the tan delta peak. In Table 3.2.3 the tan delta increases with the addition of GTR. PPT20 has an onset temperature of -7ºC that it can function sufficiently without failure at this temperature. Upon addition of 30 #, 60 # and the BFD TT, the onset temperature is shifted to 0.51,1 and 9 ºC so the blends of these GTR are not suitable for the utilization in subminimum temperatures because they are prone to shatter. Interestingly, BFD SWT has a much broader operating temperature range and this again may be attributed to the presence of BR which has properties such as rebound resilience and low temperature resistance; it can therefore withstand temperatures at -20ºC which is the lowest temperature recorded in Sutherland (South Africa). The intensity of the tan delta peak increases with addition of the GTR (Table 3.2.3) and the buffing dust SWT had an intensity of 0.7 this suggests an improved ability to absorb impact and a greater resistance to fracture this is attributed to the presence of butadiene rubber [33, 35, 40].

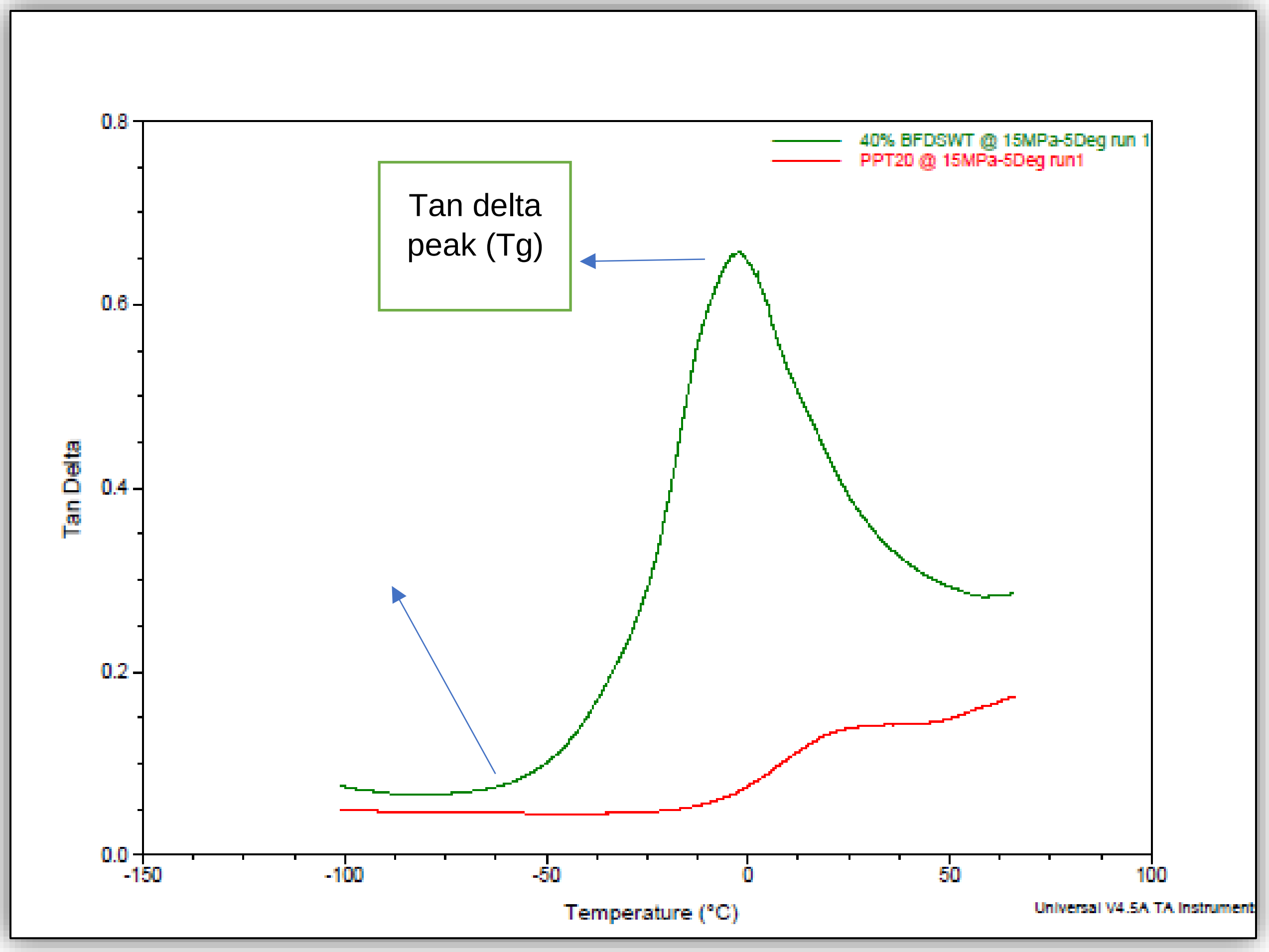


Figure 3.2.3: Tan delta analysis

Table 3.2.3: Tabulated onset temperature and glass transition (Tg)

GTR	**Onset (ºC)**	**Tg(ºC)**	**Tan delta**
PPT20	-7	26	0.1
30#	0.51	7	0.4
40#	-4	19	0.2
60#	1	10	0.3
60 # cryogenic	-8	23	0.2
BFD SWT	-31	-3	0.7
BFD TT	9	19	0.2

3.3 Failure Analysis

SEM imaging of the impact break specimen for 20% and 40% GTR content were viewed in various magnifications which ranged from low magnification (18-20) to high magnification (80). Low magnifications aid in the analysis of the nature of the matrix; i.e. whether it is continuous/ homogeneous or not, while high magnifications aid in the analysis of interfacial bonding. Upon addition of the GTR modification, the PP structure observed at both 20% and 40% result in the disruption of the continuous matrix. The micrographs show an agglomeration of rubber (Fig 3.5.6) which results in a discontinuous matrix, however yielding improved impact strength. This is phase inversion where the PP phase has been dominated by the elastomer phase since PP does not withhold GTR additions.

At lower GTR content there is a dominance in the PP matrix. This is seen as a continuous matrix which is particularly seen in the 40# blends and 60 # cryogenic (Fig 3.4.2 and 3.4.4 respectively). Since in this case a continuous matrix is attributed to the dominance of the

PP matrix impact strength, it is reduced as indicated in (Table 3.2.1.7). This is due to the brittle nature of PP, i.e. not being able to absorb energy upon impact leading to brittle fracture. It is important to note that the structural integrity of PP is not maintained at lower GTR content, which confirms the lack of performance for the tested mechanical properties for these blends. Additionally, the only blend that indicated an improvement of impact strength of 40% (Table 3.2.1.7) was the BFD SWT and this can be explained by the micrographs (Fig 3.4.6) that shows rubber inclusion at the center of the specimen which could provide the cushioning effect for impact and thus being able to absorb the energy.

Adhesion of CR to PP was achieved at 40% GTR content to varying degrees (Fig 3.5.1-3.5.6). For the 60 # cryogenic rubber surface analysis shows the formation of a homogeneous matrix with rubber particles being encapsulated in the PP matrix hence this explains the 54% improvement of impact strength which is the best improvement at this loading. BFD TT shows a decrease in impact strength of -8% and this is explained by what is seen on the surface (Fig 3.5.5); its surface is the most deformed showing voids of great depth which indicates that when the impact test was conducted the particles of this GTR are pulled out during breakage forming a discontinuous matrix.

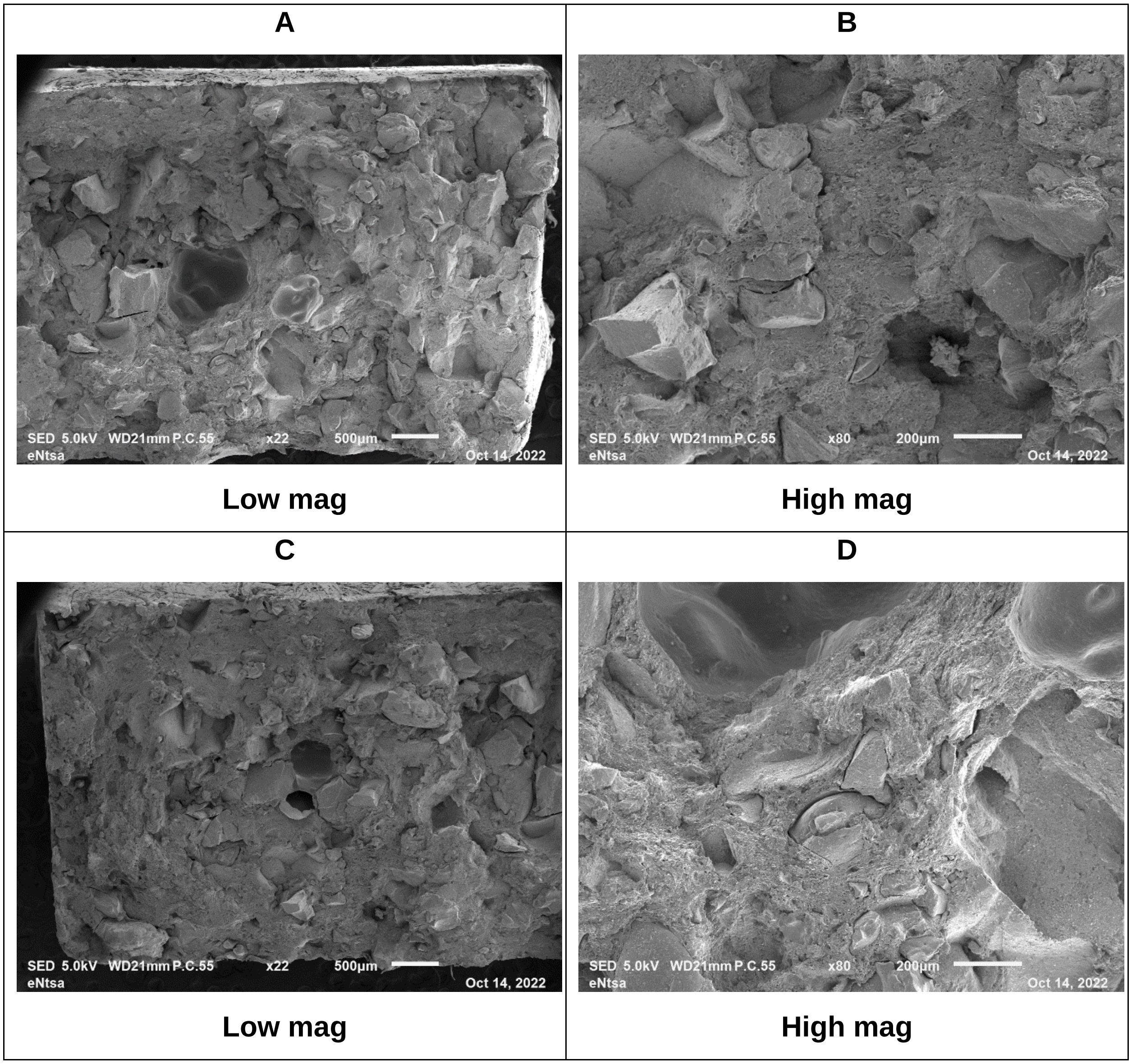


Figure 3.4.1: SEM micrographs of 30# at 20% GTR content.

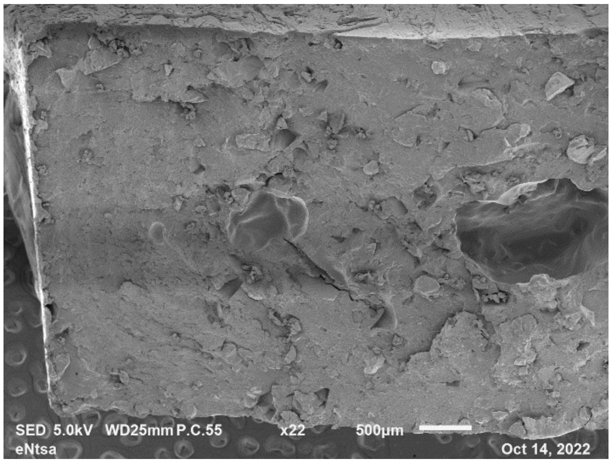
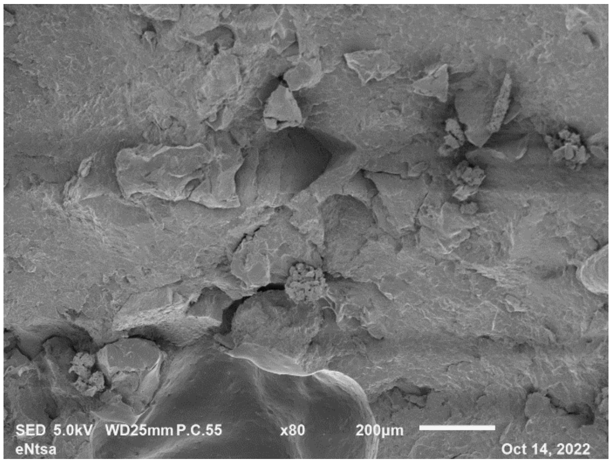
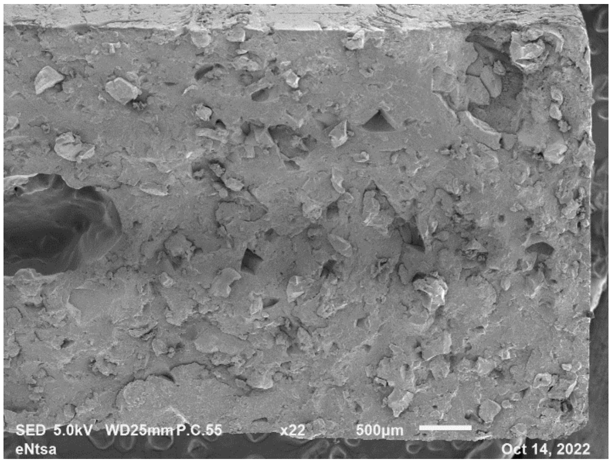
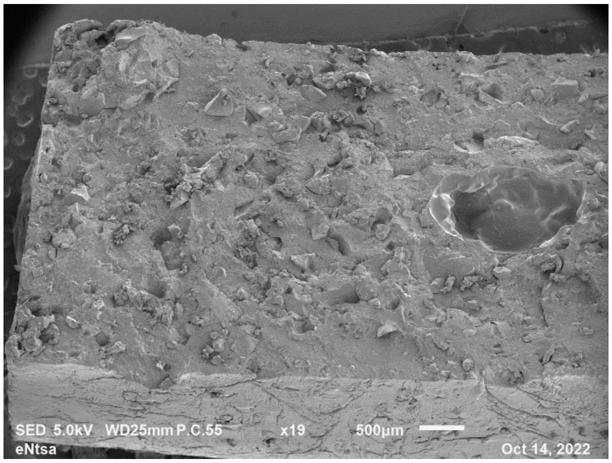
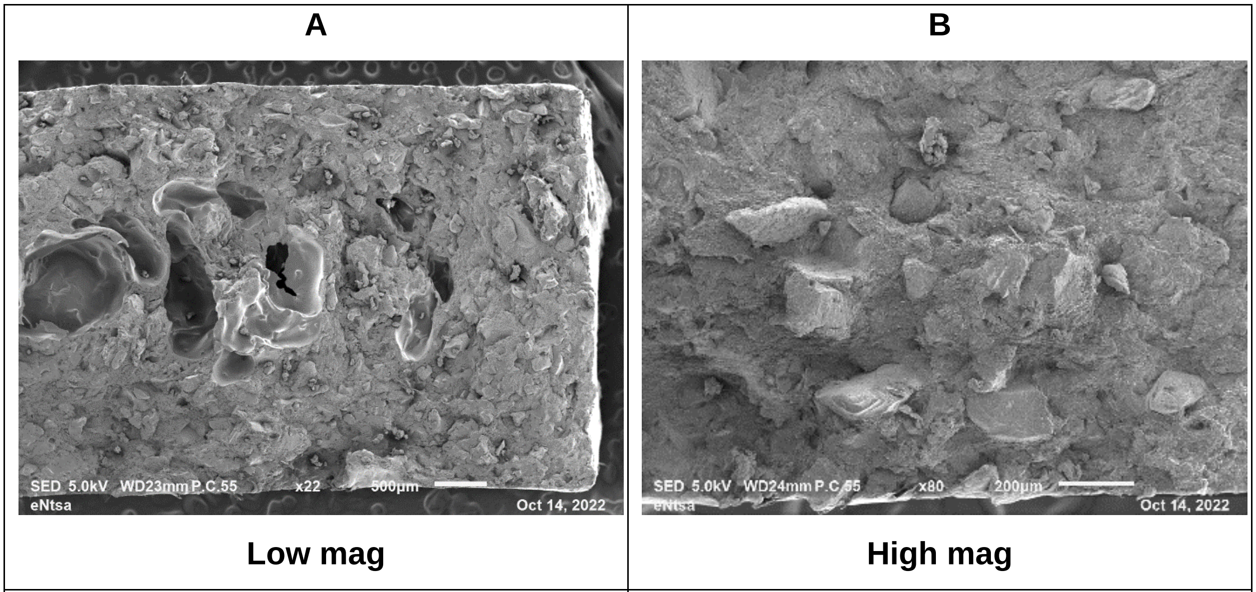
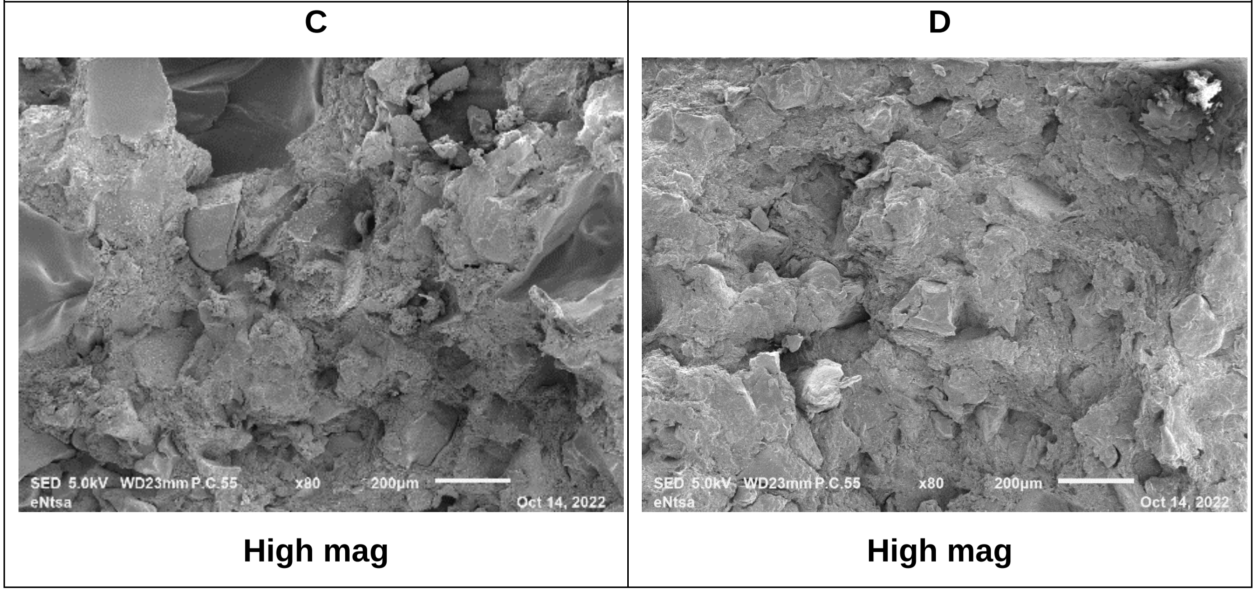
A	B
	
Low mag	**High mag**
C	**D**
	
Low mag	**Low mag**

Figure 3.4.2: SEM micrographs of 40# at 20% GTR content.



Low mag **High mag**



High mag **High mag**

Figure 3.4.3: SEM micrographs of 60# at 20% GTR content.

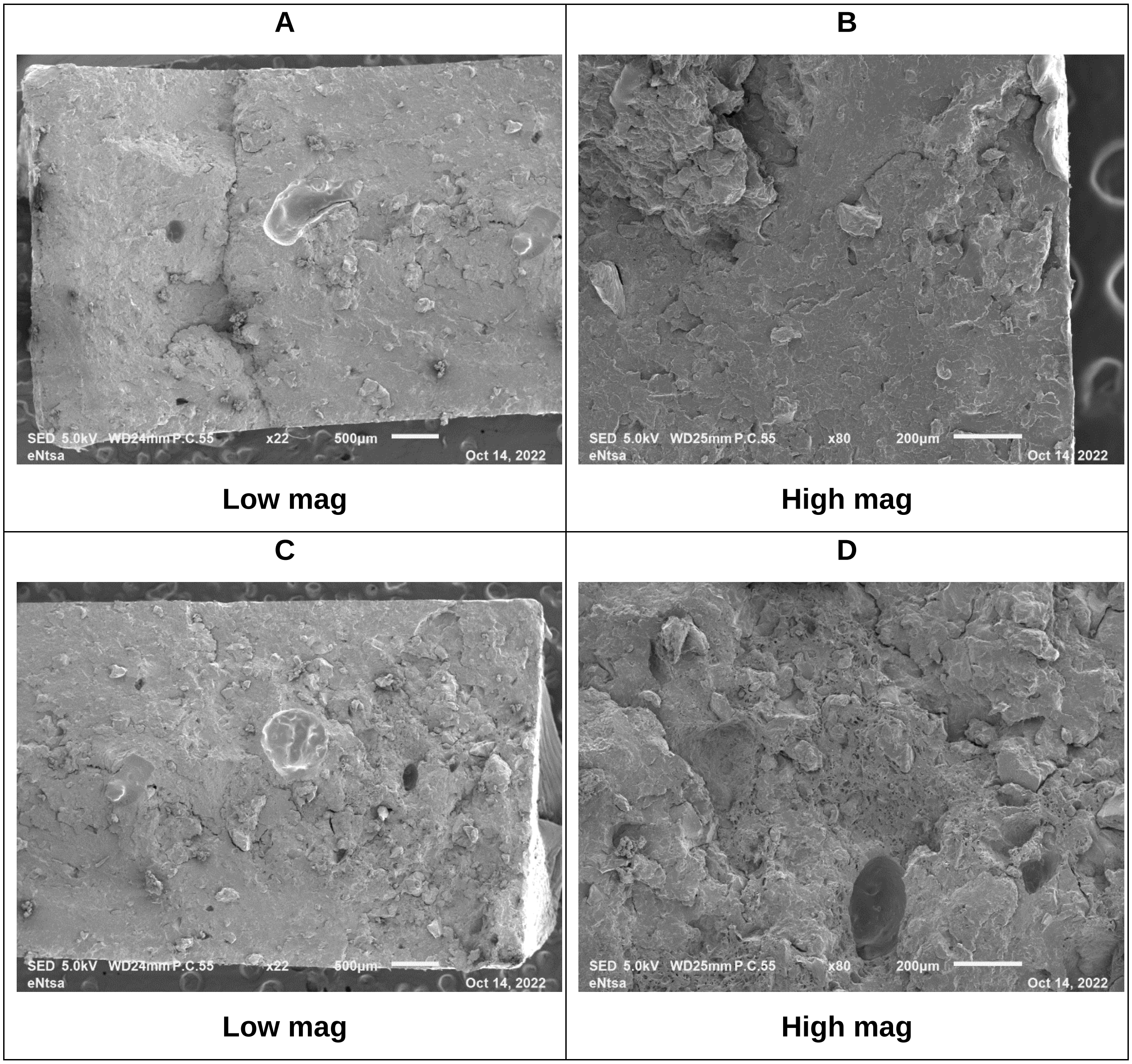
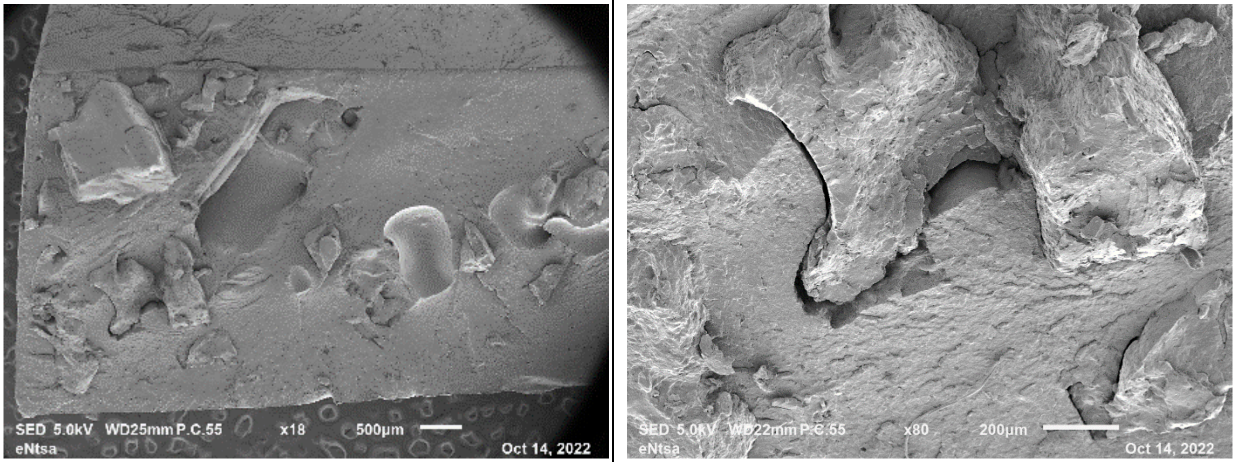


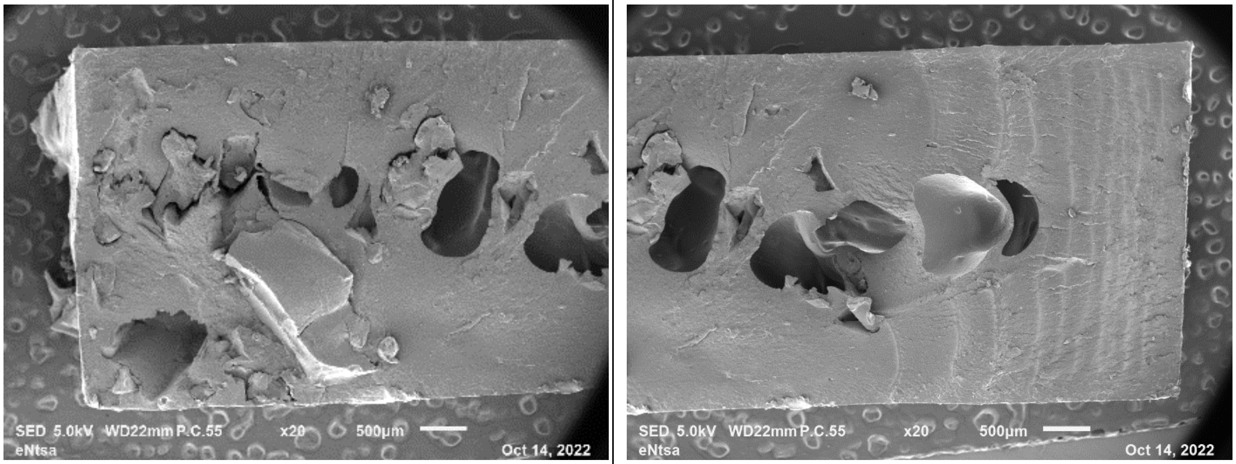
Figure 3.4.4: SEM micrographs of 60# cryogenic at 20% GTR content.

A B



Low mag High mag

C D



Low mag Low mag

Figure 3.4.5: SEM micrographs of BFD TT at 20% GTR content.

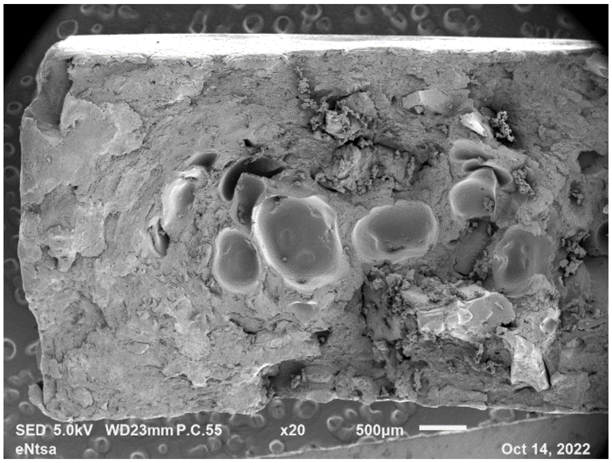
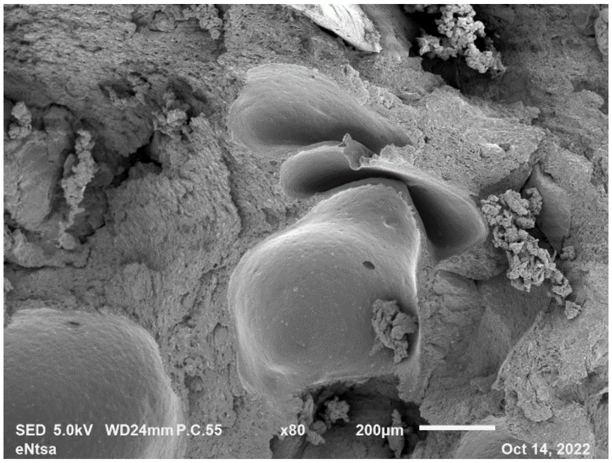
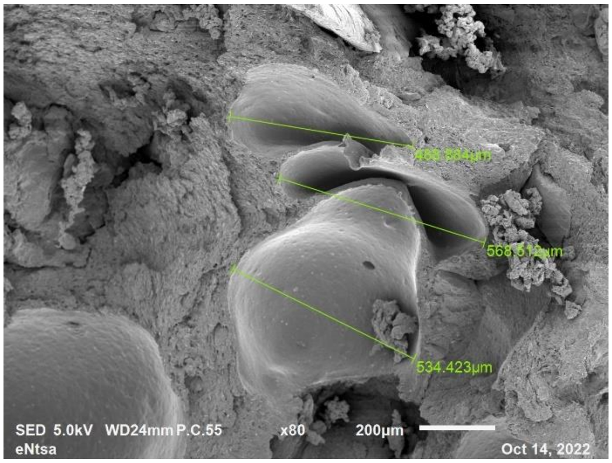
A	**B**
 **Low mag**	 **High mag**
C	**D**
 **High mag**	 **High mag measured**

Figure 3.4.6: SEM micrographs of BFD SWT at 20% GTR content.

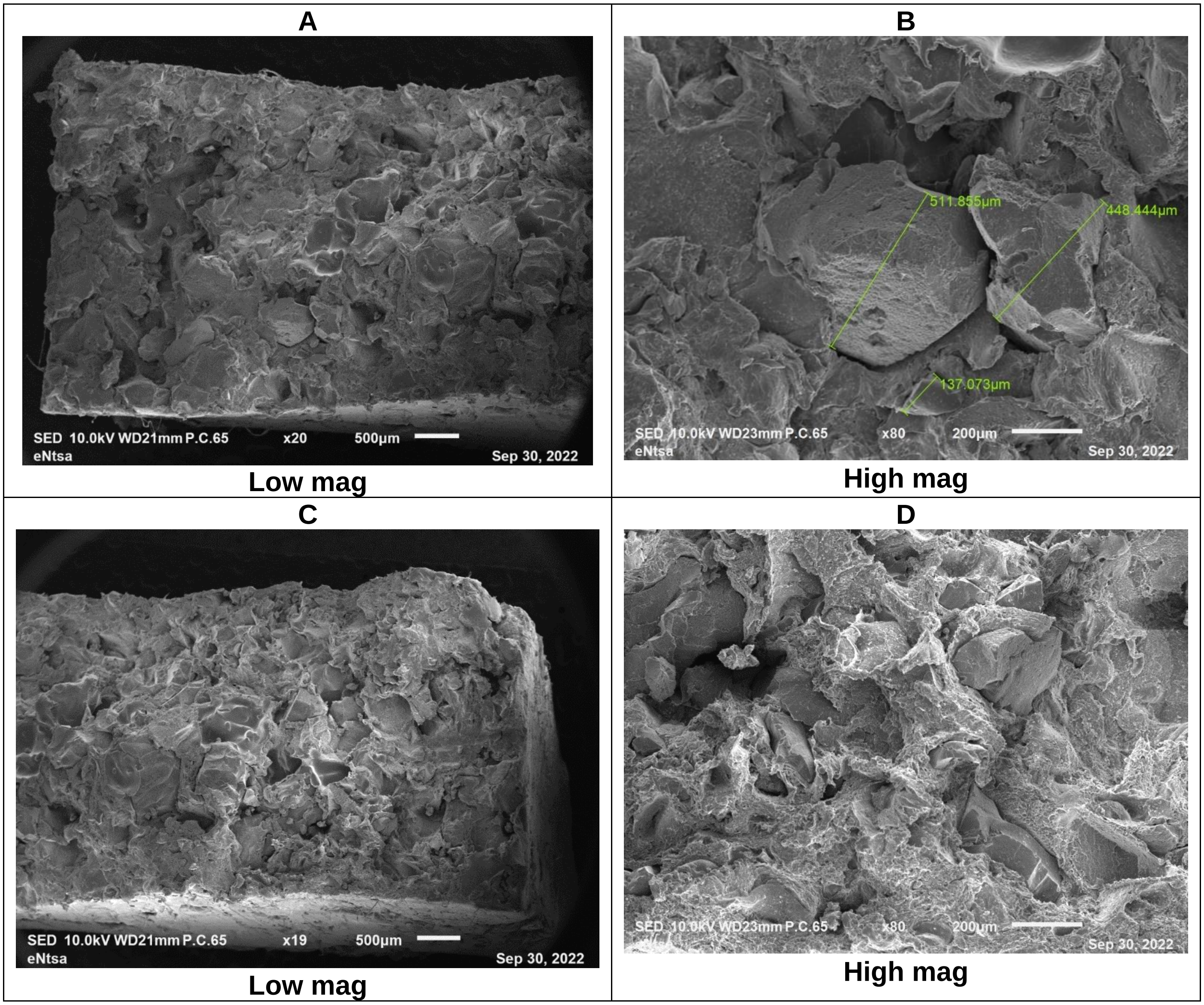


Figure 3.5.1: SEM micrograph of 30# at 40%

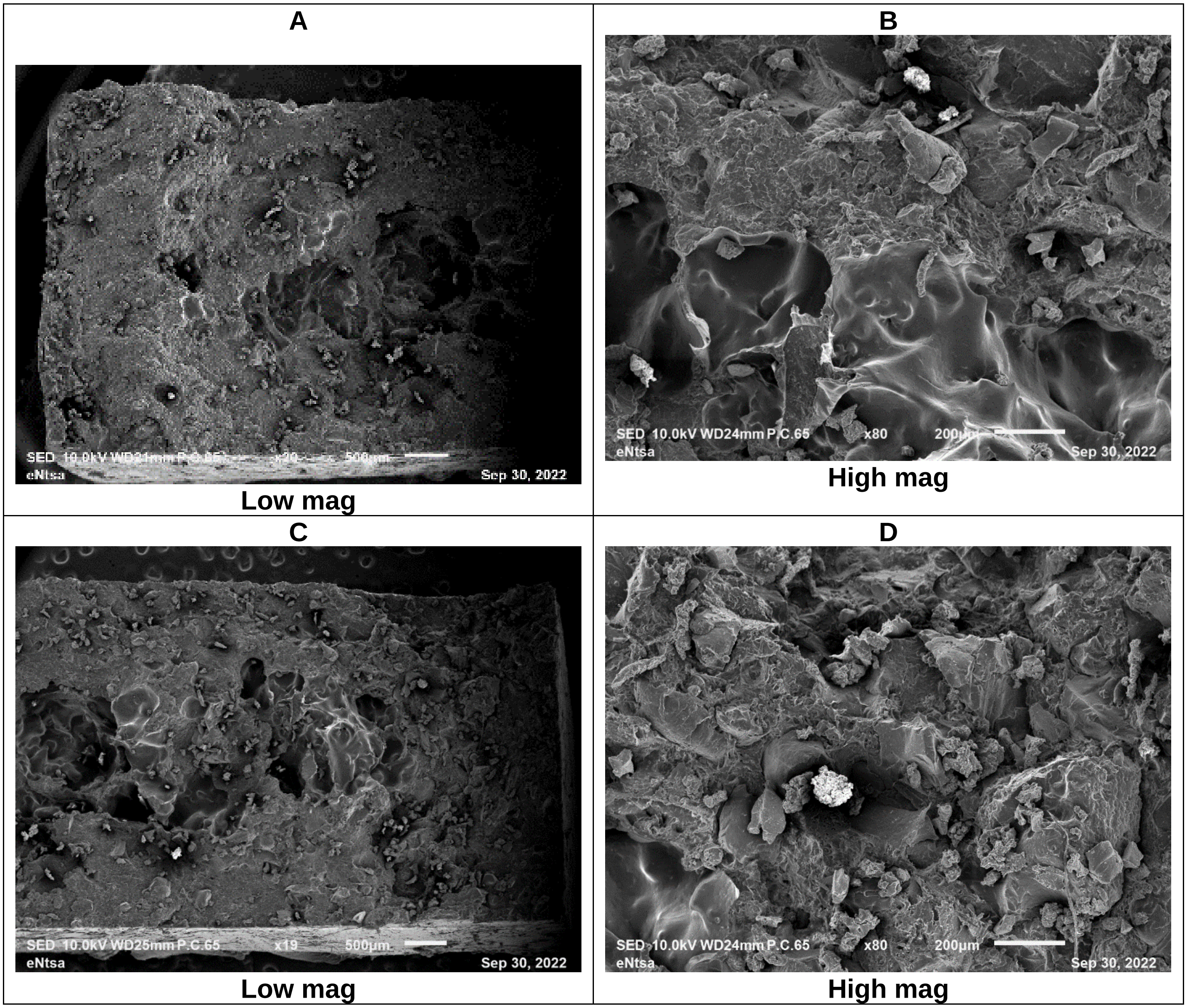
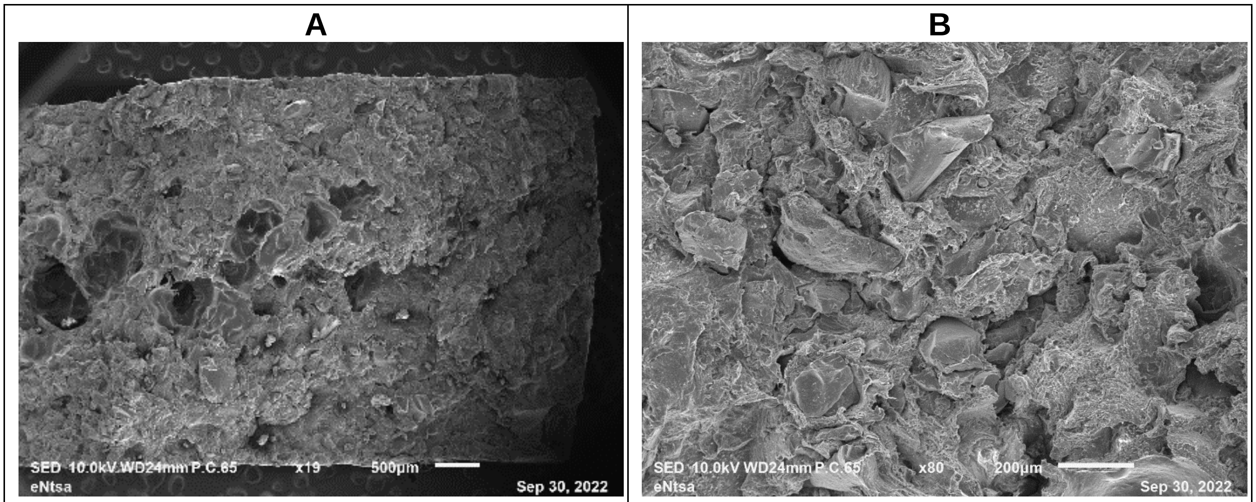
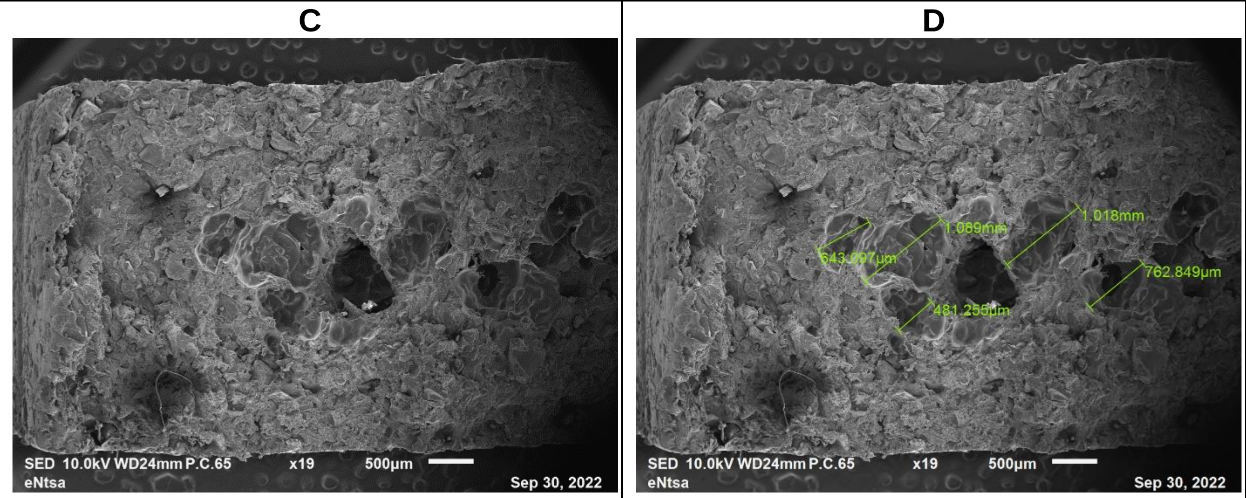


Figure 3.5.2: SEM micrographs of 40# at 40%



Low mag **High mag**



Low mag **High mag measured**

Figure 3.3.3: SEM micrograph of 60# at 40%

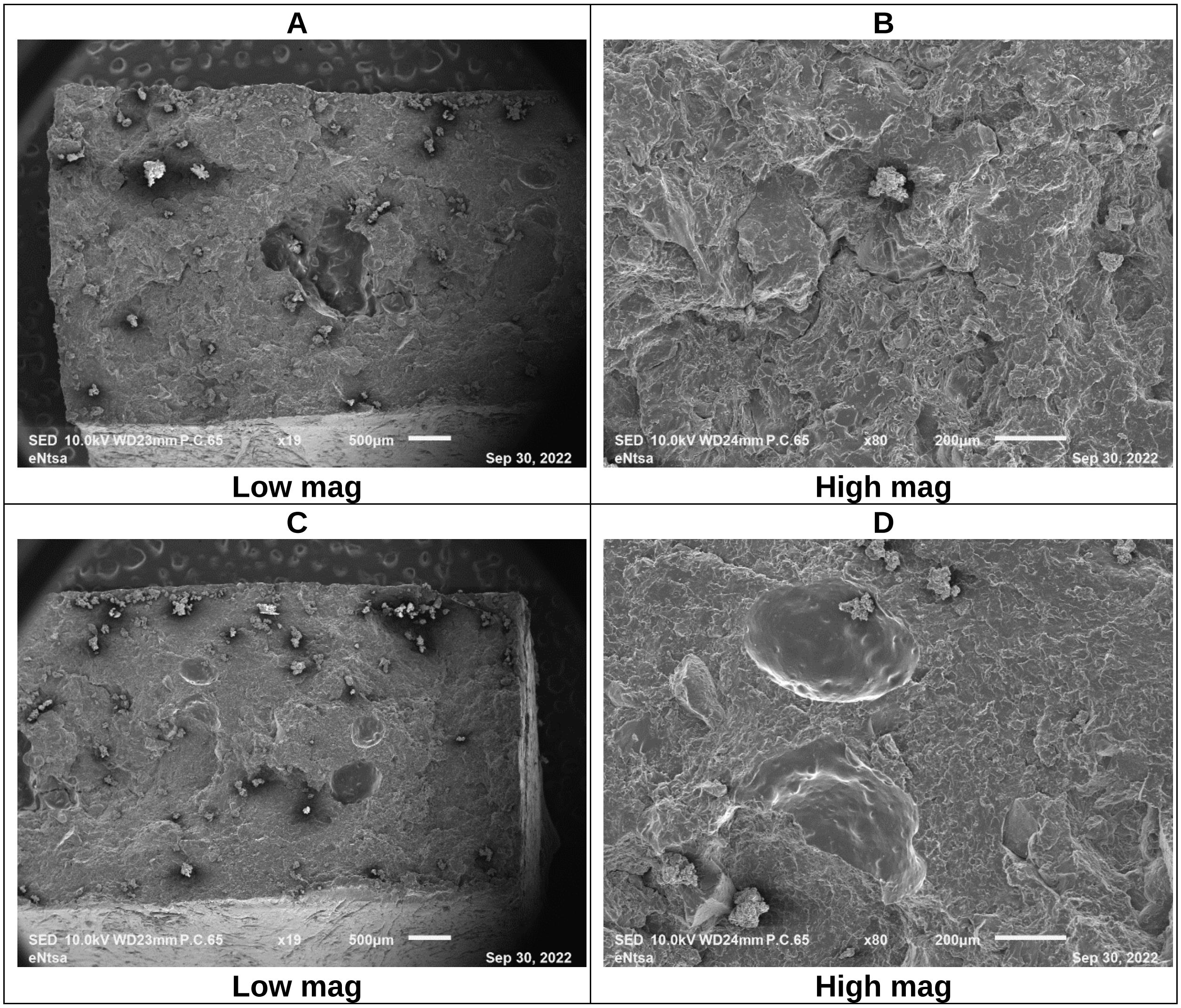
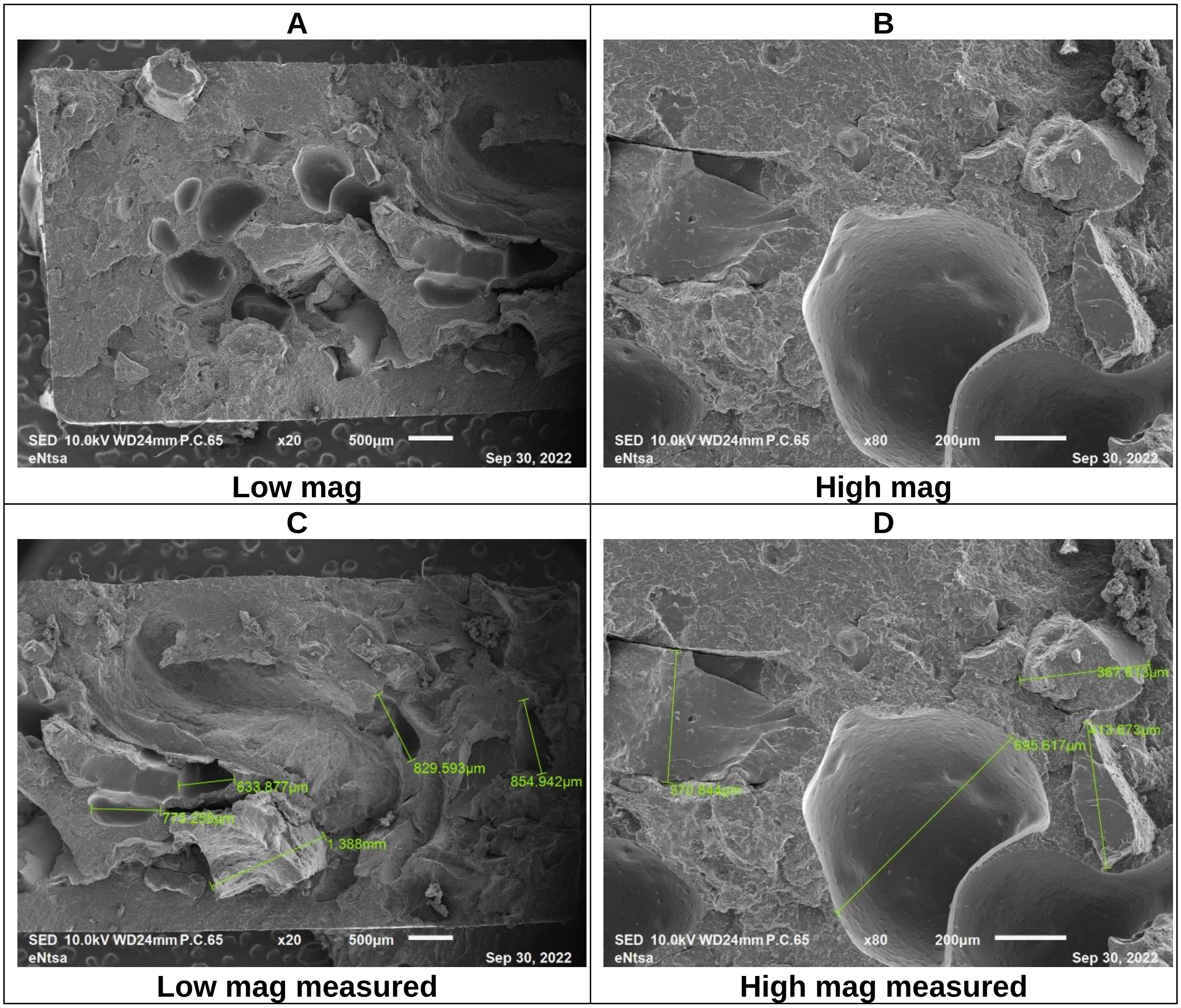


Figure 3.5.4: SEM micrographs of 60# cryogenic at 40%



Low mag

High mag

Low mag measured

High mag measured

Figure 3.5.5: SEM micrograph BFD TT at 40%

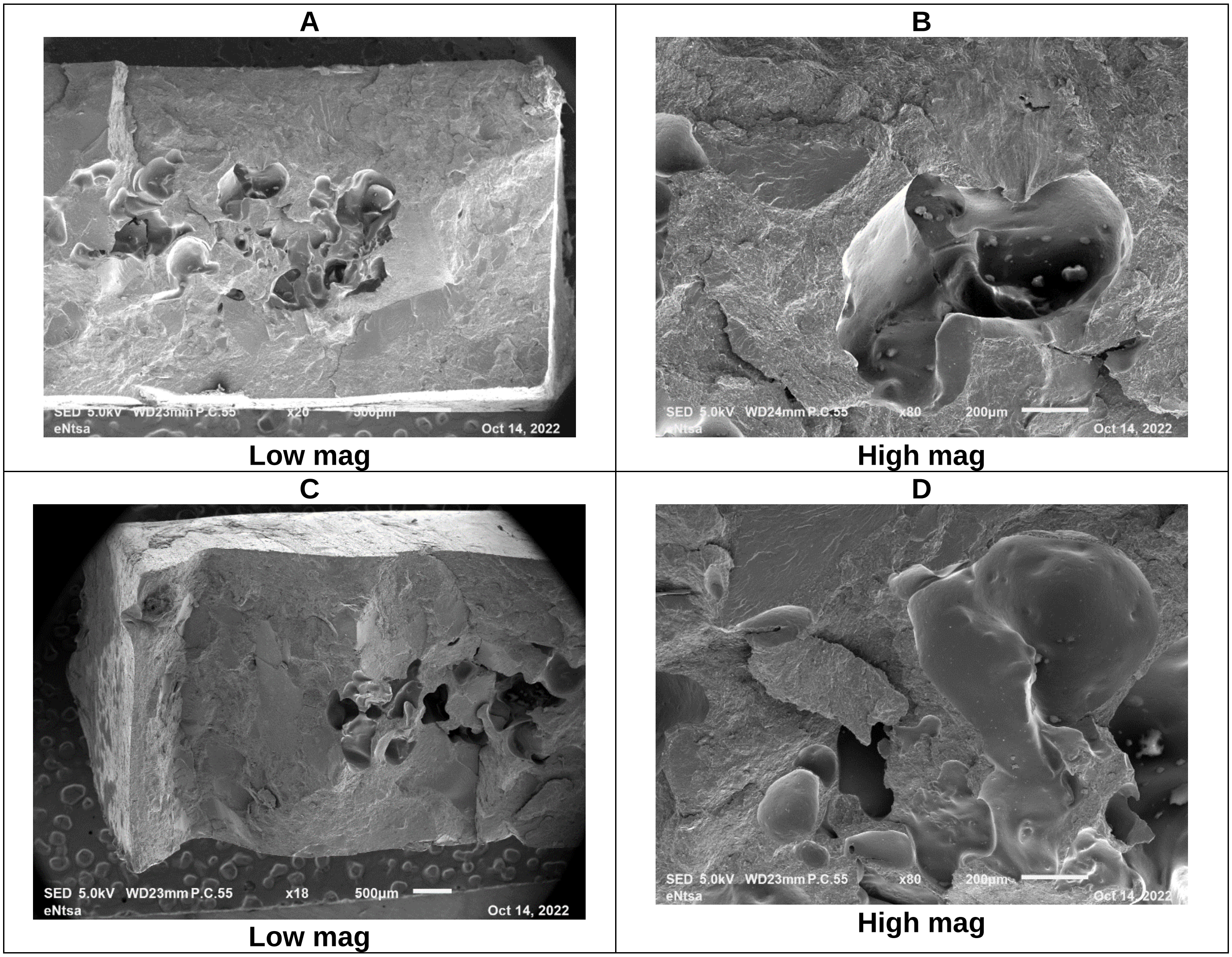


Figure 3.3.6: SEM micrograph BFD SWT at 40%

4. SUMMARY

The fundamental of this study was based on investigating the difference in the influence of GTR derived using two forms of processes mainly crumbing and buffing. In addition, the size, content, type of processing whether it is ambient or cryogenic, and the part of the tyre grounded leading to the composition (presence of Butadiene Rubber) would produce different or similar performance for the prospective TPE blends was the critical point of evaluation. Therefore, the influence of these forms of GTR's is summarized in the Tables below, showing comparison between their different variables/variants. Where Tables 4.1 is highlighting the key difference in performance for crumb rubbers, while table 4.2 is highlighting for buffing dust form of GTR's.

Table 4.1: Highlights to the performance impact of Crumb Rubber forms of GTR

Influence	Size (small to large)	Processing Type (low to high Tech)	Content (low to high)
Severely negative			
Negative	✓		
Neutral			
Positive			✓
Distinctively Positive		✓	

In the case of crumbing derived GTR's, the study showed that the addition of high dosages limited to 40% would yield positive performance, furthermore it can be concluded that high tech processing such as cryogenic grinding is preferred along with minimal particle size with a narrow particle size distribution.

Table 4.2: Highlights to the performance impact of Buffing Dust forms of GTR

Influence	Selectivity (Remould to Retread)	Content (low to high)
Severely negative		✓
Negative	✓	
Neutral		
Positive		
Distinctively Positive		

In the case of Buffing dusts derived GTR's, the study showed that small dosages limited to an amount of 20% would yield positive performance. In addition, it can be concluded that remoulded is much more preferred than the buffing dust derived from the retreading.

In summary the study showed and demonstrated that both crumbing and buffing derived GTR's can be utilzed to develop alternative TPE's replacing EPDM as an impact modifier for automotive components. However, the study highlighted that these two types of GTR's work in polar extremes, where one indicates a negative influence at low dosages while the other indicated positive influence at higher dosages. This allows us to arrive to the recommend of low dosages for Buffing and high dosages of crumb rubber.

Impact modification up to 40% GTR content and an impressive operating range making better suited for the manufacture of external parts which are continuously exposed to extreme temperatures and several impacts.

5. RECOMMENDATIONS

- It may be advantageous to prepare a 80% - 20% pelletized masterbatch of GTR-EPR prior to processing this will improve the dispersion and bonding of the GTR to the thermoplastic. Thus, improving the mechanical and thermal properties of the blends.
- The use of an injection moulding machine with a twin screw since it has good feeding characteristics and better suited for the mixing of powdered blends that require thorough mixing, melting, and forming.
- To conduct a tensile elongation test to determine the strength of the formulated blends and measure the ability of a material to resist being pulled apart.

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