



## Review

# Advances in High Performance Polymers and Composites Materials: Development Opportunities

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## Abstract

The development of high-performance polymers continues to grow in both academia and industry due to their numerous benefits for society and diverse commercial potential. Further, polymer materials with varied functional properties can be modified through blends and composites to enhance their performance. The unique functional, thermal, and mechanical characteristics, along with the ease of processing, have created new opportunities for product applications in various sectors, including packaging, agriculture, energy, automobiles, infrastructure, retail, aerospace, defense, and other growing industries. This review primarily focuses on the scientific and technological advances in high-performance materials such as polyolefins and elastomers, as well as their composites. Furthermore, it addresses the environmental concerns arising from plastic mismanagement, emphasizing sustainability aspects, including the circular economy and the development of biodegradable, bio-compostable and bio-based polymers. The review also discusses new directions in polymer science and engineering, such as life cycle management, flexible manufacturing, and the integration of artificial intelligence, machine learning, and deep learning to accelerate sustainable development.

**Keywords:** polyolefins, elastomers, bio-compostable plastics, bio-based composite, sustainability

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## 1 INTRODUCTION

Polymers constitute an important class of lightweight and high-performance materials that are prevalent in all facets of modern society, contributing to higher standards of living. The versatility of polymer materials is due to different possible combination of chemical building blocks from renewable as well as non-renewable resources. These attributes contribute to the increasing demand for polymers

and composites, which is expected to triple by 2050 from the global production of 350 million metric tons in 2018<sup>[1]</sup>. This is due to cost-effective solutions to growth sectors such as food, health, energy, transportation, defence, space, housing, infrastructure, etc.

Polyolefins are a class of synthetic polymers made from simple olefin monomers, which are hydrocarbons

containing one or more carbon-carbon double bonds. At present, polyolefins, such as polyethylene (PE) and polypropylene (PP), account for nearly half of the global plastic production<sup>[2]</sup> due to their excellent combination of mechanical and chemical properties, high durability, low cost and superior processibility. These product portfolios cover various range of applications, including construction materials, automobile parts, household materials, packaging materials such as plastic bags, bottles, containers, pipes, furniture, textiles etc<sup>[3-12]</sup>. In contrast to commodity polyolefin, high-performance specialty polyolefins are advanced polymers covered in the polyolefin family, exhibiting exceptional properties and performance characteristics. These specialty polyolefins are typically designed for niche applications where superior performance, such as electrical properties, high-temperature resistance, mechanical strength, and chemical resistance are required. Some examples of specialty polyolefins include polyolefin elastomers (POEs), thermoplastic elastomers, halogenated polyolefin, polyolefin fibres, cross-linked PE, polyolefin foams, functional polyolefin and various polyolefin-based composites<sup>[13,14]</sup>. The development of high-performance specialty polyolefins involves advanced polymer chemistry and processing techniques to tailor the material's properties to meet the specific needs industries and applications. These materials are costlier than commodity polyolefins, but at the same time they bring unique benefits in terms of functionality, durability and improved mechanical strength essential for high performance products in various industries<sup>[15]</sup>. This review covers the high-performance polyolefins grades of PP and PE produced using high performance catalyst technology, in addition to polyolefin materials for specialty applications.

Synthetic elastomers are another important class of materials with a higher growth rate in different sectors. The synthetic elastomeric rubber materials, such as styrene butadiene rubber (SBR), polybutadiene rubber (PBR), nitrile butadiene rubber (NBR), chloroprene rubber (CR), butyl and halobutyl-rubber (IIR and HIIR), ethylene propylene diene monomer, silicon rubber and ethylene vinyl acetate (EVA) rubber, have high demand in general as well as specialty applications<sup>[16-24]</sup>. Furthermore, high-performance elastomer products for self-healing and shape-memory applications are getting attention for new product development<sup>[25-28]</sup>. These developments, along with elastomeric composites incorporating carbon black (CB), graphene, carbon nanotube (CNT) materials, silica and other non-carbon-based composites useful for various applications, are discussed in the review.

Although polymers / plastics make our daily life comfortable, however, mismanagement of polymer waste causes severe environmental concern. The packaging sector and single-use plastics are mainly responsible for the plastic pollution since these kinds of plastics are discarded after its

first use. To combat environmental damage, sustainability is taking a centre stage with plastic waste as a resource in addition to bio-based polymers and composites. Post COVID-19 the legislative regulations have become more stringent and looking for alternative solutions. The use of biodegradable / biocompostable plastics seems a promising alternative for single-use application. In the last decade biodegradable polymers have grown rapidly and polymers like poly(lactic acid) (PLA), poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS), starch-based polymers etc. have become commercial reality<sup>[29-35]</sup>. The growing demand of these polymers attributed to the legislative regulations and customer awareness toward green products necessitating improved process and product development for single-use plastic applications. Furthermore, alternative solutions like plastic recycling are getting increasing attention for plastic circularity. The mechanical recycling is more dominant in the plastic recycling sector. However, the manual plastic segregation and sorting are major challenges in this area due to hazardous effects on the workers. Therefore, the new areas to adopt are artificial intelligence (AI) and machine learning (ML) based plastic segregation methods<sup>[36]</sup>. High quality automated sorting mechanism can recognize size, brands, colors and type of plastics. Furthermore, chemical recycling is equally important for polymer to recover useful chemicals and polymers from the plastic waste. The life cycle assessment of a product helps to understand its carbon footprint and to make a right choice for circularity. This review covers bioplastics, ML approaches, polymer life cycle management and flexible manufacturing for effective solutions and plastics circularity.

## 2 POLYMERS, COMPOSITES AND APPLICATIONS

### 2.1 High-performance Polyolefins

Polyolefin materials occupy top position amongst all polymers in terms of overall demand and production capacity. The polyolefin market size was valued at 243 billion USD in 2022 and expected is to increase at a compound annual growth rate (CAGR) of 5.1% for various industrial applications<sup>[37]</sup>. A number of polyolefin technologies are currently employed for the production of high-performance products. The present emphasis is to develop high through put polymerization process as well as product grades with enhanced properties. Novel proprietary catalyst technologies are developed<sup>[4-10]</sup> to produce PP and PE grades with high throughputs for different applications by polymerizing olefin with and without copolymers (Table 1).

In addition to commodity PE and PP products, a novel class of high-performance specialty polyolefin grades (Figure 1) has emerged. This class includes olefin copolymers, POEs, olefin terpolymers, polyolefin-based waxes, cyclic olefin copolymers (COC), ultra-high and high molecular weight (Mw) polyolefins, and functional

**Table 1. Polypropylene and Polyethylene Grades Developed with Advance Proprietary Catalyst Technology**

S. No.	Grades	MFI (g/10min)	Applications
<b>Homo PP Grades</b>			
Woven sacks and monofilament			
1	H030SG	3.4	Raffia tapes used in making woven fabrics
2	H026SG	2.6	High tenacity tapes
Films			
3	H100EY	10.0	Textile overwraps, general purpose packaging
4	H080EY	8.0	High tenacity tapes
Extrusion coating			
5	H350EG	38.0	Extrusion coating, lamination
Fiber and film			
6	H200FG	20.0	Staple fiber and multi filament
7	H230FG	25.0	Bulked continuous filament application
8	H350FG	38.0	Fine fiber yarn and non-woven
Extrusion and blow molding			
9	H020EG	2.0	Sheet, strappings, tubing, blow moulded container
Injection molding			
10	H110MA	11.0	Rigid packaging, furniture, and housewares
11	H050MN	5.0	Furniture and rigid packaging
12	H200MA	25.0	Thin wall container, multicavity molding
13	H200MK	20.0	Clear thin wall container, syringe
<b>Impact Copolymer PP Grades</b>			
Extrusion and blow molding			
1	C015EG	1.5	Sheet blow moulded container
Extrusion coating			
2	B250EG	25.0	Extrusion coating
Injection molding			
3	B030MG	3.0	Furniture industrial product
4	C080MA	8.0	Furniture industrial product
5	C080MT	8.0	Batteries and automotive
6	B120MA	12.0	Houseware, general purpose molding
7	C120MN	12.0	Paint pills, luggage, industrial components
8	C200MN	20.0	Automotive components, collapsible crates
9	B220MN	22.0	Appliances automotive
10	C320MN	32.0	Appliances automotive, compounding
11	B400MN	35.0	Appliances automotive, compounding
12	B650MN	65.0	Appliances automotive, compounding
13	B550MN	55.0	Appliances compounding
<b>LLDPE Grades</b>			
Film grades			
1	JF19010	1.0	Mono & multilayer films for liner bags, industrial consumer packaging, shrink film, shipping sacks, agricultural film
2	JF19020	2.0	Blown films for co-extrusion, agricultural Films, shopping bags, liners, consumer packaging
3	JF18010	1.0	Mono & multilayer blown / cast films for lamination, stretch cling films & protection films
4	JF18020	2.0	Blown & cast film for industrial packaging, stretch wrap, cling film for food or hygiene packaging, bubble wrap

Roto molding			
5	JLL36RA045	4.5	Overhead water tank, storage tank for agriculture, loft tank, litter bin, toy items
Drip lateral			
6	JD22010	1.0	Drip irrigation tubing for online laterals / flat and round emitting pipes

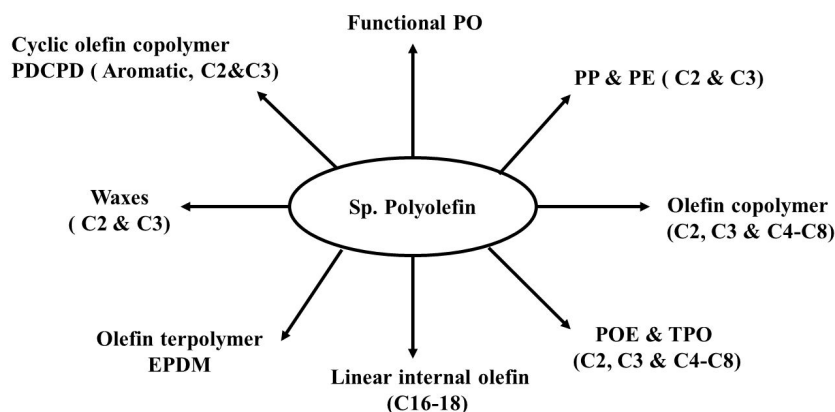


Figure 1. High-performance specialty polyolefins.

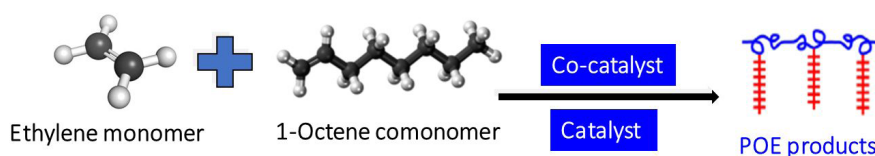


Figure 2. Synthesis of POE using ethylene and 1-octene comonomer.

polyolefin materials<sup>[11-14]</sup>. Novel properties and enhanced performance have allowed these materials to enter growing market sectors of new applications in constructions, automobiles, space crafts, EV cars, solar panel etc.

## 2.2 The Key Features of Some of the High-performance Specialty Polyolefin Materials

### 2.2.1 POE

POE are materials that can be easily molded and extruded like thermoplastics with the additional feature of enhanced elastic properties. POE offers advantages over thermoset rubbers due to mechanical flexibility, lightweight, easy processability, and recyclability. POE is produced via copolymerization of ethylene or propylene monomer with 1-butene or 1-hexene or 1-octene comonomer<sup>[38,39]</sup>. POE films provide balance of good rigidity and ductility and are more stable in terms of photo- and thermal oxidation than EVA films<sup>[40]</sup>.

The global POE market size was approximately 1.9 billion USD in 2022 and is expected to reach 3.6 billion USD by 2030, with a CAGR of 8%<sup>[41]</sup>. The top global players are Dow, LG Chemical, ExxonMobil Chemical, Sabic and Mitsui Chemical. The applications include PV cell encapsulants for solar applications, molded parts in

automobile sector, foam, wire and cable, films, etc. We have developed a solution-phase polymerization process using a metallocene catalyst for POE synthesis. Metallocene catalyst used to produce different POE grades via ethylene and 1-octene comonomer (Figure 2).

The copolymerization process parameters, such as temperature, ethylene pressure, comonomer content, cocatalyst concentration, and solvents, influence the characteristics of POEs grades, including weight average Mw, number average molecular weight (Mn), polydispersity index (PDI), comonomer 1-octene incorporation, and thermal mechanical properties etc., to produce POE grades (Table 2).

### 2.2.2 Ultra-high Molecular Weight Polyolefin (UHMWPO)

UHMWPO is a class of polymers which are produced by polymerizing olefin using Ziegler-Natta catalysts or metallocene catalyst systems. Disentangled UHMWPO class of grades offer the advantages of melt processing over entangled grades. Among UHMWPO, ultra-high molecular weight polypropylene grades are new class of materials with properties not demonstrated by ultra-high molecular weight polyethylene (UHMWPE) such as improved

**Table 2. POE Product Properties**

Properties of POE	Values
Density (g/cc)	0.86-0.88
MFI (g/10min)	3-30
1-octene (wt%)	20-40
Melting temperature ( $T_m$ , °C)	60-90
Crystallization temperature ( $T_c$ , °C)	40-60
Tensile strength (MPa)	2-5
Elongation at break (%)	300-1300
Hardness Shore D	15-20
Molecular weight (g/mol)	$30 \times 10^4$ - $80 \times 10^4$
Polydispersity	2-3

performance at a higher working temperature<sup>[42-44]</sup>. Ultra-high molecular weight polymers are used in engineering applications because of their better mechanical properties as compared to commodity polyolefin products<sup>[45,46]</sup>. Currently, UHMWPE is produced commercially with a unique set of properties and applications<sup>[47,48]</sup>. World-wide UHMWPE polymer market is growing at a CAGR of 9.1% from 1.8 billion USD in 2022 to reach 2.8 billion USD by 2027<sup>[49]</sup>. The product applications are in aerospace and defence sectors, shipping industries, and bio-medical sector.

UHMWPE materials are developed by optimizing different process parameters<sup>[11,12,42]</sup> to accomplish Mw in the range from 1 to 7 million g/mol<sup>[50-53]</sup>. The disentangled polypropylene (DPP) material is produced from the reverse micelle formation during polymerization using single site metallocene catalyst system with spherical morphology<sup>[11,54]</sup>. The general product characteristics<sup>[54]</sup> are shown in Table 3.

The low-entangled state in the semi-crystalline polyolefin polymers allows sintering and improves the processability in the solid-state. This feature allows formation of uniaxial drawn objects having unprecedented properties for DPP type materials<sup>[54,55]</sup>.

### 2.2.3 Functional Polyolefins

Functionalized polyolefins are a class of high performance olefin polymers with polar and nonpolar functionalities. The incorporation of functionalities into the polyolefin's backbone allows for improving several properties such as paintability, wettability, adhesion combability, etc. Furthermore, introduction of functionality in the polyolefin also improved the interaction with numerous materials like clay, glass fiber, CB, paint, and pigment to enhance performance of blends and composites<sup>[56]</sup>. The improved composite material of functional polyolefin has superior properties and can be used for newer applications such as fuel cells, film capacitors with better energy densities, membranes, etc<sup>[57]</sup>. Other application includes cosmetics, wires, cable, tire, healthcare, electronics, optics, surface

**Table 3. DPP Product Properties**

Properties of DPP	Values
Morphology of resin	Spherical
Bulk density (g/cc)	0.06-0.33
Melting temperature ( $T_m$ , °C)	158-165
Molecular weight (g/mol)	$1.0 \times 10^6$ - $3.0 \times 10^6$
Polydispersity	2-9

modified polyolefin films, sealing layer in co-extruded articles, food packaging, sports equipment etc.

Simple, cost-effective, and commercially viable green methodology of hydrophilic polyolefin technology has been developed (Figure 3) by post extrusion process using proprietary additives<sup>[58]</sup>. The modified fibers provide excellent flexural strength to cement sheets comparable to cement-asbestos sheets. Synthetic processes for functional polyolefin based on the polymerization of polar and non-polar monomers through Lewis Acid-mediated polymerization are also developed. The methyl acrylate (MA) with 1-octene copolymerization produces random polymer<sup>[59,60]</sup>.

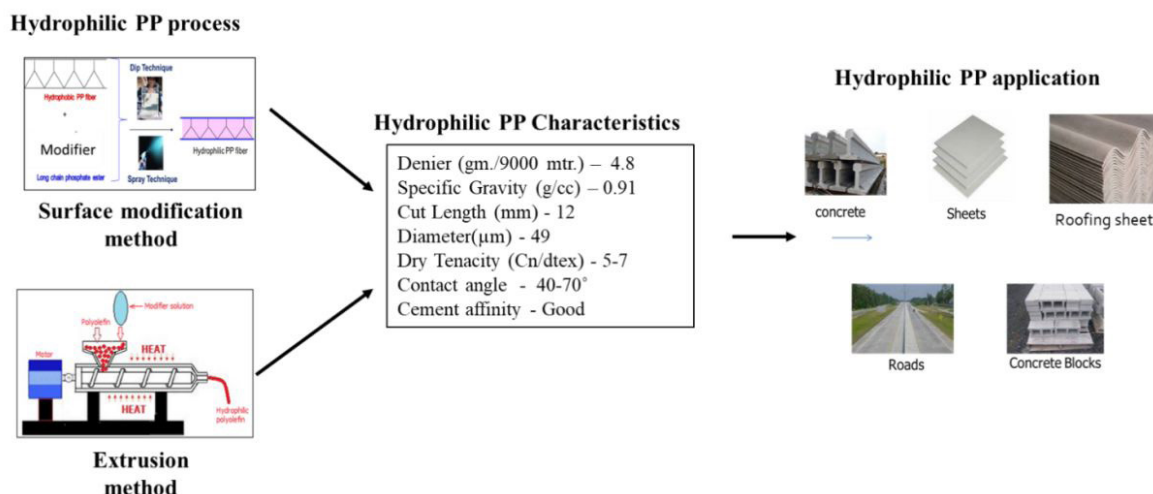
### 2.2.4 Metallocene Linear Low Density Polyethylene (LLDPE)

Metallocene LLDPE is highly demandable in film for food packaging application. In 2018, the global metallocene LLDPE market was 4.7 billion USD, with a CAGR 6%. It is expected to reach 7.8 billion USD in 2027<sup>[61]</sup>. Metallocene PE, also known as mPE, is a specialty thermoplastic produced by the copolymerization of ethylene with  $\alpha$ -olefins using a metallocene catalyst. mLLDPE has superior properties such as narrow Mw distribution, high dart impact, better tensile strength, good transparency, and down gauging properties compared to Ziegler-Natta-based LLDPE. It is mainly used in film-grade applications in addition to sheet, injection molding and blow molding products.

Metallocene LLDPE is developed by copolymerization of ethylene and higher  $\alpha$ -olefins (e.g., 1-hexene) using metallocene catalyst systems<sup>[62-64]</sup> (Table 4). The comonomer type and its amount in the metallocene LLDPE is important since it significantly impact the polymer properties such as thermal, mechanical and Mw. These characteristics are critical for deciding the end use application like film, and molding. mLLDPE exhibits superior mechanical properties such as higher tensile strength, impact, and puncture resistance than low density PE and targeted applications are different type of films.

### 2.2.5 PO-based Wax

PE wax grades are an important class of material among PO containing hydrocarbons between C20 and C50 or higher carbon numbers. The specialized metallocene-



**Figure 3. Hydrophilic PP through extrusion process for various end use applications.**

**Table 4. Resin Characteristics of Metallocene LLDPE**

Properties	Product Properties
Activity (gm, PE/gm, cat)	400-600
Bulk density (gm/cc)	0.17-0.30
MFI (gm/10min)	0.5-1.0
Melting temperature ( $T_m$ , °C)	120-123
Cry (%)	30-40
Molecular weight (g/mol)	1.1-1.5 × 10 <sup>5</sup>
Polydispersity	2.0-3.0
Comonomer (wt%)	5-7

based catalyst is used to synthesize high-performance PE wax. It exhibits oil-thickening properties due to its high crystallinity, linear polymer chain, and hardness at high temperatures<sup>[65,66]</sup>. These properties allow specialty waxes in formulations to improve their friction coefficient and gloss.

### 2.2.6 COC

COC are relatively newer polymer compared to conventional PP and PE polymers and amorphous in nature. These polymers show good chemical and heat resistance with excellent optical properties. Cyclo olefin monomers such as norbornene, cyclopentadiene, and dicyclopentadiene are used for COC production for application in optics, packaging, electronics, healthcare, etc. Market analysis shows a projection of the COC market to reach 1.4 billion USD by 2030 from 860 million USD in 2021<sup>[67-69]</sup>. Mitsui, Zeon Corporation, JSR Corporation, and Lyondell Basell are the key players.

### 2.2.7 Specialty Polyolefin Composites (POCs)

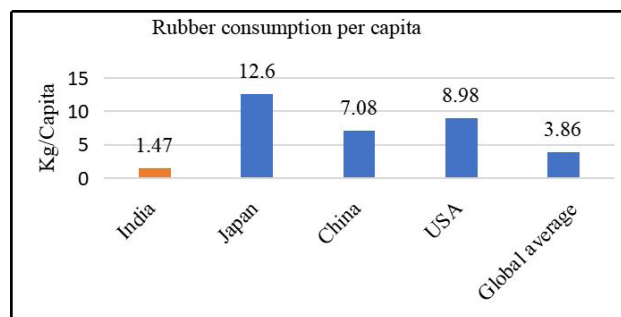
POCs materials consist of two or more phases with distinct boundaries between the two phases. The proper choice of different and unique materials results in improved structures and functions over the individual components. The challenge of POCs materials is incompatibility of reinforced filler or fiber with polymer matrix, which

results in poor adhesion between different materials in the composites. Numerous methodologies are used for resolving incompatibility issues using coupling agents, compatibilizers and modified fibers. The use of these techniques allows the development of high-performance POC with improved properties and reduced cost<sup>[70-73]</sup>. The materials are produced with improved mechanical, thermal properties, and electrical conductivity by blending polymers with highly conductive fillers, such as CB, carbon fibers, or metal particles<sup>[74]</sup>. The mechanical properties of the blend film are better than the neat polymer film properties and have good market potential<sup>[75-77]</sup>. It is well established that the different fillers<sup>[78]</sup> like alumina, CB, reduced graphene oxide, and CNTs have affected the polymer composites properties mainly dielectric properties, thermal / crystallization behaviour, toughness, and dimensional stability<sup>[79]</sup>. We have developed benzyl triphenyl phosphonium chloride based PP composite<sup>[80]</sup> with higher storage modulus and dielectric constant for potential applications in automobile and electronic industries as dielectric materials.

The availability of biofillers like natural fibers, which are relatively lower in cost and abundant in nature, has provided a significant impetus for the development of green composite materials. Natural fibres-based PP composites, such as PP / rice husk and PP / algae biomass composites, are prepared using different concentrations of fillers to enhance their mechanical properties, such as tensile strength and modulus, as shown in [Table 5](#). Compatibilizers and coupling agents play a crucial role in improving interfacial adhesion between the polymer matrix and the filler. These types of composite products can find utility in rigid packaging and the automobile industries due to their lightweight and high strength. These composites are considered sustainable products due to their lower carbon footprint<sup>[81]</sup>. Some other emerging advanced materials in the realm of POCs are also described below.

**Table 5. Mechanical Properties of PP-based Natural Fillers with and without Compatibilizers**

Sample	Tensile Strength (MPa)	Tensile Modulus (MPa)
PP	30-34	1300-1350
PP / natural fibres	34-36	1500-1800
PP / natural fibres / compatibilizers	35-40	1700-2000
PP / algae biomass	25-30	1400-1600
PP / algae biomass / compatibilizers	34-36	1500-1650



**Figure 4. Per capita consumption of rubber.**

### 2.2.7.1 Nanocellulose (NC) Composites

NC composites shows good potential as a reinforcing material owing to low density, impressive mechanical properties, nanoscale dimensions, etc. They offer low density, good mechanical performance and environmental friendliness. Furthermore, NC offers other advantages such as withstanding stress due to its high strength, serving as the nucleating agent in the crystallization of PO. The great load transfer ability of composites is attributed to a three-dimensional space network structure formed among the NC and PO<sup>[82]</sup>. The product applications include automotive components, furniture, building, home appliances etc<sup>[83]</sup>.

### 2.2.7.2 CNT Composites

POCs specially PP/CNT composites are produced by adding a small amount of CNTs with improved mechanical strength, thermal, electric conductivity, and reduced flammability<sup>[84,85]</sup>. However, PP/CNTs composites generally require a homogeneous dispersion of CNTs in a polymer matrix with good interfacial interactions. Currently, several methods are employed for the preparation of PP/CNT composites. The multi-wall CNTs as filler are appropriate materials to enhance intrinsic mechanical properties such as tensile modulus and tensile strength<sup>[86,87]</sup>. The PP/CNT applications are rapidly increasing in automobile, construction, space, medical sectors.

### 2.2.7.3 Carbon Fiber / Reduced Graphene Oxide Composites

Carbon fibers are widely applicable as effective fillers in composite materials, particularly lightweight polymer composites. Specialty carbon fibers with diameters ranging from 7-15mm are produced using processes such as hydrocarbon gas vapor growth, pitch, or polymer pyrolysis<sup>[88,89]</sup>. They are used for blending with a polyolefin matrix to enhance properties such as mechanical characteristics for various product applications, including electronics, sensors, medical devices, etc. Graphene is also a promising nanofiller<sup>[90,91]</sup> to prepare polymer nanocomposites for different applications.

### 2.2.7.4 Natural Fiber Composites

The availability of biofibres, which are relatively cheaper

and occur in abundance in nature, has provided an impetus to develop composite materials. Natural fibres are strong, light weight, and non-abrasive and can serve as an excellent reinforcing agent for plastics. The fibres come from abundant and renewable resources such as wood, grass, agricultural residues, forestry wastes etc. The challenge of compatibility of polyolefin matrix and the natural fibres can be overcome by novel methods coupled with composites preparation using extrusion, injection moulding, calendaring, thermoforming and compression moulding processes<sup>[92]</sup>. These products have very good potential for applications in the building and automotive industries.

## 3 HIGH PERFORMANCE ELASTOMERS

Global consumption of elastomers (including both natural and synthetic) is around 29 to 30 million metric tons per annum<sup>[93]</sup>, with an average per capita consumption of 3.9kg. Japan is the leading consumer with 12-13kg per capita, followed by the USA (as shown in Figure 4). Continuous efforts are focused on improving production processes and product properties to fulfill need of end use applications in different growth sectors. The major process and product development are focused for synthetic elastomers such as SBR<sup>[16]</sup>, PBR<sup>[17-20]</sup>, IIR and HIIR<sup>[21-23]</sup>, epoxidized rubbers<sup>[24]</sup> etc.

### 3.1 Key Emerging Developments in Synthetic Elastomers

#### 3.1.1 Self-healing Elastomers

Self-healing is an important and highly required characteristics for repairing cracks developed in elastomeric products<sup>[25]</sup>. This process occurs due to presence of functional or ionic groups in the elastomers responsible for reversible non-covalent or covalent interactions to heal the material (Figure 5). The lifetime of the tire, tube and other rubber articles can be improved by developing self-healable materials used in such application from the family of conjugated diolefin based elastomers (polybutadiene, styrene-butadiene rubber, butyl rubber, NBR, and CR)<sup>[26]</sup>. Majority of self-healing polymeric systems are based on dynamic covalent network or supramolecular interactions. The presence of the dynamic network further helps in the reprocessing of the rubber materials and hence reducing elastomer wastes<sup>[27]</sup>.

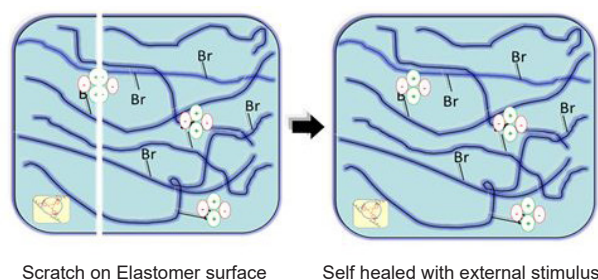
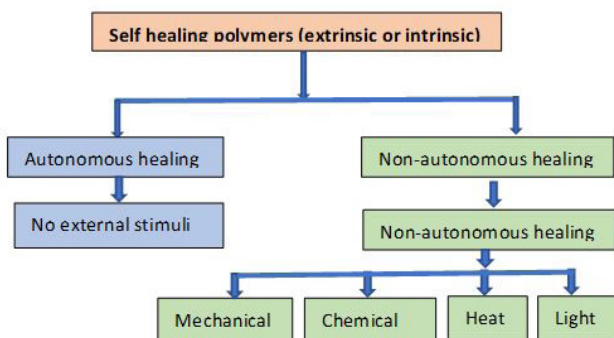


Figure 5. Self-healing processes.

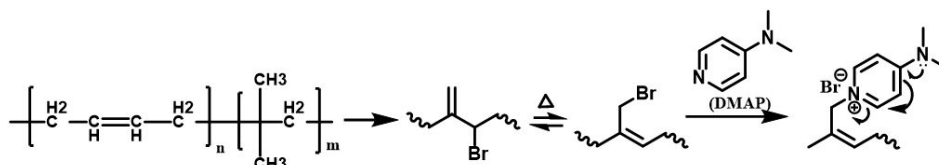


Figure 6. Reaction pathways of self-healing butyl rubber synthesis.

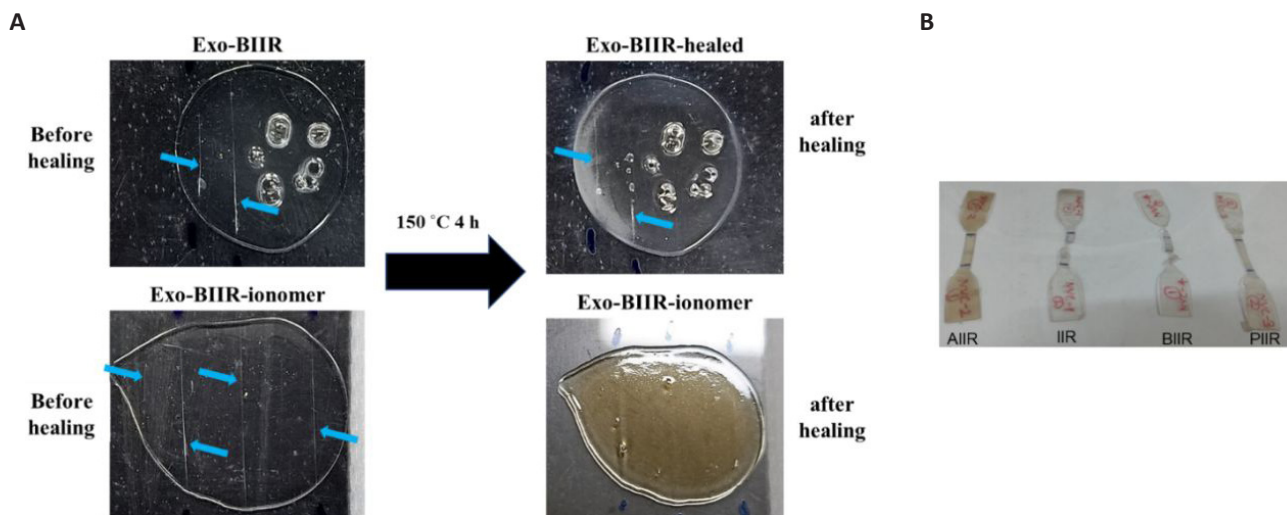


Figure 7. Self-healing characteristics of ionic butyl rubber. A: Scratch mark appears on the ionomeric film and it get healed up on exposing to high temperature; B: Elongation properties are not changed for three healing cycles.

Elastomer failure is primarily attributed to the formation of microcracks in the products. Over time, these microcracks tend to grow into larger cracks, leading to product failure. We have developed a novel self-healing ionomer based on bromobutyl rubber that can heal the product through its inherited self-healing properties<sup>[27]</sup> (Figure 6). As shown in Figure 7, when there is a crack developed in the product, crack gets healed in presence of some external stimulus like heat / temperature etc. due to the presence of ionic interactions. Self-healing properties have been studied and confirmed through mechanical and microscopic studies as shown in Figure 7. As per Figure 7A, scratch mark appears on the ionomeric film and it get healed up on exposing to high temperature. This phenomenon has been confirmed based on the studies of mechanical characteristics. It is noted that elongation properties are not changed as shown in Figure

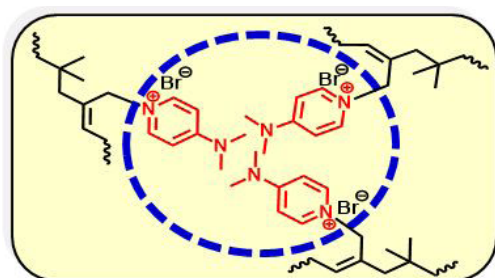
7B for three healing cycles.

Developed grades of rubber show unique properties such as superior tensile strength and hardness with respect to standard BIIR due to presence of ionic cluster in the polymer backbone (Figure 8). Air permeability properties are improved in addition to superior leaching properties in hexane and water. Higher shear strength, better resistance to needle / cone penetration, improved adhesion and low deformation are observed for sealant applications. The general characteristic of product is shown in Table 6.

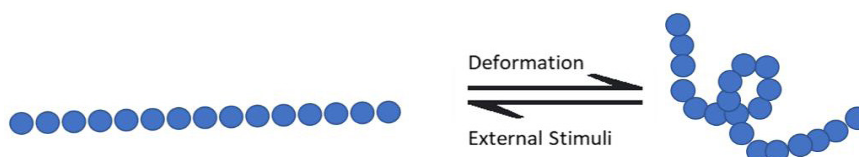
### 3.1.2 Shape Memory Elastomers (SMEs)

SMEs are an exciting category of polymeric materials, with the potential to incorporate multifunctionality. This material category has low modulus and tensile properties,





**Figure 8.** Typical structure of ionic cluster in polymeric backbone.



**Figure 9.** Shape memory process.

**Table 7.** Shape Memory Elastomers and Potential Applications

Elastomer	Trigger	Potential Applications
Polybutadiene	Thermal	Automobiles, electronics, medical, shoes, sports materials
Polyurethane	Thermal, pH, UV	Pressure bandages, smart textiles, heat-shrinkable films
Polyamide elastomers	Thermal	Intelligent electronic devices, bionic materials

along with higher flexibility. Due to their low modulus, they can be deformed to a large extent and yet regain their original shape once the force is removed<sup>[28]</sup>. Because of its special characteristics (Figure 9), they are used in multiple application in day to day life. The trigger mechanisms for SMEs can be various factor, including temperature, pressure / stress, electromagnetic field, moisture / humidity, pH or solvent (Table 7).

### 3.2 Advanced Elastomer Composites

Most of the synthetic elastomers especially SBR, PBR, IIR and HIIIR are used in tire industries. The desired physical and mechanical properties for tires are achieved by reinforcement with different filler. Various fillers such as CB, silica and graphene are used due to their superior reinforcement properties. Currently, a large quantity of CB and silica are used as reinforcement to achieve the desired properties of the composite materials for various applications.

### 3.3 Carbon and Carbonaceous Material Composites

CB is one of the most useful and extensively investigated materials to produce rubber composites. These materials are used mostly in tires due to its superior physical and abrasion

**Table 6.** Characteristics of Self-healing Butyl-based Ionomers

Properties	Values
Mooney viscosity (MU)	60
Unsaturation (wt%)	1.8
Bromine content (wt%)	1.6
Ionic content (wt%)	0.4
Moisture content (wt%)	0.4
Specific gravity	0.91

properties in addition to flex to fatigue properties. However, in recent years, other fillers, such as graphene and graphene derived nanofillers, are attracting attention due to their excellent properties and requirement of lower doses<sup>[94]</sup>. The extra ordinary property of graphene includes high modulus with excellent flexibility, lightweight, high electrical and thermal conductivity, and better gas barrier properties as compared to the other conventional fillers. These outstanding properties enable nanocomposites with superior performance. Graphene filled composites exhibit superior skid resistance in addition to lower rolling resistance and higher abrasion resistance. Superior gas barrier properties of such composites are being explored for traditional gas barrier applications<sup>[95,96]</sup>. In addition to graphene-based fillers, CNTs are also studied and used for high end applications like electrode and electronic applications.

Graphene and CNT-based functional emulsion SBR composites are prepared in an emulsion medium, as shown in Figure 10. Our studies show that performance of developed composites is comparable to that of conventional CB rubber composites (containing approximately 40-60phr of filler), even at very low concentrations of graphene, ranging from 1000ppm to 1%. In-situ graphene-functional SBR composites exhibit superior rolling resistance, better tensile and modulus properties in combination with improved skid resistance<sup>[94]</sup> as shown in Figure 11.

### 3.4 Silica and Other Non-carbon-based Composites

The high surface area of silica makes it one of the best reinforcing filler materials to improve physical and mechanical properties of the elastomers. Silica composites used for tire applications results in low rolling resistance, superior abrasion resistance and a better grip on wet and icy roads<sup>[97,98]</sup>. Due to stringent environmental norms, continued efforts are focused to replace CB filler in elastomer

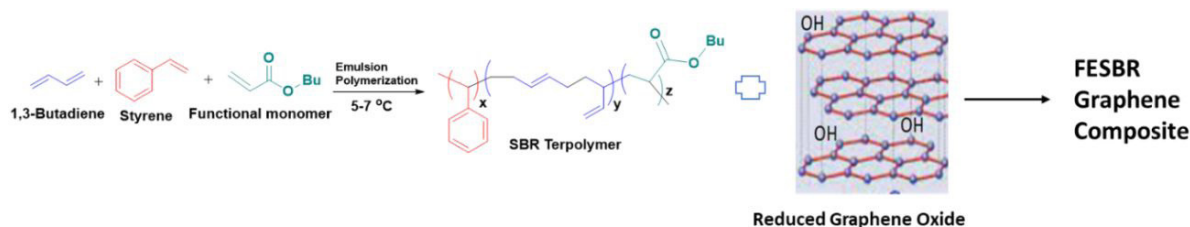


Figure 10. Graphene and CNT-based functional emulsion styrene butadiene latex-based composite.

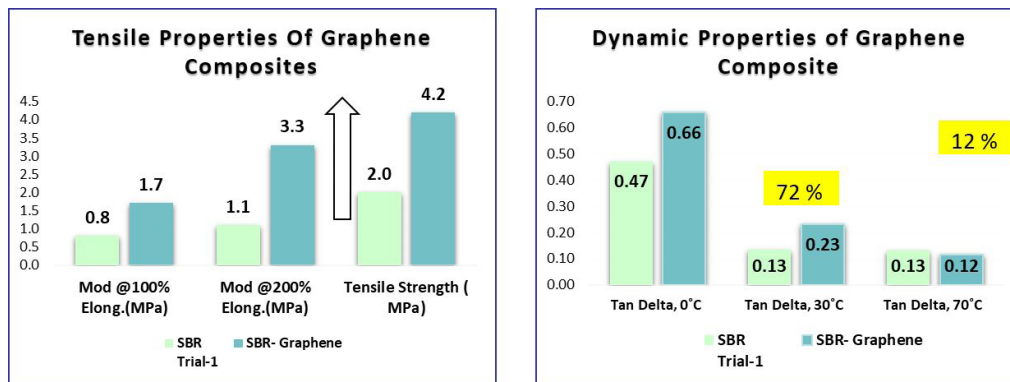


Figure 11. FESBR - Graphene composite mechanical and dynamic mechanical properties.

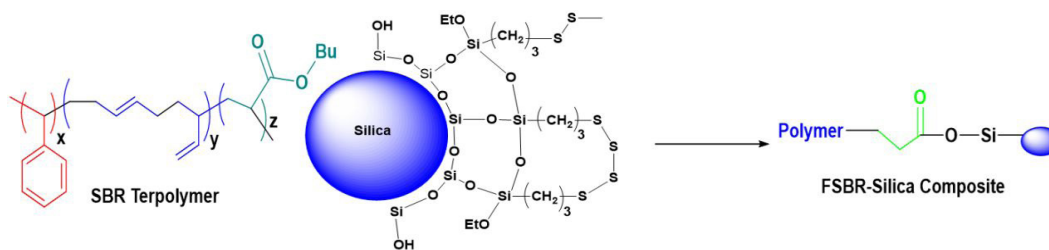


Figure 12. FESBR - Silica reactive composites.

composites with silica fillers. These composites are mostly prepared with functional polymer based on SBR, PBR and NR backbones<sup>[99]</sup>. Recent development related to high performance tires indicate more penetration of silica composite as compared to CB composites.

Novel functional emulsion terpolymers are developed through emulsion polymerization process. Synthesized rubber from emulsion is compounded with silica filler to have a carbon free composite (Figure 12).

This silica-rubber composite showed superior performances with respect to rolling resistance, abrasion resistance in addition to tensile and tear properties. Comparative performance of different SBR grades with functional SBR and silica composites is shown in Figure 13.

#### 4 HIGH PERFORMANCE BIOPLASTICS

Bioplastics are considered as one of the most important polymer segments for the sustainable development. The demand for bioplastics has increased significantly in recent years, with the bioplastic market valued at 11 billion USD

in 2021, projected to reach 46 billion USD by 2030, with a CAGR of approximately 17%<sup>[100]</sup>. Major growth is expected in the biodegradable / compostable class of bioplastics, particularly for PBAT, PBS, and poly(hydroxyalkanoates) (PHA) (Table 8), while non-biodegradable bioplastics like biobased PP and biobased polyamide are also expected to see increased production<sup>[101]</sup>.

Bioplastics are categorized into two major categories: (1) Biodegradable / compostable plastics, such as PLA, PBAT, PBS, and starch blends etc.; (2) Non-biodegradable bioplastic made from monomers derived from renewable resources, such as sugarcane, maize, and castor oil etc. Major examples of these bioplastics include bio-based PE, PE terephthalate, polytrimethylene terephthalate, polyamide etc. Biodegradable plastic can further be classified into two classes, e.g., natural biodegradable polymers and synthetic biodegradable polymers<sup>[29-34]</sup> (Table 9).

Synthetic biodegradable and compostable polymers can be prepared through chemical route of conventional polycondensation [e.g., PBS, poly(butylene adipate) (PBA)]

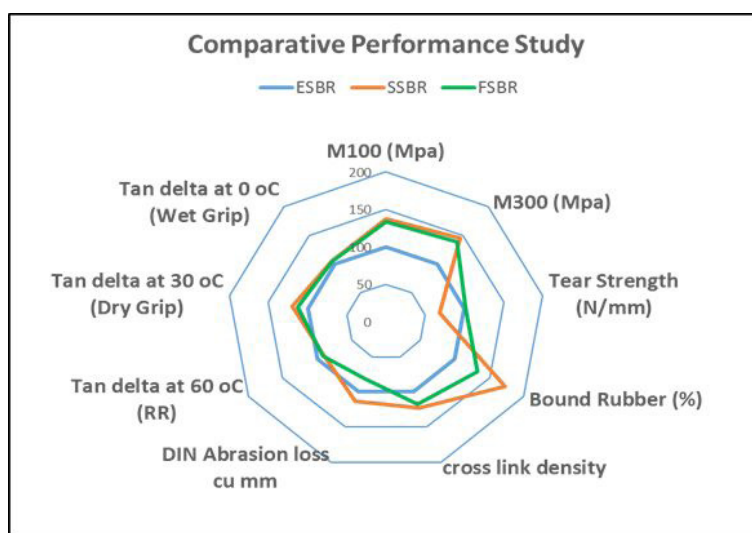


Figure 13. Silica-based functional emulsion styrene butadiene composites and ESBR and SSBR products.

Table 8. Bioplastics Production Scenario<sup>[101]</sup>

S. No.	Type of Products	Production Capacity in 2021 (KTA)	Estimated Production Capacity in 2026 (KTA)
<b>Biodegradable Bioplastics</b>			
1	PBAT	464.6	2277.0
2	PBS	84.7	1214.4
3	PLA	457.4	789.4
4	PHA	43.6	485.8
5	Starch blends	396.9	394.6
6	Cellulose films & others	106.5	121.5
<b>Non-biodegradable Bioplastics</b>			
1	Bio-PE	229.9	493.3
2	Bio-PET	150.0	91.1
3	Bio-based polyamides	220.2	1184.0
4	Bio-PP	46.0	311.2
5	Bio-based polyethylene terephthalate	196.0	197.3
6	PEF & others	26.6	30.4

and ring opening polymerization [e.g., PLA, poly(glycolic acid) (PGA), poly(caprolactone) (PCL)]<sup>[30-35]</sup>. Additionally, biodegradable polyesters can be produced through enzyme-catalyzed reactions, such as the ring-opening polymerization of lactides, lactones and macrolides, using lipase as a catalyst<sup>[102]</sup>. Furthermore, a class of aliphatic polyester, i.e., bacterial polyesters PHAs [e.g., poly(hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)] are produced through microorganisms, and a wide range of properties can be achieved through different copolymers<sup>[103]</sup>.

Biodegradable and compostable polymers are further modified for enhanced properties through blends and composite development. PBAT based blends and composites are important class of materials investigated

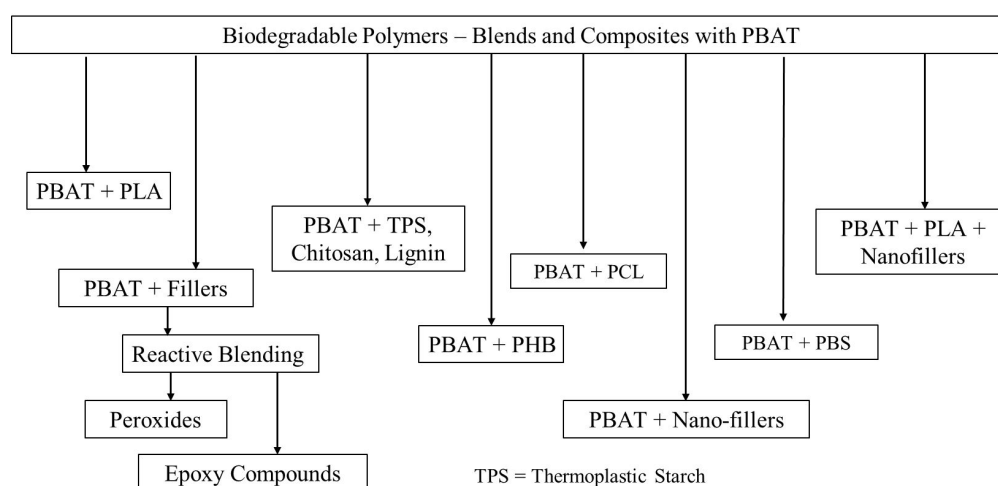
in more comprehensive manner (Figure 14). The blends and composites of PBAT with PHAs (PBAT/PHB and PBAT/PHBV) have been investigated for morphological, rheological, and mechanical properties<sup>[104-120]</sup>.

Similarly, PBAT based blends and composites are reported with PBS<sup>[121-127]</sup> and PBAT/PCL<sup>[128]</sup>. The blends and composites of PBAT with PLA have been extensively studied as compared to PBAT/PHAs, PBAT/PBS and PBAT/PCL. The properties of PBAT/PLA blends and composites (Table 10) are controlled by tailoring the blend and composite compositions<sup>[129]</sup>.

Another class of materials (Table 11) has also been developed by reinforcing various natural fibers from animal and plant sources with natural and / or synthetic

**Table 9. Classes of Biodegradable / Compostable Polymers**

Natural Biodegradable Polymers	Synthetic Biodegradable / Compostable Polymers	Synthetic Biodegradable / Compostable Polyesters
Starch	Polyesters	PBS
Cellulose	Polyamide	PBA
Chitin	Polyurethanes	PLA
Chitosan	Polyanhydride	PGA
Gelatins		PCL
Bacterial polyesters (PHA)		



**Figure 14. Biodegradable / compostable polymers: blends and composites with PBAT.**

bioplastics<sup>[138]</sup>. These products exhibit good mechanical properties and durability, which are imparted by the natural fibers and biopolymers, respectively. The Fiber (reinforcement agent) is observed in discontinuous phase, while the bioplastic forms the continuous phase of the composite, resulting in higher stiffness and tensile strength.

Lignin/PCL-based polyurethane bioplastics is another class of emerging materials. Urethane chemistry was explored for PCL and lignin-based composite for high performance bioplastics using hexamethylene diisocyanate as modifier<sup>[139]</sup>. 2,5-furandicarboxylic acid and 2,2'-bifuran-5, 5'-dicarboxylic acid in combination with 1,4-butanediol are used for the first time to prepare polyesters<sup>[140]</sup>. Further, authors reported that furan-bifuran polyesters have improved the oxygen barrier properties<sup>[140]</sup>. PGA is a class of aliphatic polyesters with potential to be used in high performance applications. The polymer chains of PGA are closely packed and have high degree of crystallinity (45-55%), high thermal properties ( $T_m=220-230^{\circ}\text{C}$ ), high stiffness and higher gas barrier properties<sup>[141]</sup>. Recently, we have published a comprehensive review covering synthetic aspect of PBAT and its modification with chain extenders and branching agents. In addition to development of thermoresponsive bio-compostable products<sup>[142-144]</sup>. Further, utilization of carbon dioxide for

the synthesis of functional bioplastics is also reported by novel synthetic pathway using butadiene and cyclic lactone. These functional polymers showed high thermal stability with good potential for biodegradation<sup>[145]</sup>.

In general, bioplastic applications include different market segments such as (Figure 15): (1) Packaging: (a) Rigid packaging: bottle, jar, and trays etc. (b) Flexible packaging: pouches, shopping / waste bags, others (net-bags). (2) Consumer goods. (3) Agriculture. (4) Automotive and transportation. (5) Textile. (6) Building and construction etc<sup>[146]</sup>.

In 2021, major portion (48%) of bioplastic global production capacities (1.2 million tons) were used for the packaging applications. It is used for single-use flexible and rigid packaging applications. PLA is becoming a choice of material for rigid packaging market. Products such as cups, mugs and tray find applications in food and catering segment<sup>[146]</sup>. Moreover, biodegradable plastics offer unique advantages in agriculture and horticulture sector. Mulching films are gathering momentum in these sectors due to ease of its use as compared to non-biodegradable plastics requiring collection from the field, cleaning off the soil and returning them for recycling. Bioplastic products are also being used in different sectors like fast-moving consumer

**Table 10. Properties of PBAT/PLA Blends**

S. No.	PBAT Content (wt%)	Composition	Tensile Strength (MPa)	Elongation at Break (%)	Ref.
1	70, 80, 90	PBAT	9.1±0.8	935.2±23	Zhao et al. <sup>[130]</sup>
		PLA/PBAT (20:80)	11.9±0.6	146.9±12	
2	30, 40, 50	PBAT	17.7± 2.3	1207.6±84.1	Correa-Pacheco et al. <sup>[131]</sup>
		PLA	52.4±2.2	8.8±0.2	
		PLA/PBAT (60:40)	13.5±1.3	17.9±1.9	
3	40	PBAT	11.4±0.9	428.1±48.4	Hernandez-Lopez et al. <sup>[132]</sup>
		PLA	44.3±2.9	14.8±1.6	
		PLA/PBAT (60:40)	29.6±3.0	20.3±8.9	
4	20, 40, 60, 80	PBAT	38.9±5.0	1245.0±33.5	Ai et al. <sup>[133]</sup>
		PLA	42.3±2.2	3.9±0.3	
		PLA/PBAT (40:60)	37.9±3.8	338.2±58.3	
5	10, 15, 20, 25	PBAT	35.0	700.0	Gigante et al. <sup>[134]</sup>
		PLA	-	7.1±2.5	
		PLA/PBAT (75:25)	-	332.3±30.3	
6	20	PLA/PBAT (80:20)	-	153±8	Urquijo et al. <sup>[135]</sup>
7	20, 40, 60, 80	PLA	43.1±3.0	16.3±2.4	Li et al. <sup>[136]</sup>
		PBAT	49.9±3.9	1251.8±26.6	
		PLA/PBAT (40:60)	38.9±3.9	414.2±46.3	
		PLA/PBAT (20:80)	39.0±7.0	529.9±54.6	
8	70	PLA	44.08±7.30	6.04±2.75	Sirisinha and Somboon <sup>[137]</sup>
		PBAT	18.77±1.63	388.24±44.81	
		PLA/PBAT (30:70)	23.79±1.99	363.58±24.43	

**Table 11. Examples of Fibre Reinforced Bioplastic Composites**

Biodegradable / Compostable Polymer	Type of Fibre for Reinforcement	Property Improvement in Resultant Biopolymer Composites
PLA	Chicken feather fibre Silkworm silk fibre Silane treated ramie fibre Hemp fibre	Tensile strength, flexural strength, impact strength
PBS	Kenaf fibre Alkali treated coir fibre	Tensile strength, flexural strength, impact strength, crystallization rate, storage modulus
PLA/PCL	Silane coupled jute fibre Palm fibre	Tensile strength and modulus
PHBV	Kenaf fibre Silk fibre	Flexural modulus, impact strength

goods, electronics and automotive. Consumer electronics examples include laptop mouse, loudspeakers, components of keyboard, mobile cases and touch screen computer cases<sup>[146]</sup>.

We have developed a process for bio-compostable plastic named PBAT. PBAT is a random polyester of butylene adipate and butylene terephthalate units (Figure 16)<sup>[3,143-145]</sup>.

The presence of butylene terephthalate unit offers the high mechanical properties in the polymer, whereas butylene adipate units are responsible for biodegradability

of the polymer. Both butylene adipate and butylene terephthalate units are randomly present in the polymer chain that make this polymer high in amorphous content. This implies that polymer chain in PBAT cannot crystallize to any significant degree since it is deprived of any kind of structural order. High amorphicity is a preferred property for a biodegradable polymer since it eases the moisture permeation in the polymer. The molar ratio of both units is an important factor to tune the right balance of mechanical properties and biodegradability. Further, the effect of terephthalic acid molar content on the melting temperature ( $T_m$ ) of PBAT is depicted in Figure 17. It is evident that

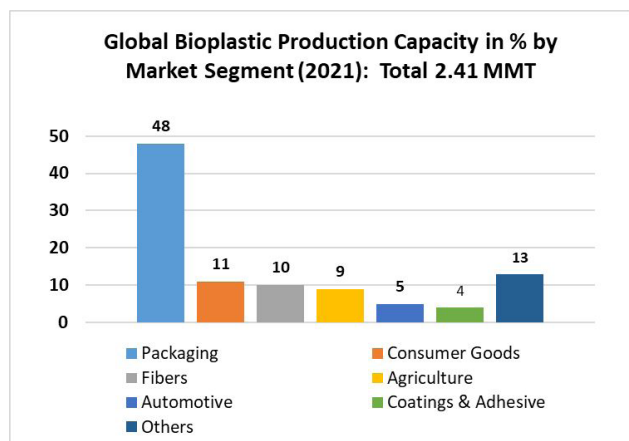


Figure 15. Application market segments of bioplastics<sup>[146]</sup>.

$T_m$  of PBAT polyester can be optimized by changing the terephthalic acid content in the polymer chain<sup>[3]</sup>.

The developed process involves catalytic esterification and polycondensation methodology for polyester development. The process involves high temperature (190-230°C) catalytic removal of by-products to obtain a pre-polymer followed by high vacuum (<1mmHg) application at high temperature (230-280°C) for high melt viscosity polymer. Further, different modifiers (chain extenders, coupling agents, and branching agents) are applied during polycondensation or post polycondensation process to obtain polymer as per target applications<sup>[3]</sup>.

Novel polyesters synthesized by in-situ functionalization using Pluronic as a secondary diol comonomer (Figure 18)<sup>[142]</sup>. Copolymers display thermo-responsive behaviour under physiological conditions due presence of Pluronic comonomer onto the structural backbone. PBAT synthesised the thermo-responsive properties of PBAT copolymer are the function of Pluronic content. This study provides a novel approach for multifunctional bio-compostable polymer with potential applications as smart materials<sup>[142]</sup>.

PBAT is a random polyester and have a low glass transition temperature ( $T_g$ ), wide melting point, low crystallinity and stiffness but high flexibility and toughness. Further, PBAT have inherent limitation which are overcome with blended / compounded products with other polymers and fillers to achieve balance of processability and properties. PBAT based blends and composites for different target applications (Figures 19 and 20)<sup>[3]</sup>.

The compostable net-bags have been developed through a process involving PBAT/PLA blends using extrusion (Figure 21). These developed bio-compostable net-bags are unique in their category since they can be produced commercially by a direct extrusion process using existing downstream machines<sup>[3]</sup>. The bio-compostable net bags

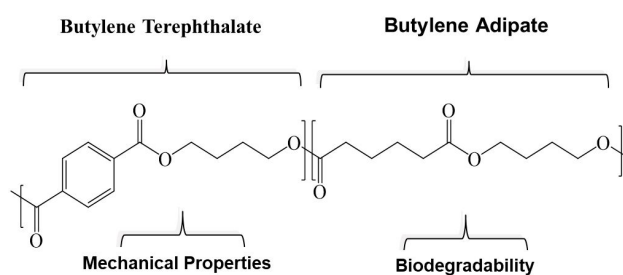


Figure 16. PBAT - A random polyester.

have application in single-use packaging for fruit, vegetable and general grocery items.

## 5 NEW DIRECTIONS IN POLYMER SCIENCE & ENGINEERING

### 5.1 Self or Directed Assembly Building Block as well as Interaction with Nano Particles for Advanced Composites

Self-assembly is the process of spontaneously organizing disordered smaller components into well-organized large patterns through local interactions between the components themselves. The advanced composites obtained from nanoparticles involve self-assembly as a consequence of interactions among the particles, aimed at reaching thermodynamic equilibrium and reducing the free energy of the system. In self-assembly, the role of weak interactions, such as the van der Waals forces and hydrogen bonding etc., is important in comparison to covalent, ionic, or metallic bonds<sup>[147]</sup>. The important aspect of self-assembly is that the building blocks can be prepared from atoms and molecules. However, they can also be prepared from a wide range of nano- and mesoscopic arrangements, using different chemical materials, moieties, and shapes. Due to the small size of nanoparticles (1-100nm), they exhibit unique properties compared to macro-scale materials<sup>[148]</sup>. The examples are the linear as well as star-shaped polymers produced by controlled ring-opening polymerization of L- and D-lactide. Further introduction of carboxylic end-groups is accomplished by the reaction of OH end-groups with succinic anhydride. The morphology of sc-PLA depends on the assembly of end group components. The stereo complexes are precipitated in solvents like 1,4-dioxane and THF. The influence of concentration of sc-PLA subunits on particles size was observed by microscopic analysis. The nanometre-sized grains of stereo complexes aggregated to form larger stereo complex nanoparticles. The properties and morphology of the final stereo complex-based materials are influenced by the end-group interaction, architecture and basicity of solvent<sup>[149]</sup>. The specific examples are: (1) Star-shaped stereo complexes microspheres with hydroxyl end-groups of 1 to 4mm. (2) Uniform stereo complex nanoparticles (~400nm) in 1,4-dioxane from the combination of star-shaped PLA functionalized with carboxylic end-groups and linear PLA

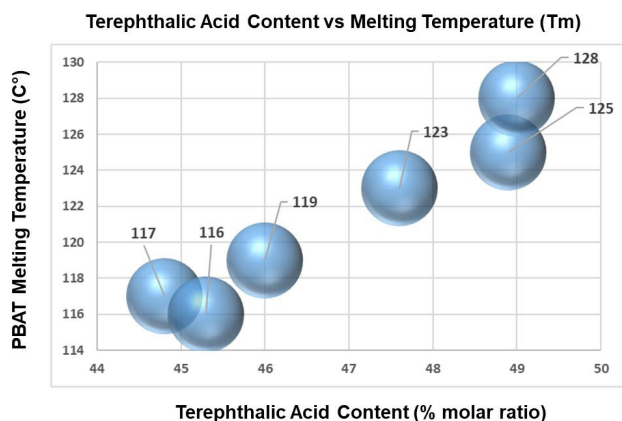


Figure 17. Effect of Terephthalic acid molar content on melting temperature of PBAT<sup>[3]</sup>.

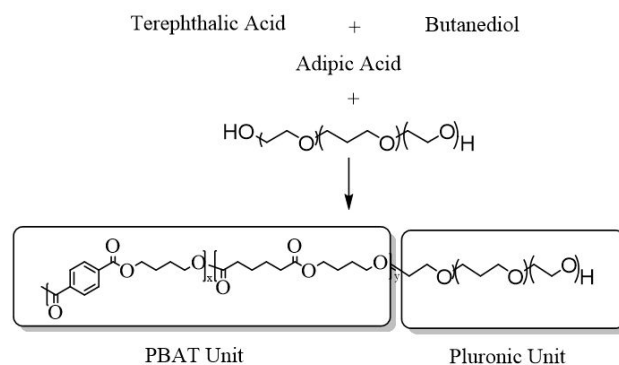


Figure 18. Pluronic-functionalized PBAT (PPBAT) copolymer.

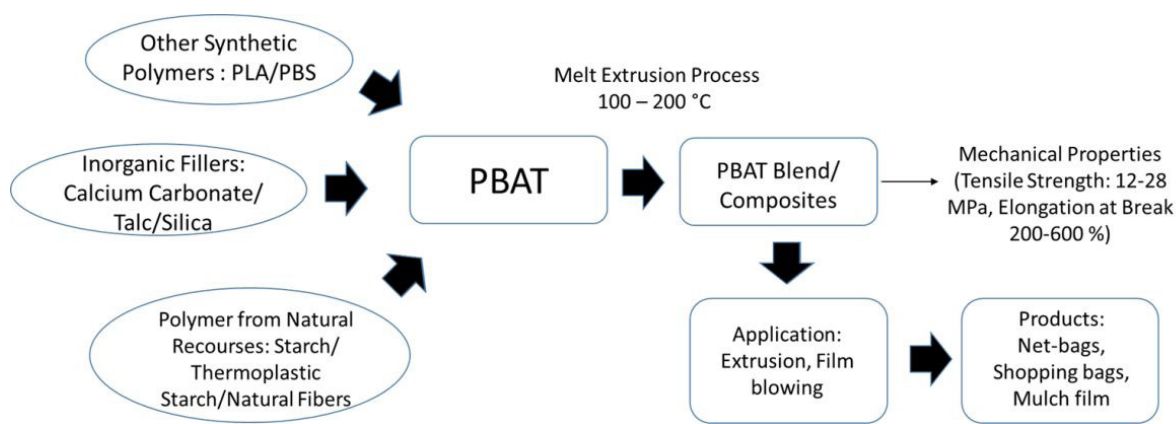


Figure 19. PBAT blends / composite, application and products.

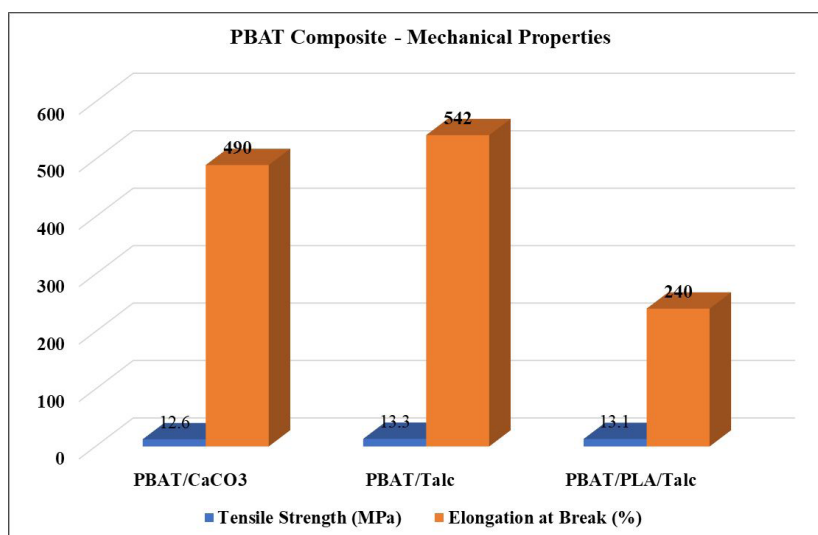


Figure 20. PBAT composites - mechanical properties.

with ionic liquid end-groups.

The formation of stable new hybrid nanoparticles in solution stage through self-assembly caused by the stereo complexation between enantiomeric PLA chains in organic-inorganic hybrid diblock copolymers is demonstrated. The

well-pattern of hybrid diblock copolymers [PLLA-*b*-P(MA-POSS) and PDLA-*b*-P(MA-POSS)] are produced via atom transfer radical polymerization of methacryl isobutyl POSS (MA-POSS) using PLLA or PDLA as a macro-initiator<sup>[150]</sup>. It was observed that, the size of the stereo complexed hybrid nanoparticles, decreases with the increasing length of the



**Figure 21. Net-bag production through extrusion process.**

(MA-POSS) block in the copolymer at given composition. The prepared stereo complexed nanoparticles remain stable over 1 month and are not affected to dilution, signifying the formation of steady hybrid nanoparticles dispersion.

The structural restructuring of cylindrical nanoparticles caused by polylactide stereo complexation has been studied<sup>[151]</sup> by preparation of stereo complex micelles from a combination of poly(L-lactide)-*b*-poly(acrylic acid) and poly(D-lactide)-*b*-poly(acrylic acid) diblock copolymers in water through crystallization driven self-assembly. Unpredicted morphological transition during the formation of stereo complex micelles is resulted in the formation of dense crystalline sphere-shaped micelles rather than cylinders. The co-crystallization of polymers with different formulations provides access to materials with improved performance<sup>[151]</sup>.

The self-assembly of PLA-based amphiphilic block copolymers [Poly(ethylene glycol)-poly(D,L-lactide) block copolymers] in water has been studied<sup>[152]</sup>. The block copolymers assemble into sphere shaped micelles and worm-like aggregates. However, the fraction of the latter apparently increases with decreasing lactide load fraction or hydrophobicity.

## 5.2 Multiscale Simulations and AI / ML / Deep Learning (DL)

Polymers are exploited in a wide range of applications, from daily products such as plastic packaging to the most advanced technologies such batteries, solar cells, and 3D printing materials. However, multitude of complex polymer synthesis processes generate large amount of high-dimensional data. Only a small part of data can be analysed by a typical researcher while the vast amount of polymer research data remains in a database with only a partial cursory analysis. Fortunately, with the aid of advancing computing power and newer data science algorithms, ML, a subfield of AI, has evolved rapidly in recent years and is efficient at processing the high-dimensional data providing new directions and increasing speed of discovery.

ML is an important branch of AI and enable data analysis for authenticity, comprehensiveness, and objectivity.

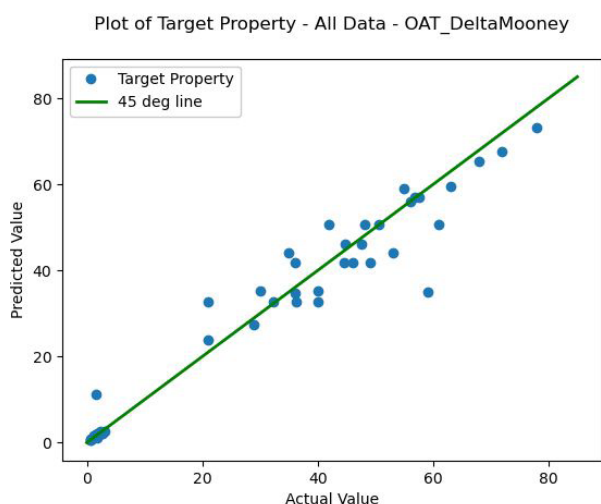
Hence, it is necessary to develop high-throughput synthesis experiments coupled with high-throughput characterization, and high throughput simulation to generate data<sup>[36]</sup>. The relevance of these tools can be reflected in some examples described below.

ML showed great potential in modelling and analysing biomacromolecules. AlphaFold, the AI model created by DeepMind<sup>[153]</sup>, can predict the folding spatial structure of protein segments from the sequence of amino acid residues. The understanding of protein folding is helpful for the design of proteins to meet specific functions. The DL models created by Senior et al.<sup>[153]</sup> utilized amino acid sequences to make predictions on both the pairwise distances between residues and the backbone torsion angles. After training with the data of nearly 30,000 proteins in the protein data bank, the model won the 13th Critical Assessment of Protein Structure Prediction<sup>[154]</sup>.

A database to summarize the characteristics and properties of 854 different polymers is prepared which includes DFT calculation results (atomization energy, bandgap, dielectric constant, etc.) and experimental data (such as permeability, T<sub>g</sub>, and mechanical properties). Information platform was created which used the ML model based on the Gaussian process regression (GPR) algorithm to link the key features and properties of polymers. The aforementioned research has been made accessible on the corresponding website (<http://www.polymergenome.org/>) to assist in selecting polymers for future investigations. Furthermore, the GPR algorithm has been utilized to forecast the properties of polymer electrolytes.

Hatakeyama-Sato et al.<sup>[155]</sup> have constructed a large experimental database for lithium-conducting solid polymer electrolytes which contains more than 104 entries including properties like conductivity, transfer number, and chemical stability. Graph neutral networks models are deployed to express the polymer molecules and GPR models to anticipate the conductivity of new material based on its similarity with historical materials in the database. On a logarithmic scale, the models demonstrate satisfactory accuracy, as indicated by a mean absolute error of less than 1. In the future, the property prediction





**Figure 22. Comparison of experimental and predicted Delta Mooney viscosity values.**

generated by ML models can help researchers to explore unknown polymer systems more efficiently.

Utilizing ML can aid in the design and identification of novel polymers. One of the key challenges in guiding experiments to find polymers with required  $T_g$  is how to navigate efficiently in a wide composition and structure space. Kim et al.<sup>[156]</sup> applied the active learning framework combined with the GPR algorithm to effectively select out the polymers with  $T_g$  greater than a certain threshold. Once the  $T_g$  of a new case has been tested, the results thus obtained are used to update the current knowledge of the system and the iteration is repeated until the desired  $T_g$  is achieved. It is noted that the ML model is more efficient in experimental design. Only several iterations are needed to find the polymers with high enough  $T_g$ . This idea can be widely used to guide the next step of synthesis in the polymer science<sup>[157]</sup>.

Characterization methods, such as mass spectrometry, nuclear magnetic resonance, and infrared spectroscopy, are commonly employed to deduce the composition and structure of polymers. However, ML methods have emerged as a promising approach to expedite the analysis of characterization data. For example, support vector machines (SVM)<sup>[158]</sup> has been applied to conduct thermal analysis of polymers. The dataset to train the SVM model is a matrix  $X$  of dimensions  $293 \times 215$  collected by the technique of dynamic mechanical analysis which could record the stiffness of samples being heated. The stiffness of 293 samples with the temperature ranging from  $-51^\circ\text{C}$  to  $27^\circ\text{C}$  in increments of  $1.5^\circ\text{C}$  is learned by the SVM model.

We have prepared a model to predict the effect of antioxidant on PBR. These modelled data<sup>[159]</sup> are validated by experimental data and found to be matching up to 90% as shown in Figure 22.

## 6 FLEXIBLE MANUFACTURING AND CIRCULAR ECONOMY

In 4th industrial revolutions combining digital, physical and biological sciences, manufacturers are trying to customize their processes to have flexibility and speed of delivery. Transformative innovation known as flexible manufacturing system (FMS) is continuously improving with various digital tools to become cost effective as well as highly flexible for production of need-based product requirement<sup>[160,161]</sup>. Flexibility in manufacturing system cover different aspects including man / machine / material flexibilities, process / product / capacity flexibilities and overall flexibilities. There are still many challenges which need to be addressed before wide implementation of FMS. Potential applications in polymer synthesis and application can be batch to continuous polymerization process for specialty polymers and injection, blow molding processing of polymers for different end uses. The recycling process involving operations of sort, shred, clean, and palletisation can be designed for FMS for different waste streams providing good-quality, consistent products at high-speed improving productivity and overall efficiency with reduce costs.

Superior properties of thermoplastics, such as their lightweight nature, durability, lower cost, and ease of processability, make them very popular for packaging materials, among other applications<sup>[162-165]</sup>. However, their high durability has also resulted in the generation of large amounts of waste<sup>[166]</sup>, which accumulates in landfills, rivers, and oceans<sup>[163,167]</sup>, adversely impacting the environment and ecosystems<sup>[168]</sup>. Landfilling and incinerating plastic waste is undesirable due to the emission of gaseous and other toxic pollutants<sup>[169-171]</sup>. Therefore, the concept of a circular economy, involving the circularity of polymers at the end of their life cycle, is opening up many new opportunities for innovation in polymer science and engineering for these materials.

Implementation of circularity is the most relevant solution for the issue of plastic waste. The circular economy involves the 6R principles: reduce, recover, reuse, recycle, redesign, and remanufacture. It promotes a sustainable plastic value chain with societal benefits, economic growth, and environmental protection. Primary and secondary recycling methodologies are commonly used for plastic waste. However, tertiary and quaternary recycling are the latest recycling methodologies that have been more developed in the last few decades. Upcycling and pyrolysis approaches result in the production of feedstock, monomers, and valuable products<sup>[172,173]</sup>. Upcycling extends the end of life of the plastic by bringing it back into the value chain, thereby adding environmental value<sup>[174]</sup>.

### 6.1 Polymers Life-cycle Management

Although an enormous amount of polymer is produced

every year<sup>[175,176]</sup>, only a limited quantity of it is recycled. Enhanced performance expectations have led to innovations such as the incorporation of oxygen barrier properties, improved mechanical properties, lightweight characteristics, enhanced durability, etc.<sup>[177]</sup>. These enhancements are achieved through the development of multilayer films, the addition of organic / inorganic fillers, etc., making them multicomponent and complex and posing challenges to recycling. Mechanical recycling / reprocessing has relatively low climate impacts and is thus a preferred route. However, relying solely on mechanical recycling / reprocessing cannot be the solution for the entire waste plastics issue due to the multicomponent and complex nature of the waste<sup>[178]</sup>. Thus, there is a need for alternative approaches towards sustainability through life-cycle management strategies that integrate circularity and the end-of-life of polymer products. Circularity involves keeping polymers within the economic activity, minimizing the use of net fossil feedstocks, and helping to reduce overall greenhouse gas emissions. Currently, a significant portion of plastics ends up in landfills, contributing to terrestrial and aquatic pollution. Incineration is another option for polymers at the end of their life, which generates some excess energy but also adds to greenhouse gas emissions.

Another class of materials have a more environmentally benign end of life such as degradable under ambient conditions (i.e., bio-degradable) or under controlled conditions (i.e., bio-compostable). These materials need to be sorted out carefully post-usage from other non-biodegradable materials. If mixed with conventional polymers, its sorting and recycle process becomes difficult, as well there is deterioration of recycled product quality due to complex nature of mixed waste<sup>[179]</sup>.

A major challenge in front of polymer science and engineering is to design a polymer with defined pathway for reuse and end-of-life recovery of used polymers<sup>[180]</sup>. Recently, a new type of polymers called “unzippable” has been reported<sup>[181,182]</sup>. These polymers have polyolefin-like macromolecules and incorporate sacrificial or degradable bonds at regular intervals. It is due to mostly adverse impact of these functional groups on physical characteristics as well as mechanical properties. Exceptions to these macromolecular modifications are designed monomers, such as long aliphatic polyester<sup>[183]</sup>. Another approach is to make degradable polyolefin by radical copolymerization. Zeng et al.<sup>[184]</sup> functionalized PE by conducting copolymerization of ethylene and cyclic ketene acetals using cobalt based catalyst. It leads to incorporation of ester groups into PE backbone. These ester groups as cleavable, making copolymer degradable under mild conditions. This is an emerging area, where functionality can be incorporated by use of other vinyl monomers.

Used polyolefin are mostly mechanically recycled,

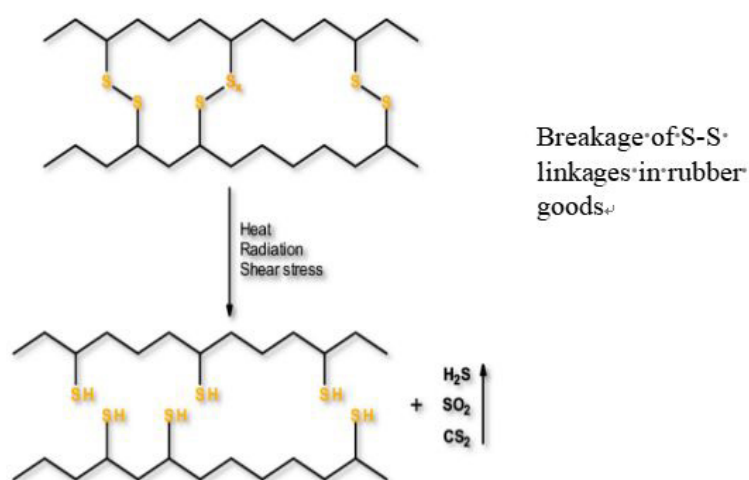
pyrolyzed to recover energy or treated via gasification. But recent developments are towards clean recycle i.e., convert it back into monomers. Hees et al.<sup>[185]</sup> presented an approach in designing polyolefins for easy recycling. It can be achieved by additives that catalyse polyolefins degradation while thermal exposure such as during melting or re-extrusion. Zhang et al.<sup>[186]</sup> reported transformation of waste PE directly into long-chain alkylbenzenes using a platinum-alumina catalyst. The resultant long-chain alkylbenzenes becomes the feedstock for detergent manufacture.

Self-healing and / or shape reprocessing polymers, such as vitrimers and covalent adaptable networks<sup>[164]</sup>, constitute another class of materials designed with triggerable chemistries. Sheppard et al.<sup>[187]</sup> applied dynamic covalent chemistry to modify unrecyclable plastics. They activated covalent cross-links in polyurethane foams, which break the foam and reshape the polymer into new products in recycling process. Properties of such vitrimers, depends upon chemical structure of the polymer as well as reactivity of the dynamic bonds. Thus, chemical reactivity of the monomers and modifiers are critical for the design of these materials. It is having higher relaxation times and creep at the recycling and application temperatures, which limits its broader applicability<sup>[188,189]</sup>. Furthermore, biopolymers (bio-degradable or bio-composable) are being seen as immediate solution to accumulation of the used plastic pollution. Some of the promising biopolymers are PLA, PGA and PHA. Mechanical recycling is first choice, but recycling routes such as alcoholysis, biodegradation and biological recycling are also explored<sup>[190]</sup>. Developing techno-economically viable circularity processes and end of life solution for demonstrated chemistries is the challenge and opportunities in polymer science and engineering.

We have developed and patented a process for devulcanization of waste tires, repurposing them for various different applications<sup>[191,192]</sup>. Through this process, sulphur-sulphur bonds in the vulcanised elastomers are broken which makes them reprocessable as shown [Figure 23](#).

## 7 CONCLUSION AND FUTURE PERSPECTIVES

Sustainable and resilient socioeconomic growth poses both a significant challenge and opportunity for the polymer industry to make impactful innovations in new materials. The increasing demand for clean and efficient energy, sustainable mobility, cutting-edge healthcare, urban infrastructure, potable water, improved security and defense systems, and other amenities presents opportunities for the development of novel polymer materials as solution providers. Among different class of advanced polymers and composites, polyolefins and elastomers continue to be area of high academic and industrial significance. Homopolymers and copolymers of PE and PP with desired characteristics are produced by polymerization processes for different end-use products, including film, fibers, injection



**Figure 23. Devulcanization of waste rubber.**

molding, rotomolding, etc. Furthermore, UHMWPOs in entangled and disentangled forms are produced with novel catalyst systems for high-performance engineering applications. The copolymerization of olefins with other comonomers results in the production of functional polyolefins, metallocene-produced LLDPE, COC, and POEs as an emerging class of materials for niche product applications. Novel POCs, incorporating materials such as nano cellulose, CNT, carbon fiber, reduced graphene oxide, and natural fibers, play a pivotal role in enhancing the performance platform of products to cater the need of new applications, thus contributing to higher growth. Synthetic elastomers, such as PBR, SBR, and butyl & halobutyl rubber, are now produced using new approaches to facilitate the commercial production of grades for different applications. Further, various novel elastomers are emerging with self-healing and shape memory type of features. In addition to this advanced elastomer composites with carbon and non-carbon-based materials are produced to widen the functional characteristics for newer applications.

Considering the significant global focus on the challenge of plastic pollution, multiple solutions are being pursued, including recycling fossil feedstock-based polymers, circular economy focusses, and relatively more benign biopolymers as well as biocompatible polymers and their composites. In view of these, the bioplastic class has emerged as highest growth materials with new innovations in synthetic methodology as well as enhanced performance for end-use applications for different sectors, including packaging. Furthermore, new directions in polymer science and engineering are emerging including self or directed assembly building block, multiscale simulations and AI / ML / DL, flexible manufacturing & circular economy as well as polymers life-cycle management. High performance polymer & composite materials development will accelerate disruptive innovations for better quality of life in the emerging fourth industrial revolution with amalgamation of physical, digital and biological worlds. This requires cross

functional skills working across traditional boundaries of science and engineering for faster realization from mind to market.

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#### Conflicts of Interest

The authors declared no conflict of interest.

#### Author Contribution

Gupta VK and Sapre AV conceptualized, wrote, reviewed, and edited the manuscript. Sapre AV also made significant contributions to the field of new directions in polymer science, specifically in the areas of AI/ML and flexible manufacturing. Both authors contributed to the manuscript and approved the final version.

#### Abbreviation List

- AI, Artificial intelligence
- CAGR, Compound annual growth rate
- CB, Carbon black
- CNT, Carbon nanotube
- COC, Cyclic olefin copolymers
- CR, Chloroprene rubber
- DL, Deep learning
- DPP, Disentangled polypropylene
- EVA, Ethylene vinyl acetate
- FESBR, Functionalized emulsion styrene butadiene rubber
- FMS, Flexible manufacturing system
- GPR, Gaussian process regression
- IIR and HIIR, Butyl and halobutyl-rubber
- LLDPE, Linear low density polyethylene
- MA, Methyl acrylate
- ML, Machine learning
- NBR, Nitrile butadiene rubber
- NC, Nanocellulose
- PBA, Poly(butylene adipate)

PBAT, Poly(butylene adipate-co-terephthalate)  
PBR, Polybutadiene rubber  
PBS, Poly(butylene succinate)  
PCL, Poly(caprolactone)  
PDI, Polydispersity index  
PE, Polyethylene  
PET, Poly(ethylene terephthalate)  
PGA, Poly(glycolic acid)  
PHA, Poly(hydroxyalkanoates)  
PHB, Poly(hydroxybutyrate)  
PHBV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)  
PLA, Poly(lactic acid)  
POCs, Polyolefin composites  
POE, Polyolefin elastomer  
PP, Polypropylene  
SBR, Styrene butadiene rubber  
SMEs, Shape memory elastomers  
SVM, Support vector machines  
UHMWPE, Ultra-high molecular weight polyethylene  
UHMWPO, Ultra-high molecular weight polyolefin

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