A Review On Recycling Of Thermosets

LS Jayakumari*, M Arun Kumar, B Arunbala, R Sailaja

Abstract - Thermosets are a type of plastics that pose a major problem when it comes to easy reusability and recycling because they become irreversibly rigid when subjected to progressive increase in temperatures. Epoxy resins, Phenol Formaldehyde, and Polyurethanes are a few of the many thermosets that are widely employed in several different fields. The rigid, brittle, opaque thermosets, in general, possess qualities like good mechanical strength at elevated temperatures, good chemical resistance in addition to even being self-extinguishing at times (mostly with the help of additives), with low smoke emissions, as highlighted by the British Plastics Federation. However, these properties which serve as an advantage to the end product also affect their recyclability, which is difficult and limited, because of their ability to undergo cross-linking on heating, which ultimately results in the formation of strong covalent bonds that cannot be broken easily. Several commercial techniques are now available for recycling thermosets, which include - Mechanical Processing, Thermal Processing and Chemical Processing. These methods demand higher amount of energy for offering feasible results. There are several studies that have focused on degradation (which is the essential first step that progressively leads to recycling) of thermosets. This review highlights the importance of such studies, techniques and methodologies on aspects including feasibility, cost, sustainability and technological innovation.

Key Words: Recycling, Thermosets, Polymer recycling, Composites, Recycling of Composites

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1 Introduction

Thermosets find numerous applications worldwide. They are one of the most produced as well as used materials- several million tonnes of thermosets are produced annually, throughout the world. In a general sense, thermosets are known for its superior mechanical and thermal properties, toughness, flame retardancy and stability which make them suitable for a wide range of applications. Currently, polymer-based thermoset products are used in every corner of the world [1], [2].

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This, in turn, is causing the accumulation of a huge amount of end-of-life product waste. So, recycling is very essential (Morales Ibarra, 2018; Kresta,1998; Yang et al., 2012).

The need for recycling is to limit the use of available resources and for implementing proper waste disposal. However, recycling of thermosets is often problematic due to their structural stability. Thermoset polymers are raising too many eyebrows as, unlike thermoplastic polymers, thermosets require more effort to recycle, that is why they are creating environmental concerns, because they are derived from petrochemicals and are harmful to the environment as they release toxic gases like styrene, which is considered a pollutant [6], [7]. Thermosets create irreversible impact on environment but there are number of methods available to recycle it which helps avoid and prevent any serious consequences [8]–[10].

The need for recycling is very essential to limit the use of available resources and the need to the waste disposal [11], [12]. Many recent developments have been made, for instance, Polyurethanes can be recycled using Bio-chemical process. Which is green practices and environmental friendly, where Polycarprolactone and toluene combination is used as a diluents for recycling [13] this paves way for its application in automotive seating and insulation. The carbon fibre based unsaturated polyester composites recycling using hydrolysis oxidation synergistic catalytic strategy. The main aim of the research is to recover the carbon fibre completely from the unsaturated polyester and it was observed that the mechanical properties were retained [14].

Suryln, a composite made of poly(ethylene-co-methacrylic acid) (PEMA) and Zn^{2+} made by using hot pressing method. Due to its excellent heat and self healing made it hard to recycle. But recycling has been carried out using dichloromethane at elevated temperature. Ester bonds in these composites were cleaved using potassium hydroxide NaOH [15]. The composite of Aluminium tri hydroxide $Al(OH)_3$) and poly(methyl methacrylate) was recycled using supercritical fluids. During this recycling process depolymerisation, decomposition, dehydration was occurred simultaneously. The excess methanol leads to the depolymerisation of polymethyl methacrylate to methylacrylate and aluminium hydroxide transforms to alumnia [16]. For creating plastic free environment chemical scale recycling method was introduced [17]. In this method mixture of plastic wastes and plant oil is continuously producing monomers like ethylene, propylene and other useful chemicals by microwave assisted pyrolysis under high temperature.

2 Review of existing literatures

2.1 Recycling of composites

The techniques employed in recycling of thermoset composites summarised in table 2. Keith et al. (2019) noted that carbon fibre reinforced composite can be recycled with supercritical acetone/water solvent mixture. The solvent supplied is in the ratio of 80:20 and the reaction is carried out using a non-stirred batch reactor. Temperature and pressures in the range of 300-380 ˚C and 16-30 MPa. Degradation reaction does start at some temperature below 300 ˚C. It is observed that 54% of fibre recovery observed at 300 ˚C for 120 min and 90% recovery at 320 ˚C for 150 min while complete reaction is achieved in another 15 min for 360 ˚C. The decomposition is demonstrated using X-ray computer tomography. The reaction rate can be calculated using Arrhenius model with shrinkage core model (SCM).

Jiang et al. (2017) conducted research on recycling of carbon fibre/epoxy resin (CF/EP) composites in mild condition. Here the author described about recycling the composites in a shorter time and much lower temperature then other methods. The CF/EP is pretreated in initially with nitric acid and it starts to decompose and forms layered structure. These layers are subjected to macrogol 400 in the presence of (NaOH) at 160 °C for 200 min. As a result, carbon fibre is separated from epoxy resin. Specifically resin removal rate is more than 95wt%. The mechanical properties are slightly decreased when compared virgin fibres. As mentioned above the recycling took shorter time under mild condition.

Yijia Ma and Steven Nutt (2018) noted that amine/epoxy composites can be recycled by chemical treatment at atmospheric pressure. The results presented demonstrate key aspects of matrix dissolution for composites (with amine-cured epoxy) using two chemical treatment methods at atmospheric pressure: (a) depolymerisation (benzyl alcohol/K_3PO_4 at 200 °C) and (b) acid digestion (acetic acid/H_2O_2 at 110 °C). Both depolymerisation and acid digestion processes dissolved amine/epoxy matrices. However, acid digestion was deemed more suitable and practical for amine/epoxy composite recycling because of 1) faster chemical reaction rate at 2) lower reaction temperature, with 3) the recovery of residue and defect-free fibres. The amine-cured epoxies having the mechanism of acid digestion or oxidative digestion, in which oxygen atom transfer to the linking aniline groups followed by bond cleavage via elimination.

Justine Beauson et al. (2016) noted that recycling of shredded composites (SC) from wind turbine blades to new thermoset composites, shredded composite obtained from the load carrying beam of a wind turbine blade was sorted manually into two fractions, done by sieving. Based on observations of large fibre or matrix, the debonding cracks at the fracture surfaces of the shredded composites and the properties that are being obtained are low failure strength and strain of the composites is due to the lack of bonding between the shredded composites and the new polyester matrix (Table 1). To tackle this problem, the application of a physical or chemical treatment of the SC or the use of an alternative resin such as epoxy, to improve bonding could be investigated.

Table 1: **Mechanical properties of the manufactured SC composites**.

	Tensile properties				
	Fibre Length [mm]	Fibre content [Vol%]	Stiffness [GPa]	Strength [MPa]	Failure strain [%]
Polyester		0	3.4±0.0	49±6	1.7±0.3
As received	0.8 - 30	4	4.2±0.2	16±3	0.4±0.1
		7	4.8±0.1	18±1	0.4±0.0
		9	5.5±0.6	20±4	0.4±0.1
Fine	0.8	4	4.0±0.2	21±5	0.6±0.1
		8	4.7±0.2	23±4	0.5±0.1
		9	5.0±0.2	23±3	0.5±0.1
Coarse	30	4	4.3±0.3	15±1	0.4±0.1
		9	5.4±0.8	18±1	0.3±0.1
		11	5.8±0.4	29±4	0.6±0.1

Hua Yan et al. (2016) evaluated that epoxy resin composites can be recycled using supercritical 1-propanol, carbon fibres with clean surface, good thermal stability and excellent mechanical properties were successfully recycled through supercritical 1-propanol from the carbon fibre reinforced epoxy resin composites. When the temperature increase, the decomposition rate of the resin in the composites increases, but the mechanical properties of the recycled fibre decreases at small amount. With the extension of reaction time, the decomposition rate decreased, and obvious deterioration in the mechanical performance of the recycled carbon fibres was observed. 1 wt% of Potassium hydroxide (KOH) additive could improve recovery efficiency of the composites significantly. Supercritical 1-propanol recycling method has many potential benefits, including the high quality of the recycled carbon fibres.

Table 2: Recycling of Composites

Ref	Technique	Procedure	Inference	Advantages/ limitations
[18]	Supercritical acetone/ water solvent mixture technique	50 ml of the solvent mixture in a stainless steel, 100 ml tubular reactor was electrically heated to temperatures ranging from 300 to 380 °C and was held at the desired temperature from 0 to 150 min.	Acetone/water solvent mixture supplied in the ratio of 80:20. Temperatures in the range of 300-380 °C, pressures from 15.8 to 30.0 MPa and reaction times up to 150 min	Clean fibres can be recovered using temperatures above 320 °C and raising the temperature results in significantly faster reaction rates
[19]	Green chemical recycling method.	The CF/EP were pretreated in nitric acid to be initially decomposed and layered, then the layered CF/EP were subjected to macrogol 400 in presence of NaOH at 160°C for 200min.	Resin removal rate was more than 95wt% the mechanical properties of recovered carbon fiber decreased slightly compared with those of virgin fiber.	Carbon fiber/epoxy resin composites were recycled in shorter times and lower temperatures
[20]	SC recycling using special vacuum infusion setup.	Weight contents of SC in the new polymer composites were set to 10, 20 and 30 wt%. In order to obtain these weight contents with a vacuum infusion process, the weight of the manufactured composite plates need to be controlled.	The three wanted SC weight contents of 10, 20 and 30 wt% were all almost achieved, except for the composite plates with the wanted weight content of 30 wt%.	The low failure strength and strain of the composites is due to insufficient bonding between the SC and the new polyester matrix.

[21]	Chemical treatment at atmospheric pressure.	The study demonstrated that chemical treatments at atmospheric pressure with two methods depolymerisation and acid digestion.	Amine/epoxy matrices with acid digestion was deemed more suitable and practical because of faster chemical reaction rate at lower reaction temperature, with the recovery of residue and defect-free fibers.	These two methods were effective for dissolution of amine-cured neat epoxy.
[22]	Supercritical treatment using 1-propanol.	The composites was carbonized completely under the inert atmosphere at 515 °C, and the mass fraction of the residual carbonized products remained 77.6%. The residue contained carbon fiber and coke from the epoxy resin.	Carbon fibers with clean surface, good thermal stability and excellent mechanical properties were successfully recycled through supercritical 1-propanol from the carbon fiber reinforced epoxy resin composites.	With the temperature increase, the decomposition rate of the resin in the composites increased, but the mechanical properties of the recycled fibers decreased slightly
(Ribeiro et al., 2014)	Shredded fillers replacement for composites.	Different contents and size grades of the glass fiber reinforced polymers (GFRP) recyclates were incorporated as replacements for sand aggregates and fillers.	Flexural and compressive behavior, were found to be improved, irrespective of the quantity and size grade of the GFRP waste.	8% in GFRP waste content constitutes the turning point value on materials' behavior trend

Ribeiro et al. (2015) assessed the re-use of thermoset composite wastes as substitutes for aggregates and fillers for composites. Here, the effect of mechanically recycled GFRP pultrusion wastes was studied, by incorporating them with polyester polymer mortars. Their impact on the mechanical behavior (flexural and compressive behavior, specifically) was analyzed, by incorporating different contents and size grades of the GFRP recyclates as replacements for sand aggregates and fillers. Both the specified properties were found to be improved, irrespective of the quantity and size grade of the GFRP waste. A "turning point" in the behavioral trends was observed when the quantity of the scraps exceeded 8%. Despite being this advantageous and economical, further research is still required in this area to determine an efficient way to prevent the agglomeration of fibres during mixing and casting. The interface adhesion between the fibre waste and resin matrix also needs to be improved. Regardless, this is a unique take on recycling thermosets waste, which very few studies have focused on.

2.1.1 Processes used to remove and recycling Carbon fibres

The following table 3 summarises the techniques where thermosets are recycled by removal of carbon fibres. Ibarra et al (2016) discovered that by recycling thermosets, the recovery of carbon fibres was highly desirable in terms of the economy as well as the environment. It was found to lead to a reduction in waste and scrap. Benzyl alcohol and water were used to recover carbon fibers from composite materials, in subcritical and supercritical conditions, for subsequent reuse in high-performance components. The reaction temperature and time duration were the determining parameters. The decomposition rate of epoxy resin reached up to 89.1% with supercritical water and 93.7 % with subcritical benzyl alcohol. Scanning electron microscope (SEM) analysis showed complete separation of the composites as indicated by the clean recovered carbon fibers. The study highlighted the advantages of HVF over mechanical method.

Table 3: Recycling of thermosets by removing of Carbon fibres.

Ref	Technique	Process	Inference	Advantages/ limitations
[24]	Chemical recycling of thermoset composite	Benzyl alcohol and water were used to recover carbon fibers from composite materials, in subcritical and supercritical conditions.	Decomposition rate of epoxy resin reached up to 89.1% with supercritical water and 93.7 % with subcritical benzyl alcohol. High Voltage Fragmentation (HVF) recyclates could have a higher degree of reinforcement in new composite products compared to the shorter fibres recovered from the mechanical method.	It was found to lead to a reduction in waste and scrap. Complete separation of the composites can be separated as indicated by the clean recovered carbon fibres.
[25]	Supercritical solvolysis.	The resin removal raised optimal amount in a batch reactor process for an optimized molar ratio.	This study revealed that the resin removal efficiency decreased with several operating parameters such as time, temperature and quantity of water. In order to improve the purity and cleanliness of the recycled carbon fibres (rCFs).	The addition of ethylene glycol, in comparison with pure water, allowed to remove a high quantity of resin without mechanical losses

Fig 1: SELFRAG high voltage fragmentation laboratory equipment (left) and Wittman MAS1 granulator [24].

For instance, the results of fibre length distribution suggest that HVF recyclates could have a higher degree of reinforcement in new composite products compared to the shorter fibres recovered from the mechanical method, though most fibres from both the techniques are of 5 mm and are suitable for short fibre applications. HVF recyclates also have smooth and clean surfaces with traces of loosely attached residual resin, whereas mechanical recyclates had higher amount of resin.

Lucile Henry et al. (2016) described about the recycling of carbon fibre reinforcement by supercritical solvolysis. The experiment is carried out with two different media (water and a water/ethanol) mixture under supercritical conditions. The different experimental conditions, nature of solvents, temperature of recycled carbon fibres were studied. The water/ethanol mixture tends to have better mechanical properties than pure water mixture.

The properties of recycled carbon fibre have slightly decreased than virgin carbon fibre.

2.2 New Techniques Employed to Recycling thermosets

Table 4 summarises the new techniques employed in recycling thermosets. Shi et al. (2015) explained their take on sonochemical transformation of epoxy–amine thermoset into soluble and reusable polymers (Fig 2). Inducing position-oriented cleavage in thermosets leads to the formation of soluble polymers (degraded products). An epoxy–amine thermoset embedded with Diels–Alder (DA) bonds could be transformed into soluble polymers by sonochemistry, under mild temperature (ca. 20 °C), for the very first time. The soluble polymers, obtained by inducing position-oriented cleavage of DA bonds of the swelled epoxy resin in Dimethyl Sulfoxide by sonication, were re-cured to form epoxy-amine thermosets by DA reaction. Sonication is a process where sound energy is applied to agitate particles present in a sample, to extract its various components. Generally, ultrasonic frequencies (>20 kHz) are used. Hence, this process is also known as ultra-sonication. This sonochemical method of producing position-oriented cleavage provided an efficient way for controlled degradation and recycling of thermosets containing dynamic covalent bonds like DA groups.

Fig. 2: Graphical representation of degradation of a thermoset by sonication [26]

Table 4: New techniques employed in recycling of thermosets.

Ref	Technique	Procedure	Inference	Advantages/ limitations
[26]	Sonochemical transformation.	An epoxy–amine thermoset embedded with DA bonds was transformed into soluble polymers by sonochemistry. It was re-cured to form epoxy-amine thermosets by DA reaction.	Sonochemical method of producing position-oriented cleavage provided an efficient way for controlled degradation and recycling of thermosets with DA groups.	Recycling of thermosets containing dynamic covalent bonds like DA groups can be done with sonochemical method.
[27]	High Voltage Fragmentation	Composites were cut into smaller pieces and were submerged in water. Tests were conducted to find out the minimum applied voltage for the release of spark energy was minimum, to make sure that only	The spark channel generated an intense shockwave with high pressure and temperature and induced internal mechanical stress which exceeded the tensile strength of solid materials	HVFs are necessary to simplify and reduce the cost of recycling while maintaining high mechanical properties.

		minimal mechanical damage occurred to the fibres.	which finally lead to material disintegration.	

Anane Fenin and Akinlabi (2017) presented a study where composites were recycled by high voltage fragmentation. It was also compared with its competitor, mechanical recycling. In general, on applying high voltage, pressure waves along plasma channels were observed, which disintegrated materials in water. For carrying out HVF, composites were cut into smaller pieces and were submerged in water. Tests were conducted to find out the minimum applied voltage for the release of spark energy was minimum, to make sure that only minimal mechanical damage occurred to the fibres. The spark channel generated an intense shockwave with high pressure and temperature and induced internal mechanical stress which exceeded the tensile strength of solid materials which finally lead to material disintegration.

2.2.1 Recycling Thermosets by (other) chemical means

The following table 5 briefs the techniques where thermosets are recycled by means of chemical reactions like sel-condensation, cross-linking, transesterification, etc.

Lin et al. (2020) stated that cleavable bond locations can be enhanced for controlled thermoset degradation. Using polydicyclopentadiene (an industrial thermoset), they demonstrated it by introducing cleavable bonds within the strands of thermosets. This was done using a comonomer additive and it was found that the mechanical properties, same as the native material, were retained, in addition to which the thermoset was found to be capable of mild degradation. The products of the degradation are soluble and recyclable, possess functionality and controllable size. However, cleavable crosslinks in higher loadings were found not to produce degradable materials.

Simon et al. (2018) described about the recycling of polyurethanes from glycolysis process. The polyurethane is thermostable and having the ability of undergoing the chemical recycling process. That is why chemical recycling process is usually preferred for elastomers like polyurethanes. Glycolysis is the most widely used chemical process. It consists of a transesterification reaction; the ester group is joined to the carbolinic carbon of the urethane. And the carbolinic carbon is interchanged by hydroxyl group of glycol. Alkane Hydroxides are used as the catalyst. Amines may react with free isocyanate, urethane group may react with water, where urea is susceptible to glycolysis. This reaction leads to the formation of polyol and unstable carbamic acid. At last due to the reaction temperature, urethane may be degraded thermally by giving out carbon dioxide, amines and unsaturated compounds.

Krug et al. (2019) conducted a study where it was demonstrated that catalytic amounts of fluoride ion at room temperature could solubilize highly cross-linked silicone resins (that were initially cured up to 250 °C). Silicone resins are conventional thermosets with an inorganic backbone. They possess chemical inertness and high thermal stability, which despite being advantageous, makes it difficult to recycle them by traditional methods. Once solubilization equilibrium is obtained, the solvent is removed so that the polymer network can be reformed. Then, aluminium substrate coatings and virgin and recycled silicone monoliths were analyzed for properties like hydrophobicity, wear resistance, substrate adhesion, and thermal stability. Silicones that were recycled under optimized conditions retained wear resistance, thermal stability, and it's adhesion property, almost completely. In some instances, the recycled coatings were even found to offer properties that were superior to the initial materials (Fig 3). This study has suggested a method for direct recycling of silicones, without depolymerizing. Furthermore, this also allows upcycling of silicones because of the improvement in wear and thermal resistance observed after recycling.

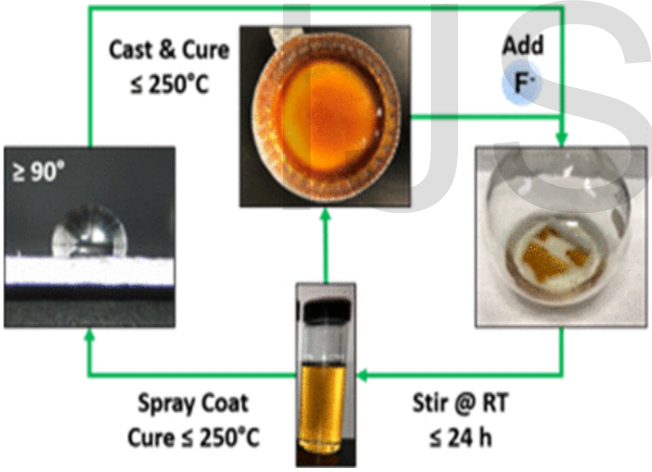

Fig 3: Pictorial representation of preparation of Silicone coatings [28]

Lin Zhou et al. (2017) conducted research on rapid degradation of disulfide-based thermosets through thiol-disulfide exchange reaction. The cross-linked Polyurethanes (PUs) were prepared (Fig 4) from 11,110-lydithiodiundecanol (DTU) as soft segment, incorporating isophorone diisocyanate (IPDI) and tris(2-Hydroxyethyl)amine (TEA) as hard segment. When immersed in 0.1 g/mL reducing agent dithiothreitol (DTT) for 12 h at 25 °C, the PUs completely dissolved. The temperature increased from 25 °C to 60 °C, the time required for the complete dissolution of the PUs decreased from 12 h to 50 min. Meanwhile, when we combined ultrasound with DTT, the Polyurethanes totally dissolved at T < 40 °C in 30 min because of the multi-stimuli synergism. These results indicate that the multi-stimuli synergistic effect can efficiently accelerate the disassembly of thermosetting PUs, which provides an effective way to detach thermosets under mild and multiple conditions. The detachable PUs will have a lot of applications in the field of disassembling thermosetting polymers rapidly and recycling the valuable adhesive components conveniently.

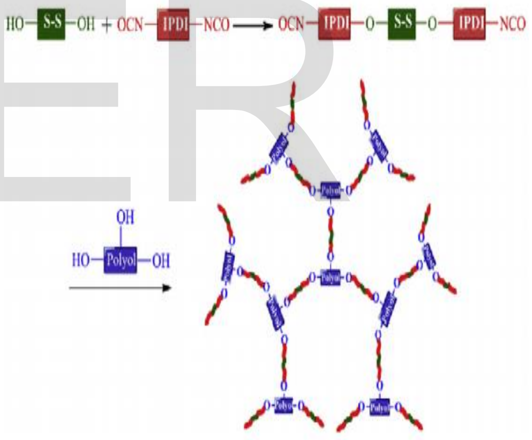

Fig 4: Synthesis of cross-linked polyurethanes containing disulfide bonds (DTU-IPDI-TEA) [29]

Antonela Gallastegu et al. (2020) conducted research in spain and evaluated that biobased Polyether thermoset which is obtained by self-condensation of Glycerol and Diglycerol can be recycled by hydrolysis under acidic condition. The thermosets were synthesized by copolymerization of Glycerol with 1,6-hexanediol using an acid-base non-eutectic mixture from methane sulfonic acid (MSA) and 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD) as organic catalyst. Glycerol-based thermosets are cross-linked polymer networks with elastomeric behavior due to their crosslinked structure these materials are not soluble or reprocessable and their ability to be recycled is strongly hindered. The glycerol-based thermosets could be polymerised simply by immersing the thermoset in water and heating it to 120 °C for 2 h. This Process was efficient at room temperature but for the depolymerisation is to be occurred for very longer time (24 h).

Lu Lu et al. (2016) demonstrated how intrinsic self-healing enables recycling of epoxy thermoset. Esterification of diglycidyl ether of bisphenol A and tricarballylic acid produced healable epoxy foam with shape memory. Healing (Fig 5) was done without using a healant (microencapsulated healing agents), catalyst or a hardener. The healing effect was imparted by a transesterification reaction that took place at the fracture surface between two epoxy blocks that were saw-cut, compression programmed and stacked in a confined space. Applying shape recovery forces on the blocks made the gap between the two epoxy blocks tightly close at higher temperatures. The amalgamation of shape memory and intrinsic healing capability within the network was found to widen the use of thermosets, especially in real-world composite applications, and also enabled recycling.

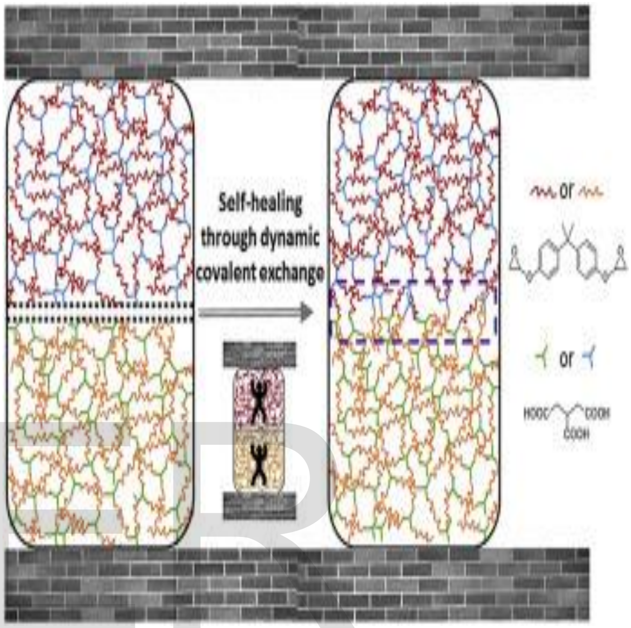

Fig 5: Graphical abstract of self-healing [30]

Table 5: Recycling by (other) chemical means.

Ref	Technique	Procedure	Inference	Advantages/ limitations
[31]	Mechanochemical degradation.	Cleavable bonds were introduced in Polycyclopentadiene within its strands using a comonomer additive.	The mechanical properties were retained. The thermoset was capable of mild degradation.	The products of the degradation were soluble, recyclable and possessed functionality and controllable size.
[32]	Glycolysis process	Bulk self-condensation of glycerol was carried out using an acid-base non-eutectic mixture formed from MSA: TBD (3:1 M ratio) as organic catalyst.	Molar ratio was chosen based on its performance and thermal stability. 0.3 mol of glycerol and 0.015 mol of the MSA:TBD mixture	This work shows not only a new method to valorize glycerol and its derivatives but also a route to the generation of recyclable biobased thermosets which could

			were heated at 90°C under agitation for 30 min.	contribute to the future circular plastic economy
[28]	Room-temperature chemical recycling Technique.	Silicone coatings were prepared and recycled. Once solubilisation equilibrium is obtained, the solvent is removed so that the polymer network can be reformed.	Silicones that were recycled under optimized conditions retained wear resistance, thermal stability, and its adhesion properties.	Direct recycling of silicones has been made possible. Furthermore, up cycling of silicones is also possible because of the improvement in wear and thermal resistance observed after recycling.
[29]	Rapid disassembly	At first, DTU with distilled THF were placed into a three-necked flask with magnetic stirrer and nitrogen inlet and outlet. The mixture was stirred to homogenization, and then IPDI were added. Prepolymerization proceeded at 70 °C for 3 h under nitrogen atmosphere.	The detachable PUs will have a lot of applications in the field of disassembling thermosetting polymers rapidly and recycling the valuable adhesive components conveniently.	The multi-stimuli synergistic effect can efficiently accelerate the disassembly of thermosetting PUs, which provides an effective way to detach thermosets under mild and multiple conditions
[33]	Hydrolysis, under acidic conditions.	3:1 mixture of MSA and TBD as a catalyst for the self-condensation of aliphatic diols leading to aliphatic polyethers. The self-condensation of Gly was performed under air at 170 °C for 24 h.	This work shows not only a new method to valorize glycerol and its derivatives but also a route to the generation of recyclable biobased thermosets	polymerization/depolymerizations of glycerol-based thermosets can be done
[30]	Intrinsic self-healing characteristics.	Diglycidyl ether of bisphenol A was esterified with tricarballylic acid to produce healable epoxy foam with shape memory. The healing effect was imparted by a transesterification reaction that took place at the fracture surface between two epoxy blocks that were saw-cut, compression	The amalgamation of shape memory and intrinsic healing capability within the network was found to widen the use of thermosets, especially in real-world composite applications, and also enabled recycling.	Applying shape recovery forces on the blocks made the gap between the two epoxy blocks tightly close at higher temperatures.

		programmed and stacked in a confined space.		
[34]	Chemical recycling	Poly(hexahydrotriazine)s (PHT) was treated with acid (pH = 0), and the decomposition rate of PHT was <10%. After it was cured at 100 °C for 36 h	The decomposition rate was about 45%, and no noticeable change occurred when further treated	The PHT could be depolymerized partly (about 45%) at low pH (pH = 0) at heating conditions.
[35]	Intrinsic self-healing characteristics.	Copolymers of styrene and furfuryl methacrylate Synthesized by atom transfer radical polymerization, and cross-linked with a bismaleimide by means of thermally reversible DA reaction, to obtain self-healing materials.	The possibility to reversibly decouple the DA adduct at relatively low temperature	The diblock copolymers did not show self-healing, but they melted.
[36]	Current recycling methods	The availability of degradable thermoset matrices, along with recovered carbon fibres (RCFs) are anticipated to bring about the essential sustainability characteristics for future carbon fiber reinforced polymers (CFRP)	Dynamic reversible bonds have been recently added to conventional thermosets such as epoxies to characteristics of being able to be reshaped and reprocessed	More radical approaches such as replacing thermoset matrix with new thermoplastics are feasible for composites in the wind turbine and other relevant sectors
[37]	Current recycling methods	Chemical sizing or re-sizing is a significant step to use recovered fibers (RFs) in new composites,	Reuse of RFs in new composites is limited due to the entanglement of fibers.	Microwave-assisted chemical recycling method is considered as a green, energy-efficient, and most sustainable recycling method.

Many new developments have been made nowadays. For instance, PHT synthesized from paraformaldehyde and p-phenylenediamine (PDA), on adding carbon nanotubes, shows amplified thermal/mechanical stability, than the original polymer [34]. These improvements make it useful in automotive, aerospace and many other suitable applications. It has also been discovered that PHT and its composites depolymerize (which implies that they can be recycled, as they are broken down) low pH, and can be degraded for about 45% at the heating condition. Aliphatic polyether thermosets that can be recycled are prepared using Glycerol as starting materials. Hydrolysis carried out in acidic atmosphere leads to depolymerization of these thermosets, back to their starting monomers.

They can further be repolymerized to get biobased thermosets, which can also be recycled by various chemical techniques. Sustainable polymer systems are being developed nowadays where complete recycling of epoxy-based thermoset composites are being made possible, with separation, recovery and complete reuse of the constituents of the composites, resins as well as the fibers [35]. Practices that can reduce wastes and re-use resources are essential. Several techniques have been developed for efficient recycling of end-of-life CFRP [36] and manufacturing wastes. The idea of recycling end of life wastes of wind turbines [37] by reusing reclaimed fiber composites of carbon fibers and glass fibers has also been explored

2.3 Recycling of tyre products

Since Tyre also comes under thermoset elastomers, the need for efficient recycling techniques analysis is required. In table 6, the techniques applied for recycling of tires (and tire products) were summarised.

Sathiskumar and Karthikeyan (2019) proposed that recycling of tires and its energy storage application of by-products. The disposal of waste tires is a major environmental and economical issue. Pyrolysis is the most promising route. Pyrolysis is the thermal decomposition of the waste tire in an oxygen free environment at 400°C. The by-product of the pyrolysis is Tire Pyrolysis oil (TPO), Pyro-gas, Pyro-char (Fig 6). TPO can be used as a precursor for benzene, xylene, toluene, and carbon nanotube and limestone synthesis. Pyro gas can be used as a combustible fuel. The gas-phase products from waste tire pyrolysis are mixture of olefins, CO_2, H_2, S, etc., where Hydrogen is considered as efficient and economically friendly fuel. Tire derived carbons can be used as electrodes in energy storage system like batteries, supercapacitors and fuel cells. Recently Pyro char has been used as electrode materials for Li, K, Na-ion battery. By this way, the waste tires can be converted into useful materials by pyrolysis process

Buss et al. *(*2017) focused on recycling Waste Tire Rubber (WTR) by microwave energy. WTR was ground to its powder form at ambient a temperature. This powder was then devulcanized by passing microwave electromagnetic energy. A new composite was then made by incorporating it into a thermoset resin. FTIR analysis revealed that rupture of Sulfur-Sulfur and Carbon-Sulfur bonds have occurred during the process. By swelling analysis, it was revealed that the microwave treatment lead to a very notable degree of devulcanization. New epoxy based composites were then prepared using GTR (Ground Tyre Rubber) and DGTR (Devulcanized Ground Tire Rubber), individually, which disclosed that DGTR imparted better mechanical properties than untreated GTR because of the excellent 'interface coherence' between DGTR and epoxy, which was confirmed by SEM analysis.

Fig 6: Graphical representation of pyrolysis of waste tires [38].

Table 6: Recycling of tyre products.

Ref	Technique	Procedure	Inference	Advantages/ limitations
[38]	Pyrolysis	Waste tire pyrolysis decomposition temperatures between 400 and 500 °C. The output product of the pyrolysis (TPO, pyro gas and pyro char) is also changed if the temperature is varied.	Usually, the low pyrolysis process favors the production of TPO while the high-temperature process favors the production of gases. . Carbon nanotubes, hydrogen are a high-cost material and it's used for energy storage application and can be derived from waste tire material.	Pyrolysis process reduces the number of waste tires while converting them into market valuable products
[39]	Microwave treatment	WTR powder was devulcanized by passing microwave electromagnetic energy. Then new composites were prepared from the ground tire rubber, as well as the devulcanized ground	Fourier-transform infrared spectroscopy analysis revealed that S-S and C-S bonds were broken, while swelling analysis revealed that the microwave treatment lead to devulcanization.	New composites prepared from GTR and DGTR revealed that the better mechanical properties because of excellent interface

		tire rubber and their effects were analyzed.		coherence between it.

The demand for judicious use of resources and extensive waste management has lead to the reusing and recycling of fiber composites by various techniques including mechanical, thermal, chemical, and even a few hybrid ones. These practices and techniques are still a subject of research and are proving to be useful.

3 Conclusion

Thermoset plastics cannot be re-used as they burn before they can be re-molded, which is contrary to thermoplastics, which can be re-molded due to their melting capability. Henceforth, recycling of thermosets is the only feasible option, when it comes to plastic waste management. Recycling is a useful and advantageous practice that takes into account, the properties and the factors of the material that helps it retain its innate reactive trail. It is essential to apply technologies that contribute to finer waste management for imperishable use of thermosets. Many new developments have been made nowadays. Also, sustainable polymer systems are being developed nowadays where complete recycling of thermoset composites are being made possible, with separation, recovery and complete reuse of the constituents of the composites, resins as well as the fibers.

Practices that can reduce wastes and re-use resources are essential. The demand for judicious use of resources and extensive waste management has lead to the reusing and recycling of thermosets by various techniques including mechanical, thermal, chemical, and even a few hybrid ones. These practices and techniques are still a subject of research and are proving to be useful. With the embarking of new technologies at quicker paces now more than ever, recycling of thermosets can indeed be made easy which is an utmost necessity considering the rate at which plastics waste are growing.

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