

BASIC ASPECTS OF COMPOSITES BASED ON EPOXY RESIN OR UNSATURATED POLYESTER REINFORCED WITH FIBERS DERIVED FROM ANCHORAGE CABLES

ASPECTOS BÁSICOS SOBRE COMPÓSITOS À BASE DE RESINA EPOXI OU DE POLIÉSTER INSATURADOS E REFORÇADOS POR FIBRAS ORIUNDAS DE CABOS DE ANCORAGEM

ASPECTOS BÁSICOS SOBRE COMPOSITES A BASE DE RESINA EPOXI O DE POLIÉSTER INSATURADO Y REFORZADOS CON FIBRAS PROVENIENTES DE CABLES DE ANCLAJE



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ABSTRACT

The reuse of waste materials for the creation of new products is fully aligned with sustainability principles and is supported by two essential premises: reducing the volume of potentially polluting waste in disposal areas and decreasing the reliance on virgin raw materials. In this context, waste containing synthetic polymers emerges as a particularly relevant candidate for repurposing, given its high potential for environmental impact when improperly discarded. Among these materials, synthetic cables—widely used in the anchoring of floating units—represent, at the end of their service life, a strategic source of high-performance fibers. When reintegrated into production processes, these fibers can act as reinforcement in thermoset-based composites, improving properties such as mechanical strength, thermal stability, and durability in harsh environments. Accordingly, this text presents the fundamentals related to the development of composites based on epoxy and unsaturated polyester resins reinforced with synthetic polyester fibers derived from post-industrial anchoring cables, which may have advanced applications in sectors such as naval structures, automotive components, structural panels, and protection systems.

Keywords: Cable Reuse. Polymers. Composites.

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RESUMO

A reutilização de resíduos para a criação de novos materiais está plenamente alinhada aos princípios da sustentabilidade, amparada por duas premissas essenciais: a redução do volume de resíduos potencialmente poluentes em áreas de descarte e a diminuição da dependência de matérias-primas virgens. Nesse contexto, resíduos contendo polímeros sintéticos despontam como candidatos particularmente relevantes para reaproveitamento, dado seu elevado potencial de impacto ambiental quando descartados de forma inadequada. Entre esses materiais, os cabos sintéticos — amplamente empregados na ancoragem de unidades flutuantes — constituem, ao final de sua vida útil, uma fonte estratégica de fibras de alto desempenho. Quando reintegradas aos processos produtivos, essas fibras podem atuar como reforço em compósitos à base de termofixos, ampliando propriedades como resistência mecânica, estabilidade térmica e durabilidade em ambientes agressivos. Dessa forma, este texto apresenta os fundamentos relacionados ao desenvolvimento de compósitos à base de resinas epóxi e poliéster insaturado reforçados com fibras sintéticas de poliéster provenientes de cabos de ancoragem pós-industriais, que podem ter aplicações avançadas em setores como estruturas navais, componentes automotivos, painéis estruturais e sistemas de proteção.

Palavras-chave: Reutilização de Cabos. Polímeros. Compósitos.

RESUMEN

La reutilización de residuos para la creación de nuevos materiales está plenamente alineada con los principios de la sostenibilidad, sustentada en dos premisas esenciales: la reducción del volumen de residuos potencialmente contaminantes en áreas de descarte y la disminución de la dependencia de materias primas vírgenes. En este contexto, los residuos que contienen polímeros sintéticos surgen como candidatos particularmente relevantes para su reaprovechamiento, dado su elevado potencial de impacto ambiental cuando son desechados de forma inadecuada. Entre estos materiales, los cables sintéticos — ampliamente empleados en la anclaje de unidades flotantes— constituyen, al final de su vida útil, una fuente estratégica de fibras de alto rendimiento. Cuando se reintegran en los procesos productivos, estas fibras pueden actuar como refuerzo en composites a base de termoestables, mejorando propiedades como la resistencia mecánica, la estabilidad térmica y la durabilidad en ambientes agresivos. De este modo, este texto presenta los fundamentos relacionados con el desarrollo de composites a base de resinas epoxi y poliéster insaturado reforzados con fibras sintéticas de poliéster provenientes de cables de anclaje posindustriales, los cuales pueden tener aplicaciones avanzadas en sectores como estructuras navales, componentes automotrices, paneles estructurales y sistemas de protección.

Palabras clave: Reutilización de Cables. Polímeros. Composites.



1 INTRODUCTION

Composite materials are a class of materials classified as advanced, consisting of the combination of a matrix and another phase called reinforcement, which usually comes in the form of fibers, particles or nanostructures. The superior properties of composites come from a synergy between their individual components, so that they can present greater mechanical strength, rigidity, thermal stability and durability, among other characteristics of interest. These advantages make composites fundamental for various applications in different productive sectors, such as aeronautics, automotive, naval, sports, biomedical, energy, among others (CAMPBELL, 2010).

In the case of polymeric composites, in which at least one component is a polymer, their application possibilities are related to the possibilities of customization for different functions, giving them versatility (SABA et al., 2016). Another interesting feature of these composites is related to the reuse of polymers, since several polymers can be recycled to form composites.

The way in which the polymer can contribute to the properties of the composite depends on its composition and shape, and there are several possibilities for reuse, such as anchor cables. Anchor cables are structural elements used to transfer tensile forces between a structure and an anchoring system, such as the cables that fix platforms at sea. These types of cable are used in large quantities in terms of length and, thinking they have a useful life, provide a large amount of post-use waste.

Based on these ideas, this text presents basic aspects about matrix-based composites of epoxy or polyester resins reinforced with anchor rope fibers, in the context of the reuse of used anchor lines.

1.1 COMPOSITE MATERIALS

Composites are multiphase materials whose mechanical performances and properties are designed to be superior to those of the constituent materials acting independently, Figure 1. The ASTM D3878-20b (2020) standard conceptualizes it as a material consisting of two or more materials, insoluble in each other, which, when combined, form a useful engineering material with properties not possessed by its constituents (ASTM International, 2020).

For a material to qualify as a composite, some requirements must be met, for example, the constituent materials must have proportions above 5%; the reinforcement and the die must have different properties, acting independently, and; The properties of the composite material will be different from the properties of the reinforcement and the matrix (Daniel; Ishai, 2006).

Figure 1

Representation of composite constitution



Source: The authors, 2024.

According to the ASTM D3878-20b (2020) standard, which makes a generic definition of composite material terms, including terms of commercial importance, it conceptualizes it as a material consisting of two or more materials, insoluble in each other, which, when combined, form a useful engineering material that has properties not possessed by its constituents.

The performance of composites is linked to their individual properties, both of the matrix phase and the dispersed phase, as well as the nature of the matrix/reinforcement interface and the geometry of the dispersed phase. Therefore, the engineering involved in composite construction is diverse, and consequently will influence the final properties of the composite (CANEVAROLO JR., 2006; CANEVAROLO; CANEVAROLO, 2019; DANIEL; ISHAI, 2006; LI et al., 2021; SWAMI; DABADE, 2021).

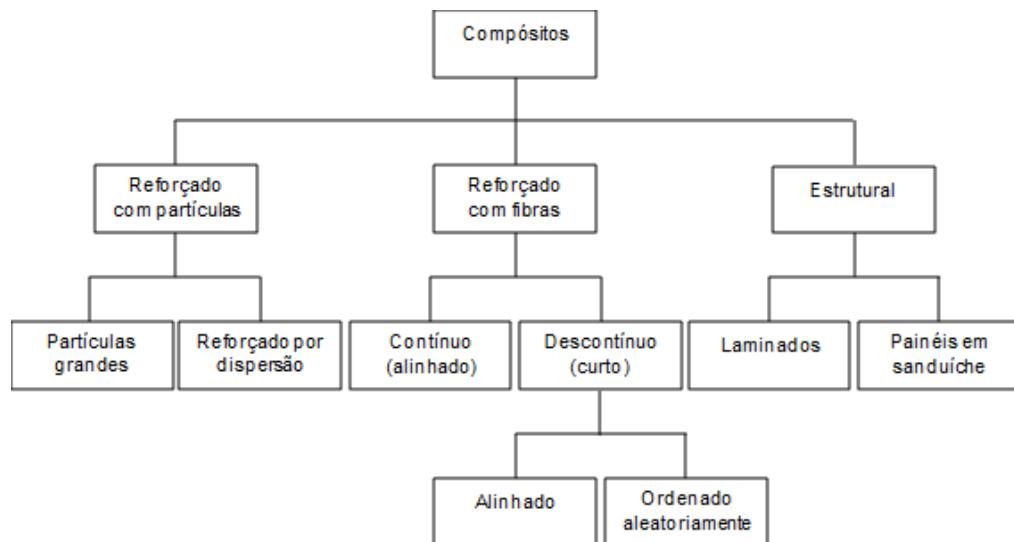
Specifically in the case of fiber-reinforced composites, the adhesion process between these materials is one of the essential criteria to ensure the efficiency of the composites obtained. This type of interaction can allow for better load transfer between the constituent materials of the composites. The larger the contact area between the materials, the better the adhesion between them, regardless of whether it is of a physical, chemical or physicochemical nature. Due to this, the selection of resin and reinforcement will depend on the requirements of the product that will be developed and the conditions to which these materials will be subjected (ZORZANELLI, 2019).

Generally, fiber-reinforced composites are prepared by impregnating the continuously and evenly distributed fiber into a resin, and the matrix that is commonly a brittle resin, can then be effectively strengthened with the high-strength fiber after curing. However, there are several ways to build composites, through the most varied types of reinforcements in addition to fibers. The most commonly used method to classify composites is by the type of reinforcement inserted in the matrix. In the organizational chart, suggested by (CALLISTER;

RETHWISCH, 2014), composites can be produced and classified according to the type of reinforcement, as shown in a schematized way in Figure 2.

Figure 2

Classification of composites according to the type of reinforcement



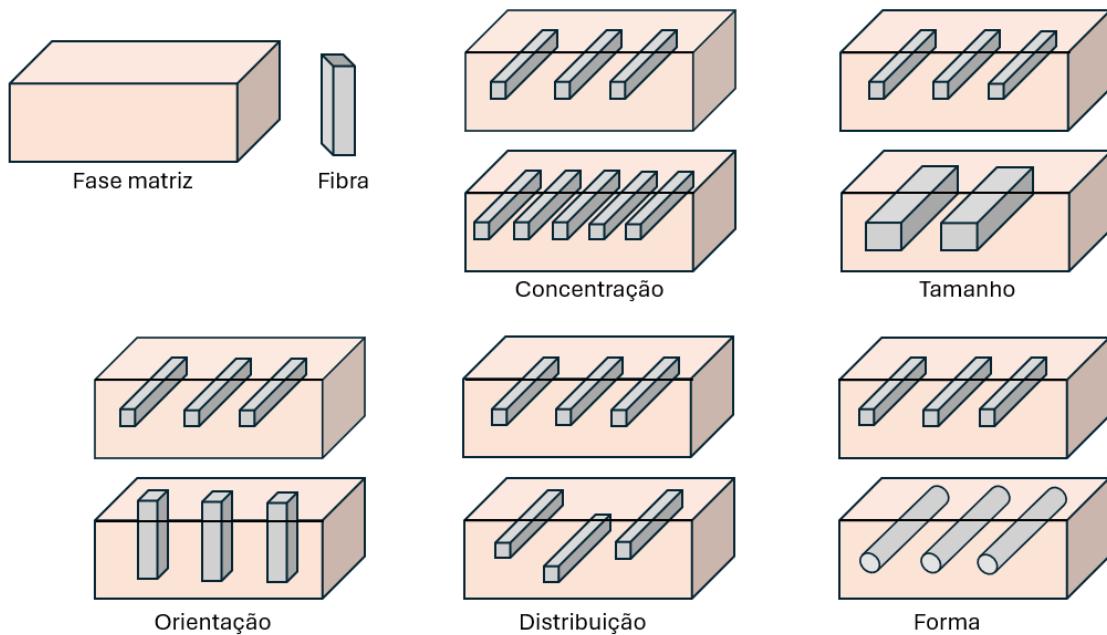
Source: The authors, 2025.

The architectures of the fibers arranged in composites have an impact on the mechanical properties of these materials. As shown in the scheme by Ventura (2009), presented in Figure 3, architecture, geometry and fiber constitution have a significant impact on the properties of the composite.

The resins most commonly used in the production of polymeric matrix composites are in descending order: epoxy, polyester and vinyl ester. The differences between epoxy, vinyl ester and polyester resins are wide, in terms of cost, polyester resin is much more affordable. But if the priority is mechanical properties, epoxy resin and vinyl ester are far superior in the requirements for resistance to force impacts, wear, corrosion, and chemical or environmental degradation (BENNETT-HUNTLEY, 2014; DEVARAJU; ALAGAR, 2019; MISKOLCZI, 2013; PUTTEGOWDA et al., 2018).

Figure 3

Simplified scheme of possible composite architectures containing the same matrices and fibers used as reinforcement, but different orientations, sizes, distribution, concentration and fiber shapes



Source: The authors, 2024.

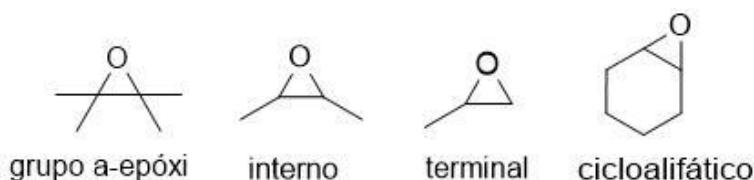
The curing process of polymeric systems is conditioned by the external temperature, with the curing of epoxy being the most critical. As far as polyester resin is concerned, the curing time will depend on the type of catalyst. Hardener, which is the type of curing agent for epoxy resin, uses a ratio ranging from 5 to 46% by weight during the curing process. The state of the resin can be affected by environmental factors such as ambient temperature and humidity (ARTUR S. C. et al., 2009; KIM; NUTT, 2020; RODRIGUES, 1992). Regarding polyester resin, the catalyst is the curing agent, which can vary from 1 to 4% to the total weight of polyester resin (SILAEX 2021). However, the use of the catalyst should be done with caution due to the exothermic process.

1.2 EPOXY RESIN AND ITS RESPECTIVE CURING AGENTS

Epoxy resin is composed of molecules that contain more than one alpha-epoxy group, and can be internally, terminally or in cyclic structures as can be seen in the structures in Figure 4. The epoxies resins used in composites are mainly glycidic ether and amines.

Figure 4

Representation of the types of epoxy structures

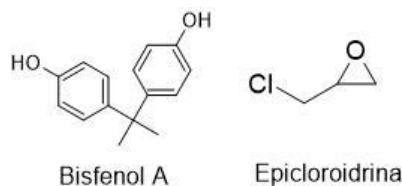


The three-membered ring that constitutes the structure of epoxy can be called ethylene oxide, oxirane, ethoxide group, and epoxide. The term glycidyl is used to characterize a terminal epoxide group.

Epoxy resins typically consist of two components that must be mixed together just before they can be applied. One of the components is a liquid prepolymer and the second, a curing agent, which reacts with the polymer causing it to solidify. Most epoxy resins are based on a prepolymer consisting of bisphenol A and epichlorohydrin (DGEBA-bisphenol A diglycidyl ether), as shown in Figure 5.

Figure 5

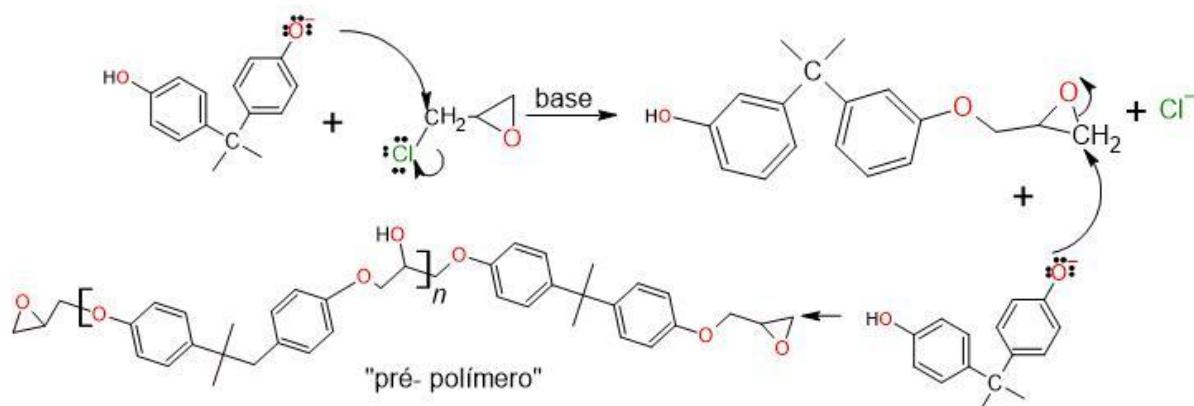
Bisphenol A and epichlorohydrin molecules used in epoxy synthesis



Under treatment with a base under carefully controlled conditions, bisphenol A is converted to its anion, which acts as a nucleophile in an S_N2 reaction with epichlorohydrin. Each epichlorohydrin molecule can react with two bisphenol A molecules, one of them by the S_N2 displacement of the chloride ion and the other by the opening of the epoxy ring. At the same time, each bisphenol molecule can react with two epichloroidrin molecules, leading to the formation of a long polymer chain. Each end of the chain in the polymer has a non-reactive epoxy group and each chain has numerous groups of secondary alcohols separated regularly along its length. Figure 6 illustrates this mechanism via S_N2 .

Figure 6

Reaction mechanism via $Sn2$ for the formation of epoxy "pre-polymer" - DGEBPA



When epoxy is to be used, a curing agent, usually a tertiary amine R_3N , is added causing the "prepolymer" chains to bind, Figure 6. This cross-linking of the chain is a reaction of opening the epoxide ring catalyzed by the base of a hydroxyl group located in the middle of the chain with an epoxide group at the end of another chain. The result of this cross-linking is the formation of a system of interpenetrating chains that has very high resistance to deformation and chemical resistance (MCMURRY, 2010; RODRIGUES, 1992).

Epoxy resins can be cured with a range of curing agents, also called hardeners, including Lewis acids, depending on the curing and product needs. Curing agents can be catalytic or co-reactive. A catalytic curing agent acts as the initiator of the epoxy resin homopolymerization, while the co-reactive curing agent acts as a co-monomer in the homopolymerization process. This agent can react with the hanging groups in the resin structure via cationic mechanism (RODRIGUES, 1992; ROMÃO et al., 2003).

The curing agent must be chosen carefully as well as the temperature, because it will affect the type of chemical reaction, shelf life of the mixture and final properties of the material (BAGHERPOUR, 2012; ROMÃO et al., 2003). Composites made with epoxy resin of vegetable origin reinforced with jute fiber and carbon fiber were studied by Niedermann et al. (2015), using different curing agents, verified by DMA analysis, that the type of curing agent directly interfered with the storage module (E'), both for composites reinforced with jute fiber and for those reinforced with carbon fiber (GANESH GUPTA K et al., 2021; GUPTA; SRIVASTAVA, 2014; NIEDERMANN; SZEBÉNYI; TOLDY, 2015).

The material properties and curing time can be formulated according to the required application, as the type of curing agent and the resin/hardener stoichiometric ratio influence the mechanical properties of the composite (NIEDERMANN; SZEBÉNYI; TOLDY, 2015; ROMÃO et al., 2003). The high viscosity of this resin limits its use in certain processes, such as molding, filament winding and manual preparation. It is also known that exposure to room

temperature conditions for long periods can increase the degree of curing and increase the viscosity of the resin, factors that can prevent the total infiltration of the fiber bed during curing (BOSZE et al., 2006; KIM; NUTT, 2020; LORANDI et al., 2016).

Among the most commonly used curing agents are amines and anhydrides, but polymercaptans, modified amines or polyaminoamides are also popular on the market, and have high reactivity and chemical resistance. The main known cross-linking promoters in the market will be presented in Table 1 (SILAEX, 2021).

Table 1

Cross-linking promoting agents used in the crosslinking of epoxy resin

| Healing agent | Description |
|------------------------------|---|
| Aliphatic Amines | Low viscosity liquid. Small, volatile molecules that react with free hydrogen radicals. Fast-curing at room temperature. Good chemical resistance, easy homogenization with resin. Disadvantages: High critical mixing ratio. Mist defect or superficial "blush" oiliness. High toxicity. Example: ethylene amine (EDA), diethylene triamine (DETA). |
| Amine adducts | They are the result of mixing epoxy resin or reactive diluent with an amine excess. Larger and less volatile chain production. Less critical mixing ratio. Fast curing. Medium toxicity. |
| Polyamides | Obtained by dimerization reaction of aliphatic amines such as diethylenetriamine (DETA) with diacids or long-chain fatty acids, resulting in high molar mass polymers ranging from a viscous liquid to a solid. The non-critical mixing ratio, long working time and good water resistance. Disadvantages: High viscosity, low thermal resistance, low chemical resistance, intermediate cost, long curing time, and dark colors. |
| Cycloaliphatic Amines | These agents are less volatile due to the presence of cyclic rings in their structure. Light stability, low reactivity and great color retention. Low viscosity, good chemical resistance, easy homogenization with the resin, little susceptible to blush. Disadvantages: High cost, crystallization and medium thermal resistance. Example: Isophorondiamine (IPDA) with the use of reaction accelerators. |
| Anhydrides | Anhydrides are used in a hot curing system. They have a long latency time when incorporated into the resin and provide excellent thermal resistance. Long working time, low viscosity, easy to mix with resin, high gloss without blush. Disadvantages: High cost, dark colors. Example: hexahydrophthalic anhydride (HHPA), chlorenic anhydride (HET). |
| Polyamimides | Polyamimides come from a reaction of polyamide with stoichiometric amine excess. This results in a product that will have intermediate characteristics |

| | |
|--|--|
| | between a polyamide and an aliphatic amine. Suitable in cases where greater tenacity and adhesiveness are desired with better fluidity and greater reactivity. |
| Aromatic Amines | Aromatic amines are usually solids that need to be melted and hot mixed with the resin and then cured at high temperatures. Due to this process, large amounts of corrosive and toxic amino vapors are emitted. When cured, this system exhibits good chemical and electrical resistance, excellent hydrolysis resistance, and good thermal resistance. Examples: p-p'methylene dianiline (MDA), metaphenylene diamine (MPDA), diaminodiphenyl sulfone (DADS). |
| Polysulfides | Polysulfides are rarely used products, since they have high toxicity, difficult acquisition and high price. Its main characteristics are flexibility, impermeability and good adhesion to glass, but they can be replaced by other hardeners that confer a similar characteristic with less toxicity. |
| Polyoxypropylamine or polyetheramines | Polyoxypropylamine are hardening agents that combine the flexibility and adhesion of polyamides with the good color retention and light stability and transparency of cycloaliphatic amines. However, they have low reactivity and high cost. |
| Polymercaptans | Polymercaptans are generally used where rapid curing is required, without much need for chemical and thermal resistance. It is widely used in quick-drying doughs for home use. (e.g.: Ultra-fast Durepoxy). They have a high odor and high toxicity. |
| Dicyandiamide and boron trifluoride | Dicyandiamide and boron trifluoride are solid hardeners used in special systems for single-component compounds for heat curing, since they have a long latency period in storage. |

2 UNSATURATED POLYESTER RESIN AND ITS STRUCTURAL VARIATIONS

Unsaturated polyester resins are one of the most widely used thermoset polymers, with a wide range of applications, due to their low cost, versatility, and ability to undergo various post-polymerization reactions. The synthesis of unsaturated polyester resin is achieved by a bulk or azeotropic polycondensation reaction (KOVAČEVIĆ et al., 2017).

Unsaturated polyester resin-based compounds are commonly used in marine and automotive structures due to their favorable water resistance and mechanical properties (BENNETT-HUNTLEY, 2014; GOBIKANNAN et al., 2021; KANDOLA et al., 2020).

Unsaturated polyesters have double covalent bonds between carbon atoms, which can be joined by cross-links to form thermosets. In combinations with fibres, these polyesters can be cross-linked to form high-strength reinforced composite materials (SMITH; HASHEMI, 2012).

Unsaturated polyesters are complex esters formed by the reaction of a dialcohol (usually ethylene glycol) and an anhydride or dibasic acid, with the release of a water

molecule. Polyesters and polyamides occur by the mechanism of polymerization in stages, this is because each bond in the polymer is formed independently of the others. It is a reaction that occurs by the mechanism of nucleophilic substitution of the acyl group, catalyzed by an acid, of a carboxyl acid.

Unsaturated polyester is produced from reagents containing unsaturations, usually by maleic acid or anhydride, as well as by its isomer fumaric acid.

According to Embrapol, for the formation of three-dimensional networks, the unsaturated polyester that is dissolved in styrene must react in the presence of a catalyst, where the various molecules of styrene monomers, through their double bonds, unite with the double bonds of the polyester base, giving rise to a compound that does not undergo fusion, infusible.

In the case of applications that require high mechanical stress and nobler rheological properties, such as the fibers used in anchor cables, it is necessary to perform the polycondensation step in the solid state, which produces an increase in the molar mass of the polymer, crystallinity, intrinsic viscosity and consequently influences the final cost in the resin (MIRANDA, 2014).

The mechanical and thermal properties of unsaturated polyester resin products are relatively poor, which limit their use in advanced composites. The dynamic-mechanical, thermal and flame resistance properties of these resins can be improved by adding various types of organic/inorganic reinforcements, such as glass fibers, inorganic minerals, natural and synthetic polymers among others (KOVAČEVIĆ et al., 2017).

Unsaturated polyester resins in their soluble phase, usually in styrene, is a liquid resin system that can be catalyzed at room temperature or with a small temperature rise to become thermostable, that is, without the need for complex catalyst systems. The double bonds are broken by the action of a catalyst that can be an organic peroxide, but the polymerization reaction can also be activated by heat and radiation and thus promote the reaction between the molecules, to react again with each other, giving rise to a three-dimensional polymer with thermostable characteristics and, therefore, infusible and irreversible.

According to information extracted from Embrapol — an industry that engaged in the manufacture of orthophthalic and isophthalic unsaturated polyester — the structure of unsaturated polyester is generally composed of four basic components: saturated acid (25-35% by weight), unsaturated acid (10-20% by weight), glycols (15-25% by weight) and monomer (30-45% by weight).

The chemical resistance of a polyester is mainly linked to its molar mass, acid value, number of groups formed and density of cross-links. These acids determine the degree of

spacing or contraction of the unsaturated acid molecules along the chain and determine the type of resin (EMBRAPOL, 2022).

The polyester resins found in the market are: (i) orthophthalic, with lower cost for basic non-noble use; (ii) isophthalic, which has better mechanical, chemical and thermal properties than the previous ones; (iii) PET, which are ethylene terephthalate resins, and have physical strengths slightly higher than orthophthalic and low resistance to ultraviolet radiation and (iv) bisphenolic.

The orthophthalic resins in their composition are processed with modifying acids, phthalic or its anhydride. Its mechanical and chemical properties are inferior to the others, due to the difficulty of obtaining polymers with high molar mass. Phthalic anhydride has a strong tendency to regenerate from phthalic acid ester media (reversible reaction), a fact that increases the presence of species with low molar mass, highly sensitive to chemical attack.

Isophthalic resin does not form cyclic anhydride, does not suffer from regeneration disadvantage, as in the case of orthophthalic resins, and consequently, polyesters with high molar mass can be obtained, that is, with longer chains. Such chains give the product greater mechanical resistance as they absorb impacts better. Consequently, they become polymers with greater chemical and thermal resistance. Generally, to improve the hydrolysis resistance properties of polyester, glycol is replaced by neopentyl glycol, because during the manufacturing process of polyester resin, there is an accumulation of residual glycols, in the case of neopentyl glycol, there is a low content of free hydroxyls, which disfavor the hydrolysis of polyester and its consequent degradation; These resins are more suitable in situations where the polymer will be continuously exposed to moisture (BRAUN et al., 2013; BRO; MENDES, 2004; ODIAN, 2004).

Bisphenolic resin comes from the reaction of propylene oxide and bisphenol A, resulting in propoxylated bisphenol A that reacts with unsaturated acid, which gives the resin low hydroxyl content and thus disfavors hydrolysis. Because it has a more closed structure due to the presence of aromatic rings, it makes the polymer more resistant to temperature and chemical attacks (BRAUN et al., 2013; DEVARAJU; ALAGAR, 2019; MIRANDA, 2014).

Regardless of the origin of the monomer, the mechanism involved in the production of PET is a pre-polymerization followed by a polycondensation, responsible for the growth of the chain, step polymerization. Depending on the monomer adopted, it can be rationalized as esterification (involving terephthalic acid) or a transesterification (involving dimethylterephthalate). The resins produced have non-noble properties to be exploited by the industry. Thus, to increase the physicochemical and mechanical properties of PET, a polymerization step is carried out in the solid state, which is carried out by heating the pellets

close to the melting point (220-230°C) in the presence of an inert gas (DANIEL; ISHAI, 2006; NISTICÒ, 2020).

The properties of polyethylene terephthalate (PET) depend directly on the grade and quality of crystallinity. The crystallization of this resin occurs over a wide temperature range. Polyethylene terephthalate samples with the same degree of crystallinity at different temperatures have diverse melting characteristics, and often exhibit multiple endothermic fusions. Polyester resin has crystalline melting temperature between 255 and 265 °C and density of 1.38 g.cm⁻³ at 25°C. (ANDRADE et al., 2021; NISTICÒ, 2020).

3 ANCHOR ROPES MADE OF POLYESTER FIBRES

The anchoring system is a set of structural elements capable of supporting a floating production storage and offloading unit (FPSO) in an equilibrium position, without the aid of propulsion. These units are exposed to the action of bad weather (wind, current and waves). The main function of the anchoring system is to restrict movements in the horizontal plane, ensuring proper positioning of the floating unit. This system consists of a set of lines, each line being composed of a fixed point on the seabed (anchor or pile) and floating elements that connect this point to the unit. The connecting elements are composed of a combination of moorings, steel cables or polymeric cables (LACERDA, 200).

Anchor cables formed by steel legs are generally used in water depths smaller than 500 meters, in catenary configuration. However, for depths greater than 500 meters, the weight and cost of these steel cables make them unfeasible to use for this purpose. As an alternative, polymeric anchor cables are used to replace steel cables, which can be: polyester, aramid, nylon and high modulus polyethylene. For each type, various grades, with varieties of properties are commercially available.

During the design of a floating platform, the anchor rope type is evaluated primarily by the Minimum Breaking Strength (MBS) property. Among other requirements in the design phase, the following stand out (WICHERS, 2013): strength of the constituent fibers; robustness and flexibility for offshore handling; long-term exposure under water for more than 20 years; have an efficient method of termination and interlacing; ability to be made into large diameters and long lengths, protective coating and particle barrier; resistance to potential mechanical damage and wear (ship deck, handling equipment, sharp edges); resistance to chemicals (oils, salts, bases, salts); heating effect and ultraviolet radiation; withstand the action of compressive forces, cyclic loads, fatigue, etc. (MIRANDA, 2014).

The properties evaluated in the manufacture of ropes and anchor cables are: rupture stress, modulus of elasticity, elongation at break, melting point, abrasion resistance, creep

resistance, etc. Among the polymeric fibers evaluated, polyester fiber is the one that best presented a balance between its properties and cost. Polyester fibers have a high melting point (~265 °C), preserving their stiffness even above 150 °C, good resistance to salt solutions, organic acids and solvents and oxidants. In addition, there is good elastic recovery capacity, resistance against ultraviolet (UV) rays, exceptional fatigue resistance. However, in ultra-deep water depths (over 2000 meters), polyester cables are no longer used, due to the high diameter required to withstand the mechanical forces requested. From 2000 meters onwards, high performance polymers (HMPE, LCP and aramids, due to their high rigidity) are required, which allow the construction of cables with smaller diameters, and consequently lower weight (AYERS; RENZI; AKSU, 2010; DAVIES et al., 2008).

The technical specifications for the construction of high-strength polyester ropes can be verified by the ISO18692 standard "Fiber ropes for offshore maintenance – polyester". Modern offshore mooring lines are constructed from multifilament strands composed of twisted fibers ranging in diameter from 10 to 50 micrometers. The properties of synthetic materials used in fiber ropes include a wide range of stress-strain ranges.

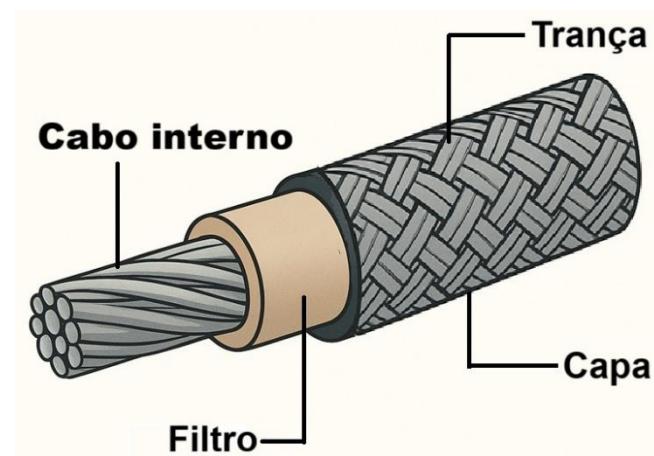
These cables are built at hierarchical levels as shown in Figure 7, and the internal cables are in turn formed by internal cable cords, which are also made of polymeric wires. The torsion angle is used for high-load applications with multiple braided assemblies surrounded by a filtering screen and protective braided jacket to prevent abrasion or damage to the internal elements of the cable (WELLER et al., 2015).

The technology of synthetic fibers, generally based on silica or resins derived from petroleum, was developed with the aim of improving the properties provided by vegetable fibers and expanding their variety of application. These fibers have greater mechanical strength and greater modulus, but their cost is high (HAACH; POITEVIN; BASTOS, 2010; LORANDI et al., 2016). The fibers used in anchor ropes are more stretched than the fibers used in the textile industries, which gives the fiber greater strength and stiffness combined with reduced stress to failure.

The mechanical properties of the fibers justify their use in cable construction, as these cables have breaking loads of up to two thousand tons and consist of many millions of fine synthetic fibers. WELLER et al. (2015) show in their work the deformational behavior of some polymers used in the manufacture of anchor cables, through stress-strain results, which is a qualitative means of comparing synthetic materials. Compared to steel, these materials have very high strength to weight (or toughness) and float almost neutrally in seawater. Toughness is obtained by integrating the area under the stress-strain curve until break. Deformations (ϵ) in seepage and breakage define the power of polymeric molecules during stretching.

Figure 7

Basic components of a polymer mooring rope



It is worth noting that the linear density is the amount of mass per unit length, this is defined by the direct titration system. Since the variable is expressed in denier or tex, the most commonly used unit is the decitex, which is the submultiple of the tex scale. Toughness is obtained by dividing the breaking strength by the titer, not considering the area of the material evaluated. The breaking force is determined by mechanical testing. Generally, the units of measurement used are the Denier (gf/den) or the Tex (mN/tex).

The deformational behavior is governed by the molecular structure of the polymer. Evaluations of viscoelasticity, relaxation, creep, and hysteresis properties are important as they provide data to predict the behavior of fibers used as anchor cord during use and response during environmental conditions, and are all dependent on the molecular structure of the polymer. The mechanical performance of polyester is strongly influenced by several parameters, such as the degree of crystallinity of the polymer (the lower the degree of crystallinity, the greater the elongation at break), the processing (orientation), and the shape (bottle, films and fibers) (MANIKANDAN et al., 2012; NISTICÒ, 2020).

The explanation of this deformation-induced phenomenon is attributable to the specific chemical structure of PET and, in particular, to the presence of aromatic rings and polar functionalities (esters) along the main chain. In detail, once the macromolecule chains are subjected to such strain-induced orientation, these functionalities are able to interact with each other, through the π - π coupling between the aromatic groups and the H-bond between the esters, and favoring a crystalline organization, with the progressive orientation of the aromatic rings parallel to the direction of the strain (HANH, 2019; IGN, 2008; NISTICÒ, 2020).

The required service life for mooring cables is on the order of twenty years, during which they are subjected to high loads that vary continuously due to sea and climate conditions. The failure must be avoided, as it puts lives at risk, would make the platform

unstable and would interrupt oil production. Fibers, which are not elastic, inevitably undergo changes due to the loads imposed, so creep and possibly other processes of deformation and failure must be understood in order for their use to be extended (LECHAT et al., 2006; LECHAT; BUNSELL; DAVIES, 2011).

Polyester ropes are not subject to significant creep in loads usually experienced in lashing applications, which means that they are generally not flawed due to creep breakage. Therefore, creep or creep rupture analysis is not necessary for the mooring project. However, changes to the mooring rope may be necessary during the life of the project due to the deformation of the rope. In addition, sufficient length of the upper segment of the chain should be maintained to allow for future adjustments to the cable. Estimation of future line adjustments can be performed based on the creep rates of the creep plateaus from the near-static stiffness test (ABS, 2014; AYERS; RENZI; AKSU, 2010; LECHAT; BUNSELL; DAVIES, 2011).

Unlike the tension relaxation property, creep consists of the application of an instantaneous and constant charge, being influenced by temperature, and the variation of the strain is followed as a function of time. Creep rupture in polymeric materials is a result of combined events such as viscoelastic deformation, primary and secondary bond breakage, chain slippage, among others. Temperature, tension, and time are also crucial factors for the viscoelastic response of polymeric materials.

Polyester ropes have a higher fatigue resistance compared to chain and steel ropes, which means that fatigue assessment is usually concentrated on the upper segment of the chain, which has a short service life.

The creep tests, carried out by Lechat, compared the average life times of the synthetic fibers with those obtained under cyclical conditions. The fibers were subjected to cyclic loads for short cycles of maximum load. The results showed that the useful life is considerably longer than that recorded for constant loads at the maximum cyclic load level, if it were the creep process that controlled the failure. The two typical morphologies related to fracture of PET and PA fibers are related to the type of failures to which they were submitted, being due to creep or traction and after fatigue (LECHAT et al., 2006; LECHAT; BUNSELL; DAVIES, 2011).

The results of Lechat's lifetime prediction pointed out that the effects of maximum load applied is that the higher the maximum load, the shorter the lifespan. However, the fracture morphology data showed a behavior similar to that obtained by creep, when subjected to maximum load. Fatigue morphology is only compatible for loads below 80%.

The creep that occurs in polyester cords due to their viscoelastic nature can be separated into several categories (CANEVAROLO JR., 2006; FLORY; BANFIELD; PETRUSKA, 2004; SUDAIA, 2015).

In composite materials, parameters such as fiber/matrix or particle/matrix interfacial resistance affect creep resistance. The viscoelastic behavior of the matrix and its function in the debonding mechanism in fiber-reinforced composites, this type of defect occurs due to the plastic deformation that occurs when materials are subjected to stress and temperature, for a period of time (LORANDI et al., 2016).

It is important to emphasize that the selection of the type of fibers will depend on the application of the composite. For example, aramid fibers are strong and heat-resistant, and are employed in military and aerospace applications, for ballistic-graded fabric armor (bulletproof vest) and ballistic composites, in marine twine (ropes, cables, and chains), marine hull reinforcement, in these cases modulus, tensile strength and high fracture are the most desirable properties, as well as weight reduction. This effect is known as "fiber addition reinforcement" and is widely used commercially to improve the mechanical performance of polymers and allow their use in applications where the pure polymer would carry a high risk of failure (CANEVAROLO JR., 2006).

In the case of fracture resistance, the presence of composite fibers makes the crack path longer, reducing the risk of failure, unlike metallic materials, where the energy dissipates in the crack region in a non-elastic way, causing practically immediate failure. This, however, depends on the bonding/interaction strength between the fiber and the matrix (CHOI et al., 2017; DEVARAJU; ALAGAR, 2019; YINH et al., 2021).

For structural applications, one of the most important properties that must be evaluated is the dependence of the elastic modulus on temperature, especially of rigid materials. This is the case of cured epoxy resin, which usually serves as a matrix in composites, or as an adhesive in structural reinforcements, and is used in various temperature conditions (LORANDI et al., 2016).

4 FIBER-REINFORCED POLYMER SYSTEMS: EVALUATION BY MECHANICAL TESTS

Fiber-reinforced composites are generally composed of synthetic, natural, mixed fibers; It may contain other types of incorporated materials such as mica fillers, carbon black, clay, graphene, carbon nanotube. The production of lightweight, high-performance, low-cost polymeric composites has been the subject of intense research in recent years. The analysis of the mechanical properties of composite materials can be done in a static or dynamic way. In addition, the evaluation of the mechanical behavior can be carried out, regardless of the

occurrence of material failure. The properties of elastic modulus, tension and strain in the flow, maximum stress, among others, are parameters characterized without reaching polymer failure. On the other hand, stress and strain at break, impact strength, number of fatigue life cycles are mechanical properties determined at the limit of the destructive strength of the polymer or composites.

The most used mechanical tests in the characterization of composites are highlighted: hardness test (ASTM D785 - Rockwell hardness test), tensile test (ASTM D3039 or ASTM D638), compression test (ASTM D695), 3-point flexure test (ASTM D7264 or D790), impact test (ASTM D4812 - Izod test) and torsion (ASTM E143). (ABU TALIB et al., 2013; MATHUR et al., 2020; SARWAR et al., 2020; SONG, 2015; VALENÇA et al., 2015). Among the mechanical tests mentioned, one of the main ones is the bending test, which is widely used in engineering and materials science, this test evaluates the mechanical properties of a material when subjected to an applied load that induces bending. Flexural strength analysis plays a key role in evaluating the structural behavior of polymeric materials, allowing us to understand their strength, stiffness and ability to withstand applied loads.

Polymeric composites consisting of fibers, especially structural carbon and glass, have been replacing aluminum and titanium alloys, as chloride ions in seawater and salt spray can penetrate through the concrete covering, destroy the passivation layer on the surface of the oxidized steel, and thus deteriorate the performance of the steel bar due to the development of rust. The annual economic loss due to marine corrosion can reach hundreds of billions of dollars.

Li et al. (2021) found that the use of polymeric fibers in composites presents improvements in different material properties, for example, in terms of tensile strength and fracture, in addition to the advantage of having excellent integrity and formability.

Li also evaluated the resistance of these composites by immersion in alkaline environment and seawater at different temperatures, the results showed that the tensile strength of the composites decreased by 89.3% in the temperature range of 25-40°C, to 81.6% to 63.1% in the temperature range of 40-50°C and 50-60°C, respectively. The results pointed to the increase in porosity of the composites indicating the development of degradation. The degradation of the matrix, fiber and interface are the main factors that affected the mechanical properties of composites (LI; ZHOU; OR, 2021; LI et al., 2021; LORANDI et al., 2016; SRINIVASULU; TEJASWI, 2012).

Lorandi et al. (2016) evaluated the behavior of polymeric composites through the technique of dynamic-mechanical analysis (DMA), making it possible to determine the

thermomechanical properties of elastic modulus and viscous modulus, as a function of temperature, frequency or time of composite materials quickly and efficiently.

They evaluated the flexural and tensile properties of aramid fiber-reinforced epoxy matrix composites and composite composites of aramid and particulate graphene, in different proportions of aramid fiber ranging from 0.1% to 0.4% by mass and graphene 0.3% by mass. The results indicated that for composites reinforced with 0.3% aramid fibers the flexural strength is maximum, which is 102.77 MPa. The additional increase of fiber to 0.4% decreased the flexural strength to 77.77 MPa. The flexural strength increased by 48% for the sample with 0.3% m/m, which is the maximum among all samples with only aramid fiber. For hybrid composites consisting of aramid and graphene, the flexural strength increased by 20%, which is lower when compared to the composite reinforced with only aramid fiber (HALLAD et al., 2018).

The investigation of the effect of orientation on the mechanical properties of tensile and quasi-static compression of Kevlar/epoxy composites through the universal testing machine. Abu and colleagues evaluated the hole effect in aramid fiber-reinforced epoxy matrix composites. The work also involved the investigation of varieties of angles in the orientation of the fibers in the matrix, with variations of +45°/-45° and 0°/90° load versus displacement curves for all specimens, with and without holes, the results indicated that in all cases the laminates with symmetrical angle layers of (0°/90°) suffered the greatest inelastic deformation before failure. (ABU TALIB et al., 2013; VALENÇA et al., 2015).

Gobikannan et al. (2021) evaluated the flexural strength of fiberglass-reinforced composites, the matrices used were thermoplastic resin, epoxy resin, and dicyclopentadiene-based polyester resin and found that they are comparable (in the range of 916-942 MPa), and the effects of conditioning on both liquids are similar for each of the three materials. The study pointed out that water reduces flexural strength by 19%, 23%, and 17% for epoxy resin, polyester resin, and thermoplastic resin, respectively, while diesel reduces flexural strength by 8%, 3%, and 5% for epoxy, polyester, and thermoplastic resin.

Yang et al. (2017) investigated the relationship between structure and mechanical properties of composites reinforced with aromatic polyamide fibers, Kevlar, with different arrangements evaluated under tensile load. It was reported in their studies that the modulus of the fiber was governed by the overall degree of molecular orientation, composites reinforced with more open mesh fabrics (auxetics), showed a significant reduction in the damaged area compared to composites reinforced with closed-mesh fabrics. Impact tests indicated that the auxetic fabric-reinforced composites had a significant reduction in the

damaged area compared to the traditional construction fabric (YANG; CHALIVENDRA; KIM, 2017).

Meshram and collaborators evaluated the mechanical properties of nylon/epoxy composites and pure epoxy based on their modulus of elasticity, yield strength, elongation, and maximum strength. Evaluation of the performance of laminated Kevlar/epoxy composites through fracture and impact testing, which demonstrated a significant reduction in the damaged area compared to the woven counterpart and, on the other hand, influenced the reduction of impact energy absorption (MESHRAM et al., 2018).

Nash et al. (2019) evaluated the performance of an infusible thermoplastic die system compared to the most commonly used die materials in marine structures under various immersion conditions. Commercially available infusible thermoplastics, vinyl ester, polyester, and epoxy resin systems have been used to manufacture laminated fiberglass composites using vacuum-assisted resin transfer molding (VaRTM). The results indicated that the infusible thermoplastic resins used showed results that made them competitive with the candidates for replacement of the resins usually used in the industry. The thermoplastic resin had the highest glass transition of all the materials tested and interlaminar shear strength properties comparable to epoxy. The resins used in these articles are listed in Table 2.

The interest in hybrid composites prepared by the combination of multiple fibers in conventional resins has been studied, the incorporation of polymeric fibers (Kevlar and polyester), glass fibers and carbon fiber when combined present the best results with regard to specific mechanical strength, such as flexural and impact resistance. (ANIDHA; LATHA; MUTHUKKUMAR, 2019; DA COSTA MATTOS et al., 2014; DI et al., 2019; SARWAR et al., 2020; SONG, 2015; VALENÇA et al., 2015).

Table 2

Cured resin properties according to manufacturer's data sheets

| Description | Epa | VEb | PEc | Tpd |
|-------------------|------------------------|------------------------|------------------------|------------------------|
| Name | Prime 27 | Leo-M-8500 | Synolite 8488-G-2 | Elium 150 |
| Healing agent (B) | Prime 20 Slow Hardener | Butanox M-50 | Butanox M-50 | Perkadox CH-50X |
| Mass ratio (A:B) | 100 : 28 | 100 : 2.5 | 100 : 1.5 | 100 : 2.5 |
| Density | 1.08 g/cm ³ | 1.04 g/cm ³ | 1.05 g/cm ³ | 1.19 g/cm ³ |
| Viscosity | 190–200 mPa s @25 °C | 300–400 mPa s @20 °C | 80–90 mPa s @23 °C | 100 mPa s @25 °C |

| Gel Time | 2h 40min @25 °C | 1h 50min @20 °C | 1h 30min @23 °C | 25min @25 °C |
|--------------------------------|-----------------|-----------------|-----------------|---------------|
| Curing time to the environment | 24 hours | 24 hours | 24 hours | 24 hours |
| Post-curing temperature | 60 °C | 80 °C | 40 °C | Not necessary |
| Post-cure time | 7 h | 6 h | 4 p.m. | Not required |
| Heat deflection temperature | 60 - 62 °C | 105 °C | 64 °C | 109 °C |
| Tensile strength | 74.3 MPa | 95 MPa | 70 MPa | 76 MPa |
| Traction Modulus | 3.5 GPa | 3.6 GPa | 3.8 GPa | 3.3 GPa |
| Elongation at break | 4,5% | 6,1% | 2,3% | 6% |

aEP: Epoxy - PRIME™ 27 by Gurit

bVE: Vinylester - LEO Injection Resin 8500 from BÜFA (this resin is part of the Saertex LEO® fire retardant composite system)

cPE: Dicyclopentadiene based polyester - Synolite 8488-G-2 by Aliancys

dP: Thermoplastic – E illum® 150 by Arkema

The investigation of the mechanical properties of hybrid Kevlar/Flax/epoxy composites using a "sandwich structure" configuration produced by multiple layers of pure kevlar fibers and pure flax fiber, in which it was found the increase in the performance of these materials through the hybridization of synthetic and natural fibers (SARWAR et al., 2020).

Valença et al. (2015) evaluated epoxy matrix composites reinforced with fabric, kevlar fiber and fiberglass manufactured by hand with different architectures. In this work, the tensile, flexural and impact properties of composites consisting of only one of the Kevlar and glass reinforcements and the Kevlar/glass mixture in fabric format, figure 18, shows the aspects of the fibers and resin after mechanical testing, were evaluated. Composites with a hybrid Kevlar/glass structure in the reinforcing fabric showed the best results with regard to specific mechanical strength as well as bending and impact energy (VALENÇA et al., 2015).

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