A review on research, application, processing, and recycling of PPS based materials

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Abstract

Among the engineering thermoplastics, poly(phenylene sulfide) (PPS) stands out for its excellent properties and mainly for processing at lower temperatures. The requirements requested by industries can be made by improving mechanical strength, weight reduction, and durable components by reinforcing the PPS matrix with fiberglass (FG) and carbon fiber (CF). This review intends to present the most current research related to the physical, mechanical, and thermal properties of PPS and the PPS/FG and PPS/CF composites most currently used by the aerospace, automotive, and energy industries. In addition to presenting the feasibility of mechanical and thermal recycling processes for PPS-based waste to reinstate a high market value thermoplastic into the industrial production cycle, thus contributing to the minimization of waste destined for landfills and incinerated or even improperly disposed of in the environment.

Keywords: applications, carbon fiber, composites, fiberglass, poly(phenylene sulfide).

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1. Introduction

The diversified aerospace, automotive, and energy industries have similar requirements and interest in high-performance materials that are lightweight but strong enough to take high loads. Thus, the use of engineering thermoplastics, such as poly(phenylene sulfide) (PPS), poly(ether-ether-ketone) (PEEK), poly(aryl-ether-ketone) (PAEK), and poly(ether-imide) (PEI), has been arousing great interest in these industrial sectors[1].

PPS has stood out among these engineering thermoplastics due to its low processing temperatures (~280 – 320 °C)[1]. Furthermore, PPS is a semi-crystalline polymer formed by alternating sulfur atoms and aromatic rings. Due to this configuration and the stability of the molecular structure, unique characteristics are granted, such as good thermal stability, low thermal degradation[2], high flame resistance, superior mechanical properties (high modulus, tensile strength, good dimensional stability, good fatigue resistance), good chemical stability (resistant to solvents), and low moisture absorption. These properties make PPS an exciting and essential engineering polymer[3,4].

In 1888, Friedel and Crafts discovered the PPS. In 1967, the production methodology was developed, and only in 1972 was PPS commercialized by Phillips Petroleum Company[5,6]. Since then, it has been produced and used widely and commonly in several areas, such as in aerospace[7], automotive[7], and wind energy industries[8].

PPS-based materials, such as composites and blends, have been widely used to meet high-performance requirements, for example, in aerospace structures such as wings, tails, fuselages[9], in the automotive industry, in motor vehicle engine compartments, pump housings, lamp and headlight bases, and in the renewable energy sector[10], in wind turbine blades[10].

To meet the requirements of industries, thermoplastics can be reinforced with fiberglass (FG) and carbon fiber (CF). So, it is possible to obtain the structure lightness, excellent mechanical resistance, and, consequently, more durable components due to its high strength-to-weight ratio[11,12]. PPS can also be used in blends when a physical or chemical mixture of different polymers is sought to obtain a material with similar or superior properties, thus complementing each component or even achieving a specific set of functional properties. Therefore, through the appropriate choice of matrices, it is possible to obtain a material with greater ease...
of processing, more tenacity, greater strength, lightness, and low cost, among other qualities\[13\].

The thermal properties of PPS-based materials must be understood because its great importance in the conformation and processing steps of components. Proper processing parameters are essentials in obtaining good mechanical and physical properties of the produced components.

Machining of PPS-based matrix composites with fiber-reinforcement, mainly FG and CF, has been studied in recent years\[14-16\]. Lack of experience in machining fiber-reinforced PPS is a factor that affects the quality of the machined pieces, which can harm finished parts in terms of mechanical strength, fatigue resistance, and dimensional accuracy. The anisotropic property of reinforced PPS changes the material removal mechanisms during the machining, compared to conventional metal machining. The main problem is the delamination of the layers that form the composite. Searching optimal cutting parameters for minimal delamination occurrence with minimal tool wear and higher production are the biggest challenges in composite material machining research.

The excellent characteristics of engineering thermoplastics, especially PPS, have increased their demand and, consequently, the generation of waste from the production process to the end of the product’s useful life. Composites and blends based on PPS have high technology in the manufacturing process combined with processing complexity. Recycling often becomes unfeasible, resulting in the destination of sanitary landfills and incineration of these residues\[17\]. However, due to environmental pressures, industries that consume these materials have been showing interest in recycling, aiming not only at waste and environmental concerns but also at the possible recovery of valuable capital from these materials. It is currently possible to recycle PPS-based materials through mechanical and thermal recycling, which may be a viable, lucrative, and ecologically correct solution for the disposal of waste based on PPS, in addition to minimizing the destination of these wastes in landfills and incineration\[18,19\]. These solutions can an economic return from these residues, which may be reinserted in the production process of the same sectors generated or even used as raw material for other industries, as indicated in Figure 1.

Thus, this review article focused on the feasibility and possible application of the PPS in components in the aeronautics, automobile, and renewable energy industries. Furthermore, the present review article reports the latest studies (2018–2022) related to the application, processing, thermal properties, welding, and feasibility of recycling PPS, aiming to show viable and profitable recycling processes for PPS waste with a high market value.

2. Applications

PPS is a high-performance thermoplastic and semi-crystalline polymer with excellent mechanical and thermal properties. Alternating para-substituted rings of phenylene and sulfur atoms form its linear and rigid chemical structure (Figure 2), which confers its particular characteristics, as per example, its high melting temperatures, being between 270-290 °C; glass transition, approximately 90 °C; of thermal decomposition around 508 °C, and coefficient of linear thermal expansion of 49 μm/m°C\[3,20\].

The exceptional properties of engineering thermoplastics combine high performance, relatively easy processing for structural parts with complex geometry, lightness, and consequently reduced consumption of fossil fuels, which leads to a reduction in the release of greenhouse gases into the environment, in addition, to being corrosion-resistant. Thus, due to the numerous qualities of thermoplastics, the demand and replacement of many metals and metallic

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**Figure 1.** Feasibility of the economic and environmental cycle of PPS-based components.
alloy components have gradually increased day by day\cite{21}. Figure 3 shows the possible applications of PPS-based materials in the aerospace, automotive, and energy industries.

2.1 Aerospace

Currently, the aerospace sector leads the consumption and application of thermoplastic and thermoset composites. Approximately 50% of polymer composites are applied in aircraft structural parts, and 40% are manufactured carbon composites\cite{6,9}.

Boeing 787 was the first aircraft that used composites as the primary material in constructing its structure, mainly in the main wing and fuselage. The payoff of included materials composites, about 50% composites by weight (80% by volume), is a 20% reduction in fuel consumption compared to similar-sized conventional aircraft\cite{22,23}.

A few years after the presentation of the Boeing 787, Airbus launched the A350, made up of precisely 53% of composite materials, distributed among fuselage, wings, landing gear, windows, doors, keel beam, and the empennage, consisting mainly of reinforced polymers with CF, and with savings of up to 25% in fuel consumption\cite{24,25}. Other Airbus aircraft, such as the A320 and A340, feature 15%, and the A380 features 25% composite materials, mainly PPS/CF. Polymeric composites are applied in ailerons, rudder, flaps, spoilers, elevator, vertical, and horizontal stabilizers, wing panels (leading and trailing edges), landing gear doors, nacelles, flap fairing, and wing box, and on the A380, it is the first aircraft ever equipped with a central wing box made of composite material.

In both aircraft mentioned, PPS is used in the composition, since currently the PPS is widely applied in aircraft components, such as interior parts, passenger seats, overhead cabinets, aerodynamic stabilizers, and wing trailing edge panels\cite{9}. Other aircraft that have PPS in the components materials is the Fokker 50 and Gulfstream G650 use PPS/CF composites on critical control surfaces (rear rudder and elevator)\cite{6,26}.

These are some of the examples of the growing use of these composite materials in aircraft structures.

2.2 Automotive

Polymers are widely used in the automotive industry due to their numerous qualities highlighting lightweight, good dimensional stability, excellent fracture and fatigue resistance, ease of processing, and corrosion resistance. Approximately 24% of thermosets and 50% of thermoplastics are used in this sector; polypropylene (PP)\cite{27} and polyurethane (PU)\cite{28,29} are the most used thermoplastics in the automotive industry\cite{7,30,31}.

GF and CF reinforced thermoplastics are always widely used in some external components of automobiles, such as crash boxes, leaf springs, bumper beams, fenders, spoilers, and spare wheel wells and are intended to reduce the weight of automotive components further, in addition to having the advantages of reduced manufacturing cost, due to shorter processing time\cite{32}. The reinforcement of thermoplastics with CF is intended to facilitate the integration of parts, low cost,
and weight reduction. Regarding the application of CF in thermoplastics, advances in manufacturing technology are required to obtain an excellent cost-benefit ratio for large quantity production, in addition to the high cost\textsuperscript{[34]}.

PPS is relatively still little used; however, it is possible to observe an increase in automakers based on scientific research\textsuperscript{[35]}. As one of the results of these studies, Bosch verified the feasibility of applying PPS (Rytton\textsuperscript{®} PPS, Solvay) in an active vacuum brake booster connecting the piston for use in sports vehicle braking systems. With this replacement, Bosch verified a cost reduction of 84\%, in addition to a weight reduction of 78\%\textsuperscript{[21,35]}Moran, Lake, and Dole\textsuperscript{[36]} used PPS (Fortron\textsuperscript{®}, Ticona) to manufacture pumps used with harsh fluids at elevated temperatures. The authors chose to use PPS due to its excellent mechanical properties, resistance to cracking and deformation, in addition to its resistance to high temperatures (200 °C), and because of its chemical stability, since the pump was in contact with corrosive substances.

PPS is already being used in structural components, such as motor vehicle engine compartment, fuel rail, pump impellers, thermostat housing, throttle body, ignition coil bobbin, micro-precision injection molded parts, encapsulation of computer chips, and other sensitive electronic components, lamp and headlight bases, pump housings\textsuperscript{[33]}.

Furthermore, in the automotive sector, blends are widely applied. According to the study carried out by Begum, Rane, and Kann\textsuperscript{[32]}; the automotive industry is responsible for the greater use of polymer blends being applied to the exterior, interior, and underhood components of automobiles.

2.3 Energy

In the renewable energy industry, wind turbine blades have always been made of polymeric composites, approximately 80\% of which are thermosets, due to the high strength, stiffness, and ease of processing processes\textsuperscript{[37]}. The wind turbine blades require that the material composition has good mechanical strength to resist gravitational and wind forces, greater rigidity to provide stability, and good fatigue resistance to support the cyclical load that the turbine blades are subjected\textsuperscript{[38]}.

Currently, the use of thermosets leads the application in wind turbine blades. However, the blades have been suffering from erosion that causes a significant loss in the aerodynamics efficiency of turbine blades and consequently reduces the wind turbine’s annual performance by between 2 – 25\%\textsuperscript{[39]}. Based on this problem, carried out a comparative study of the replacement of thermosets by thermoplastics, such as PP and PU, as they are more ductile and thus, increase the lifetime of wind turbine blades\textsuperscript{[30,41]}.

The application of thermoplastics in wind turbine blades has shown great potential, together with many advantages\textsuperscript{[42,43]}. Thermoplastics have more excellent ductility reducing degradation, thus avoiding erosion than thermosets\textsuperscript{[40]}. Thermoplastics have shown excellent aerodynamic performance, and reduced gravity forces may have lowered manufacturing costs. If they need any repair, welding is possible, eliminating the need for adhesive bonds between blade components and increasing the overall strength. Thus, they grow the valuable life of wind turbine blades, and in addition, can be recycled after a product has served its useful life\textsuperscript{[44,45]}. Complying with European regulations\textsuperscript{[46]}; as the European Union Directive on landfill waste, prohibit the disposal of large parts of composite materials, such as wind turbine blades, in landfills\textsuperscript{[47]}. Given the problems exposed by the use of thermosets and the advantages of thermoplastics, the interest of industry and research in incorporating thermoplastics in the composition of wind turbine blades has been increasing. Research using thermoplastics is still minimal; however, given the existing solutions, a material with properties of high tensile strength, high ductility, and high elongation at break is necessary. As mentioned above, some thermoplastics are already being used, such as PP and PU. However, there are other strong candidates for the composition of wind turbine blades, such as polycarbonate (PC), polyethylene terephthalate (PET), polyamide 69 (PA69), polyamide 11 (PA11), and the PPS\textsuperscript{[33,39]}.

4. Processing

PPS has relatively easy processability compared to other engineering thermoplastics. Thus, components made of PPS can be molded or extruded, and currently, they are processes widely used industrially\textsuperscript{[48]}. According to Zuo et al.,\textsuperscript{[2]} processing by injection is not feasible due to the high fluidity of PPS in the molten state, which requires the use of a closure nozzle and curing with sealed mold.

PPS has a high melting temperature (between 270 - 290 °C) requiring high processing temperatures (close to 350 °C), which can often be an obstacle in the use of the material due to the need for unconventional processing equipment, which operates in high temperatures, which often lead to increased costs in the final product\textsuperscript{[20,49]}. Another problem in PPS processing is the atmosphere in which it is carried out, since the presence of oxygen in contact with the polymer at a high temperature can lead to a degradation of its chains, reducing the properties and useful life of the final part\textsuperscript{[20,49]}. Compression molding is widely used industrially, mainly for PPS composites with some fiber, such as GF and CF\textsuperscript{[50]}. This processing occurs through the lamination of semi-pregs, which are mats with the fiber fabric already impregnated with the polymer matrix. Brujin and Hattuam\textsuperscript{[51]} used compression molding to make the panel door for a rotorcraft from the recycling of PPS/CF composites. Zhao et al.,\textsuperscript{[52]} produced high-performance PPS/CF composites with a high content of reinforcing fabrics (80\%) through the hot compression molding.

On the other hand, the extrusion process is more used to process the polymer with loads of smaller sizes or obtain polymer blends\textsuperscript{[53]}. To prepare lightweight and high-performance polymer foams with tailored morphologies and excellent properties, Ma et al.,\textsuperscript{[54]} used extrusion processing to improve the homogenization of the PPS/PEEK blend. In the study of Lin et al.,\textsuperscript{[55]} extrusion processing was used to homogenize the PPS/PA blend with graphene.

As with all thermoplastics, a drying process before extrusion processing is always recommended. For PPS, the literature shows that drying must be carried out at a temperature of 120 °C for 3 h\textsuperscript{[38]}. If the PPS has some
carbonaceous load, drying is essential, as water absorption increases in these cases\textsuperscript{52,59,67}.

Another relatively new process widely used for thermoplastics is three-dimensional (3D) printed through fused deposition modeling (FDM). It can manufacture high-performance components, including parts from PPS-based materials. However, this method involves a complexity associated with selecting its appropriate manufacturing parameters. Many processing parameters can be adjusted to optimize the process to reduce printed parts' time, cost, quality, and mechanical performance in high-performance components.

According to the study carried out by Geng et al.\textsuperscript{56}, FDM has several challenges due to its inherent crystallization and thermal crosslinking properties of PPS. When the authors verified the degree of crystallinity (Xc) and crosslinking of the PPS, they observed that the thermal history affects the properties of the PPS when printed in three dimensions. Therefore, the authors presented in their study that the accuracy of 3D published PPS samples can be improved using forced-air cooling in the molten deposition modeling. Thus, the balance between mechanical strength and ductility can be improved through changes in heat treatment conditions.

El Magri et al.\textsuperscript{57} studied the influence of response surface methodology, nozzle temperature, print speed, and layer thickness to optimize output responses, namely Young's modulus, tensile strength, and Xc through the use of FDM. According to the results obtained by the authors, layer thickness was the most influential printing parameter on Young's modulus and Xc, as optimal factor levels were reached at nozzle temperature at 338 °C, print speed of 30 mm/s, and layer thickness of 0.17 mm. The authors carried out the reprocessing using various temperatures to eliminate the residual thermal stress generated during the FDM and improve the Xc of the produced parts. The authors found that a temperature of 200 °C for 1 h could improve PPS printed pieces' thermal, structural, and tensile strengths.

Yeole et al.\textsuperscript{59} showed that PPS/CF pellets are excellent raw materials for additive manufacturing. The authors showed that the high printing temperatures (between 285 and 400 °C) did not degrade the CF and did not oxidize the PPS, something that is very worrying for the final properties of the pieces. Furthermore, the authors found that the printed works did not show many voids and that the last properties in all the printing techniques analyzed could be improved by increasing the concentration of CF in the pellets.

5. Machining of PPS/Fiber composites

The thermoplastic matrix reinforced fiber leads to higher mechanical strengths, boosting the composite applicability but damaging the machining\textsuperscript{65,66,68}. In general, reinforced components require a high surface finish and dimensional accuracy only by machining processes affirm that most GF and CF reinforced composites components in the industry are manufactured lacking precision dimension, demanding different finish or semi-finish adjustment machining\textsuperscript{69}. Moreover, according to Chen et al.\textsuperscript{13}, the addition reinforces fibers in the PPS matrix modifies the tribological properties and electrical and thermal conductivity of the PPS blends and composites. Therefore, the machinability study should also consider several variables, such as the variation of composition and properties.

5.1 Main characteristics of machining PPS/fiber composites

Fiber-reinforced thermoplastic composites are generally manufactured close to the final dimensions, and therefore it is necessary to apply a machining process to meet the dimensional requirements. Carbon fiber-reinforced polymer (CFRP) pieces, used in the aeronautic industry, are assembled by riveting and bolting. To fix components and structure, holes are needed in the CFRP parts, and the most used process for this is conventional drilling\textsuperscript{61,62}.

High hardness, strength, abrasion resistance and thermal conductivity reduce efficiency, machining quality and accelerate tool wear. Poor machining quality reduces strength against fatigue, compromised structure integrity, and prejudices assembly tolerances\textsuperscript{63}.

The high abrasiveness of the reinforced constituents, such as CF, make composite materials more difficult to machine than traditional metal materials. Chip formation is also different in machining ductile metals and polymer matrix composites. While machining ductile metals results in curled and continuous chips, the polymer matrix fiber-reinforced composite machining forms crumbled and fragmented chips by fracture of fibers, failure of the matrix, and debonding between the fibers and matrix\textsuperscript{61}.

Several difficulties are observed in machine PPS composites. One of them is the high strength-to-weight ratio of the PPS matrix, limiting its machinability. Although favoring high-end applications, the correlated anisotropy and the heterogeneity causes serious difficulty in achieving a satisfactory quality of machined components considering surface integrity, dimensional and geometrical tolerances\textsuperscript{64}.

According to Korugic-karasz and Farugia\textsuperscript{65}, the anisotropic property of reinforced PPS changes the material removal mechanisms during the different machining phases of the composite structure, and the cutting process favors a specific tendency of damages.

Another common factor is the lack of experience in machining fiber reinforced PPS since the knowledge of machining conventional materials cannot be applied to GF and CF reinforced thermoplastics\textsuperscript{66}.

The most related issue during machining fiber-reinforced polymers matrix is delamination\textsuperscript{14,16,67,68}. Delamination is the interlaminar cracking between fiber-reinforcement and polymer matrix, resulting in stiffness and strength loss. Delamination is related to the cutting forces of the machining processes. In drilling, when thrust force exceeds a critical value, pull-out fibers occur in the cutting tool's entrance, and push-down occurs in the hole's exit\textsuperscript{16,69}. Good machining parameters, tool geometry, and tool material effects cutting forces and are investigated to avoid delamination\textsuperscript{15,62,70,71}. In the drilling process, the most used composite material machining for aeronautics and automotive industries, the delamination problem is reduced by high rotations speeds and low feed rates\textsuperscript{14,68,70}.
According to Iliescu et al.,[72] a way to improve drilling is to use diamond-coated tools that can allow from 10 to 12 times longer tool life than carbide tools with three times higher cutting speeds. However, the application of higher cutting speeds can lead to an increase in temperature. According to Sorrentino et al.[73], during drilling, the maximum temperature peak is located close to the drill exit, which can favor material push out and delaminations. Furthermore, the progression of temperature increase is proportional to the composite layers damaged.

Nomura et al.[74] observed a strong influence of cutting depth and feed parameters on the burr formation of small holes drilling in PPS for drilling machining. The authors also stated that an increase in feed (from 3 to 12 mm/min) and cutting depth (0.5 to 4.5 mm) decreased the burr formation leading to a better straightness profile of the drilled hole.

Basso et al.[75] recommended a drilling strategy between chip thickness and drill cutting lips edge radius to minimize uncut fiber/matrix regions for high feed values in the micro-drilling of PPS/CF composites using a 0.6 mm diameter twisted drill.

PPS presents better machinability than other high-performance composites.[71] However, factors such as temperature, fiber orientation, and the type of applied lubrication can significantly impact the machining response of fiber-reinforced thermoplastic composites.

An important parameter to consider is the temperature since the thermal influence of machining on the polymer matrix must be below a load-critical extent. The process parameters must be adjusted to not exceed the thermoplastic matrix’s glass transition temperature (Tg). An efficient way to evaluate the temperature during machining is to apply thermocouples. However, thermal behavior may vary according to the sensor position. Therefore, regions of non-homogeneity matrix deposition or fiber displacement must be avoided.[76]

Another factor to consider is the type and quality of reinforcing fiber added to the thermoplastic. According to Khashaba[77], reinforcement and the cutting speed and tool feed govern the maximum temperature level and heat dissipation during machining. Higher temperatures reduce the matrix stability, leading to stress concentration to matrix smearing, or material loss.

The type of applied lubrication during machining can also influence and facilitate the machining of thermoset reinforced composites. The study carried out by Iskandar et al.[78] verified that Minimum Quantity Lubrication (MQL) application for milling reinforced laminates reduced flank wear by 30%.

6. Influence of thermal properties on PPS processing

The knowledge of the thermal properties of thermoplastics is essential, as it aims to establish the best processing conditions and know the parameters that influence the final properties of the material.

In the study by Batista et al.[79], the influence of the cooling rate on the degree of crystallinity (Xc) of PPS/CF composites was verified. The authors evaluate the Xc of 6 laminates, made by hot compression molding, obtained under the same heating parameters (ambient temperature ~25 °C to 315 °C) and with three different cooling rates ((1) cooling natural (or free cooling), (2) slow (1 °C/min) and (3) fast (10 °C/min)). According to the authors, DSC analyzes have shown that slower cooling creates higher Xc values (free cooling (61.9 ± 1.9) %, slow (58.5 ± 0.8) %, and fast (51.1 ± 1.0) %, as the polymer crystallite chains will have higher time to create more ordered regions. The authors also observed larger melting peak areas for lower cooling rates because they have higher crystalline content, hindering the melting process. Another point marked was that the slower rate had two endothermic peaks, which probably represents the fusion of crystallites and transcristallinity. This event occurs when fibers influence the crystallization in the interface region between the polymer and the fiber, hindering the growth of spherulites, forcing the longitudinal change of the crystal in the direction perpendicular to the fiber, and generating an increase in binding interfacial between fiber and the polymeric matrix. Therefore, the authors concluded that lower cooling rates favor greater crystallinity in the material and that, at lower cooling rates, CF assists crystalline nucleation.

The study carried out by Costa et al.[80] presents an interesting perspective, three PPS/CF laminates with six layers of fabrics were formed by hot compression molding after being subjected to heating by infrared radiation from room temperature to 320 °C, followed by forming at different temperatures (100 °C, 170 °C, and 210°C). The authors reported that 170 °C was the temperature recommended by the manufacturer. In contrast, the two other temperatures served as a basis for the study to understand material behavior in different situations. The authors verified the crystallinity in the three laminates in three different regions. Batista et al.[79] confirmed these results because the material when taken to conformation, at 320 °C and coming into contact with a colder mold, its cooling rate is higher. Therefore, its crystallinity will be lower for the three regions studied in each laminate. The results attest to the explanations given, for the three regions of each laminate, the crystallization values obtained are, mold at 100 °C against the metallic region 14%, against the rubber region 13.3% and median region 20.9%; for mold at 170°C, 18.5%, 20.2%, and 24.2%; mold at 210°C, 21.2%, 20.3%, and 23.1%, respectively, indicating that the cooling rate is inversely proportional to the crystallinity obtained. Taketa et al.[81] also observed similar results in their investigations.

Even in a study conducted by Geng et al.[82] that processed PPS through a 3D printer, it has been proven that the cooling rate is also linked to crystallinity. As a comparative option of techniques, in the study carried out by Furushima et al.[83], another equipment for crystallinity analysis was used, the Fast Scanning Calorimetry (FSC) or Hyper DSC, as the DSC has limitations regarding the scan rate, and thus it is possible to apply a slower temperature scan rate, being able to verify the structural changes of metastable crystals. Furthermore, with the FSC, it is possible to overcome these limitations and investigate the kinetics above without undesired crystallization. Even though it is more profound,
this analysis follows the same line as previous studies regarding the cooling rate of crystallinity.

Batista et al.[83] performed tests with the same cooling ranges Costa et al.[80], but with the uniform temperature distribution mold, and they obtained the same conclusions. It is essential to mention the cold crystallization curve, which appears in thermal analyses of thermoplastic polymers before the melting temperature. This event occurs when a high cooling rate is used in the composite manufacturing process. When the same composite is heated above the Tg of the matrix, the polymer chains gain mobility and begin to organize themselves. Therefore, when the cooling occurs quickly, the chains become more disordered, generating a partial amorphization in the matrix. This phenomenon can be observed in DSC analysis in the first heating, as a history of insufficient processing. To remove this history, it is necessary to submit the material to the heating and cooling cycle because, after the first heating, the amorphous chains start to move. When cooled with suitable parameters, they begin to reorganize and generate a greater degree of crystallinity, and then in the subsequent warming, this record (cold crystallization) will no longer exist.

In the study carried out by Chukov et al.[84], the authors demonstrate these characteristics, presenting DSC analyses with neat and previously unprocessed material, with only one endothermic peak. Two endothermic peaks appear only on the first heating for PPS/CF composites, which were already processed. Soon after the material is cooled to 10 °C/min, second heating is done, and cold crystallization no longer appears, reporting that the material was processed with the best parameters.

In the case of the PPS matrix reinforced by GF (PPS/GF), it is possible to verify the exact characteristics of change in the structure of the material as observed with CF reinforcement, mentioned above, as presented in the studies of Wang et al.[85]. These authors give information on the crystallization and fusion behavior of PPS/GF. The survey carried out by Zuo et al.[86] also proposes an analysis of the material, making a comparison between PPS/GF with and without thermal aging. The results point to what was previously described, until a specific time of aging, the crystallinity is increased, after a certain period, the crystallinity starts to decay, the virgin material has 44.2% crystallinity, with 20 h aging 45%, 96 h 55.8% (highest value), 144 h 52.9% and 1080 h 36.6%. Another study related to PPS/GF composites was developed by Zhao et al.[53]. However, the authors used a very high content of GF and the results show the exact characteristics of transcristallinity.

Batista et al.[87] experimented to understand the behavior of the crystallinity of PPS/CF composites when exposed to three different types of conditioning (hydrothermal, salt spray, and condensation/ultraviolet) and with three cooling systems (slow, fast). The composites were dried in an oven at 60 °C, and at each weighing, the samples were dried with a paper towel to remove surface water residue. During hydrothermal conditioning, the samples were exposed to 90% relative humidity at 80 °C for eight weeks, the salt fog was made in a salt spray chamber, and the samples were exposed to a spray of an aqueous solution of 5 wt% NaCl at 35 °C for three weeks. UV/condensation conditioning was performed in an accelerated weathering tester with ocular solar irradiance control for 900 h, using ASTM G 154 standard[88]. The authors observed that the hydrothermal conditioning showed a 17% increase in crystallinity. The polymer chains could move and reorder to form new crystal structures by remaining at a higher temperature during the process. However, the results showed that the higher the crystalline content, the lower the water penetration, with little difference. In UV conditioning/condensation, a process called chemi-crystallization occurred due to the amorphous chains being broken by UV radiation and gaining mobility to form new crystals. The salt spray conditioning caused salt crystals to start on the sides of the material, indicating that NaCl probably migrated from the inside to the outside of the structure and caused some carbon strands to come out, following this process of salt migration. Samples with higher amorphous contents showed a higher amount of salt.

In another study, Batista et al.[89] investigated, through the techniques of immersion in water and ultraviolet radiation (UV) climate chamber, the influence of temperature, humidity, and UV radiation on PPS/CF composites. Hot compression molding produced the composites in a temperature range from 280 °C to 290 °C. The artificial photodegradation process was carried out according to ASTM G 154[88], where the samples were submitted to the aging process for periods of 200, 600, and 1200 h. The moisture absorption and diffusion behavior were analyzed with the immersion of the material in water and periodic weighing. The analysis with UV radiation showed an improvement in the compression effort for short periods of exposure, which can be explained by the stiffening caused by crosslinking through the action of UV, temperature, and humidity. For more extended periods of exposure, there was deterioration in mechanical properties, which can be explained by photolysis and photo-oxidation and the embrittlement process caused by extensive crosslinking. DMA and compression tests show an increase in the Tg as the exposure period increases, indicating reduced mobility and narrowing of networks. Since temperature activates the diffusion process, it was found that water absorption increases with temperature.

At the same time, Faria et al.[90] evaluated the influence of hydrothermal conditioning on the viscoelastic properties of PPS/CF laminates. Plasticization of the polymer matrix is one of the most pronounced effects of moisture absorption, reducing the glass transition temperature. Then, hydrothermal conditioning was carried out, according to ASTM D 5229/D 5229-04 standard, and the control of the moisture gain of the sample was carried out with weekly weighings. DMA analysis showed that the integrity of the laminates was not affected by moisture absorption. However, the glass transition temperature and dissipation energies increased after conditioning in the climatic chamber. Thus, the crosslinking effect appears caused by the presence of water molecules, which compete with the plasticizing impact in the system, increasing the glass transition temperature and, consequently, expanding its service temperature.

7. Recycling

From the growing concern with the environment, the need to reduce CO₂ emissions, and the new legislation
Feasible methods of recycling PPS-based materials. The study of Bruijn and van Hattum[51] was developed at the TPRC in the Netherlands, using the PPS/CF waste recycling methodology proposed by the TPRC. According to the study, the authors demonstrated a viable and novel recycling route for thermoplastic composites (PPS/CF). They processed an integrally-stiffened access panel door for a rotorcraft, selected for detail design, testing, and current flight testing.

One of the studies carried out by Vincent et al.[99] was the mechanical recycling of PPS/CF composites. The authors ground the PPS/CF residues into flakes and used a low-shear blend to homogenize, then extrusion and hot compression molding using a press. After this process, the study aimed to characterize the recycled material heterogeneity and compared it with the commercially available material that is compression molded by long fiber thermoplastics (LFTs) that have been on the market for decades. The authors found that the recycling process was efficient in homogenizing the matrix and fibers. The results were similar to those of LFTs for fiber orientation, percolation, variation of the fiber fraction, and fiber friction. Furthermore, the authors were able to obtain ribbed plates using this methodology. According to the authors, industrial applications of this recycling route will benefit from this similarity, increasing confidence in the combination of material and process.

Another process for recycling PPS was developed by Hao Wang et al.[100]. The authors recycled PPS filters used mainly in the thermal energy and metallurgical industries and are replaced frequently, generating a large volume of waste. The process consisted of collecting the filters and removing residues that were adhered to the filter. Afterward, the PPS filters were ground until the formation of a fine powder. Then they were incorporated and homogenized with epoxy resin to act as a flame retardant. The authors found that using this composite (recycled PPS/epoxy resin) as flame retardants resulted in a reduction in CO and CO₂ emissions and, consequently, reduced the smoke’s toxicity compared to the burning epoxy/CF composites. Furthermore, the authors observed that the presence of PPS contributed to the formation of a layer of carbon on the surface of the composite, acting like a protective layer, blocking heat.

However, if mechanical and thermal recycling of PPS-based materials is not feasible, Li et al.[101] demonstrate a biodegradation regarding the disposal of materials, European policies[91,92] of solid waste, which determine the recycling of all plastic components of end-of-life vehicles and the treatment of waste to avoid negative impact to the environment and human health, led industries to increase investments in reuse and recycling of materials[93].

The recycling of thermoplastics is favored over thermosets, mainly due to their greater efficiency in the process. In the presence of temperature, they soften and can be reprocessed in different geometries[33]. The recycling processes can be divided into primary, being carried out only the polymer reprocessing, secondary or mechanical recycling, tertiary or chemical recycling, and quaternary being the energy recycling[94].

The most common process for recycling PPS is the mechanical process, in which the material is milled, homogenized, and reprocessed. Another thermal recycling option, depolymerization, occurs at high temperatures, around 550 °C, from splitting the sulphydryl groups in the main chain, decomposing mainly into the monomer, benzenethiol. However, thermal recycling can be economically viable with the intention of CF recovery, for example, from PPS/CF composites[95,96,97]. Chemical recycling of PPS is not carried out due to its chemical resistance and insolubility in organic solvents[98]. Figure 4 presents the most viable recycling processes for PPS-based materials.

PPS is also widely used for GF and CF reinforcements, mainly in the aerospace and automobile industries. And with the growing use of PPS/CF composites, the volume of waste from the processing steps is also increasing[99].

One of the methodologies related to recycling PPS composites with CF was developed by ThermoPlastic Composites Research Center (TPRC), a consortium of industry and academic members with industrial composites located in the Netherlands. This research center used a methodology based on the mechanical recycling of thermoplastic composites that starts with comminution and then reprocessing. Initially, the PPS/CF composites are ground into large flakes so that the fibers maintain a long length, and then this material is reprocessed. It is carried out by mixing the crushed material with a virgin matrix, followed by melting, which has the same purpose of maintaining the fiber length. The final step consists of reprocessing via hot compression molding. The process consisted of collecting the filters and removing residues that were adhered to the filter. Afterward, the PPS filters were ground until the formation of a fine powder. Then they were incorporated and homogenized with epoxy resin to act as a flame retardant. The authors found that using this composite (recycled PPS/epoxy resin) as flame retardants resulted in a reduction in CO and CO₂ emissions and, consequently, reduced the smoke’s toxicity compared to the burning epoxy/CF composites. Furthermore, the authors observed that the presence of PPS contributed to the formation of a layer of carbon on the surface of the composite, acting like a protective layer, blocking heat.

However, if mechanical and thermal recycling of PPS-based materials is not feasible, Li et al.[101] demonstrate a biodegradation...
methodology by *Pseudomonas sp.* for PPS, the most difficult kind of plastic to be degraded due to the excellent physical and chemical stability of this thermoplastic. The study presented by the authors shows the feasibility of biodegradation of PPS beads by *Pseudomonas sp.*, verifying that the process can be carried out in 10 days. According to the authors, the developed method can be used to verify the biodegradation efficiencies of different kinds of plastics within a shorter reaction time, but also provides the possibility to be used for screening and identifying new bacteria strains of various types of plastics.

8. Conclusion

PPS-based materials have been used in the aerospace, automotive, and wind energy industries. PPS reinforced with FG or CF-based components presents a high strength-to-weight ratio, leading to lighter structures and components with good mechanical resistance.

Due to its high melting temperature, the processing temperature is an obstacle in manufacturing PPS-based components. Its process demands equipment that operates in higher temperatures, leading to increased production costs. PPS fiber-reinforced composites are usually produced by compression molding and lamination of semi-pregs and mats with fiber fabric impregnated with the polymer matrix. FDM process has been used recently for printing pieces with PPS filaments.

In addition, the PPS processing parameters need to be controlled, as the cooling rate directly affects the material’s crystallinity, where higher cooling rates lead to less crystallinity. Higher polymer crystallinity results in more brittle components, affecting the performance of the PPS-based material parts.

The high hardness of the reinforcement materials, high strength, good abrasive resistance, and thermal conductivity make PPS-based composites difficult to machine material. Drilling and milling are the most used machining process, and the major problem is the occurrence of delamination. Delamination occurs when the forces involved in the machining process exceed a critical value, which serves as a point of attention in developing strategies to avoid this phenomenon. The works analyzed exposed strategies to minimize the delamination related to the geometry of cutting tools, different materials for cutting tools, and the adequacy of cutting parameters, mainly the use of high cutting speed and low feeds.

One of the significant advantages of applying PPS in the industry is that its residues can be recycled mechanically or thermally. In this way, it is possible to manage and develop technologies that aim at the minimum destination of waste to landfills and incineration, contributing to preserving the environment and natural resources.

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