



Review

Polymer composite materials: A comprehensive review

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ABSTRACT

Herein, in the present review we developed and investigated a comprehensive review of advanced composite materials based on thermoplastic polymers, elastomer polymers and thermosetting polymers. These advanced composite materials were reinforced by organic and/or inorganic fibers and formulated using various fillers such as organic, mineral and metallic. Further, we present the development and the synthesis of several macromolecular matrices namely polycarbonate, polyhexamethylene sebacic, polyether sulfone, polyether ether ketone, polyether ketone ketone, polyether imide, polyethylene terephthalate, phenoplasts, epoxy resin and polyurethane. The advantage of composite materials formulating is to have excellent mechanical performances, high thermal resistance, good fire behavior, high impact resistance, best abrasion resistance, exceptional electric insulation and good rigidity. Then, composite materials formulation were examined and discussed in detail.

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1. Introduction

The concept of formulation is very broad since it concerns all industries which develop intermediaries or finished products by mixing several raw materials [1–5]. More precisely, the formulation can be defined as all of the knowledge and operations implemented when mixing, combining or shaping ingredients of natural or synthetic origin, often incompatible with each other, of so as to obtain a commercial product characterized by its function of use and its ability to satisfy a predetermined specification [6–10]. Among the constituents of formula, a distinction must be made between the active ingredients which fulfill the main function sought and the formulation aids which play accessory roles [11–13]. The formulated product consists of a fine dispersion of several immiscible phases which appears homogeneous on the macroscopic scale and heterogeneous on the microscopic scale (paints, cosmetic creams, mayonnaise and composite materials); to the previous requirements are added those of the preparation and the stability of the mixture [14–16]. Composite material can be defined as the assembly of two or more materials, the final assembly having properties superior to the properties of each of the constituent materials [17–22]. Composite materials are now commonly called reinforcement arrangements (also called fillers) which are embedded in a matrix [23–25]. The matrix ensures cohesion and orientation of the load. Also, it is possible to transmit to the load the stresses to which the composite is subjected. The materials thus obtained are very heterogeneous and often anisotropic [26–28]. The nature of the matrix and the charge, the shape and proportion of charge, the quality of the interface and the production process used are all parameters that can influence the properties of the composite material [29–34]. The matrix and the reinforcement can be metallic, ceramic or plastic, which makes it possible to envisage a multitude of combinations [35–38]. The composite material is composed in the general case of one or more discontinuous phases distributed in a continuous phases. In the case of several discontinuous phases of different natures, the composite is said to be hybrid [39–41]. The continuous phase is called the matrix and the discontinuous phase is called the reinforcement or reinforcing material. In composite materials components with complementary physical and mechanical properties are combined [20,37,42,43]. The insertion of reinforcements of good tensile strength, of very high modules in a polymer matrix, makes it possible to improve the mechanical

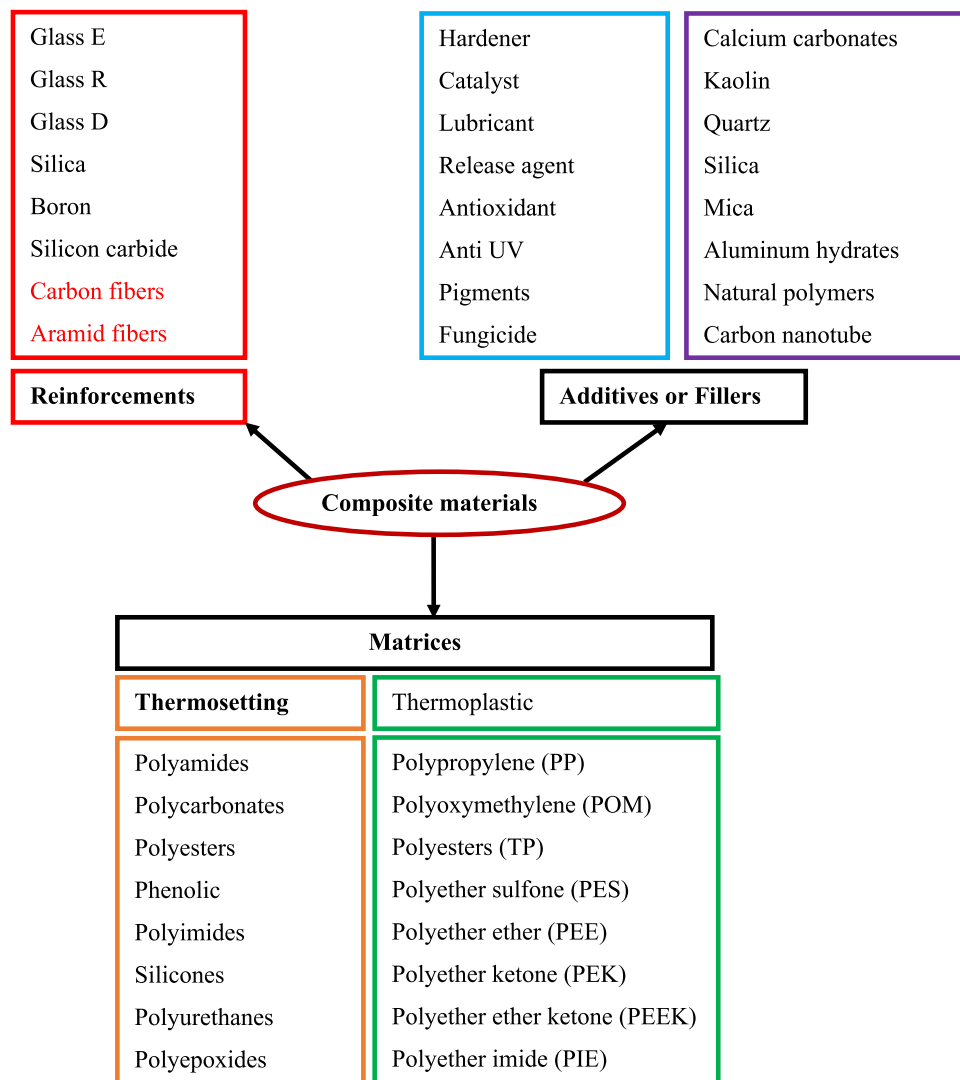
and thermal qualities [44–54]. The advantage of composites with a polymer matrix, compared to metals, is the manufacturing process which allows the production of parts of complex shape including their lower density, hence a lower fuel consumption (for aviation and automobile), higher speed in competitive sport or longer range for missiles and higher payload (in transport) [55–58]. The composite materials are classified according to the type of matrix into three categories, namely organic, mineral and metallic. Among the organic composites, there are cardboard (resins and cellulose fibers), laminated tires (rubber, steel, organic resins, glass fibers, carbon and boron) and reinforced plastics (resins and short fibers) [39,59–62]. Amongst the mineral composites we find concrete (cement, sand and additives), carbon–carbon composites (carbon and carbon fibers) and ceramic composites (ceramics and ceramic fibers) [63]. And also, the last are the metallic composites (aluminum/boron fibers and aluminum/carbon fibers) [64–66]. These composite materials affect several fields of application, namely packaging, automotive, light structures, civil engineering, aviation, sports, biomedicine, thermomechanical components and aerospace.

2. Different composite materials types

To access the description of the composite material, it will be necessary to specify three natures such as the nature of the constituents and their properties, the geometry of the reinforcement and its distribution and the nature of the matrix–reinforcement interface. The composite material is therefore a system formed of a relatively large number of constituents [11]. The number of possible realizations from this range of fundamental elements is therefore practically infinite. The nature of the matrix, the types of reinforcements [14,67], the additives and the relative quantities of these elements entering into the formulation, as well as the process of implementation, have a decisive impact on the characteristics of the finished product. There are two main classes of materials such as large diffusion composites and high performance composites.

2.1. Large diffusion composites

Large diffusion composites are the most common, generally made from fiberglass and unsaturated or phenolic polyester resin. They con-



Scheme 1. Composite materials formulation.

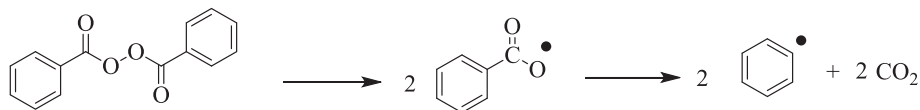


Fig. 1. Formation of radicals.

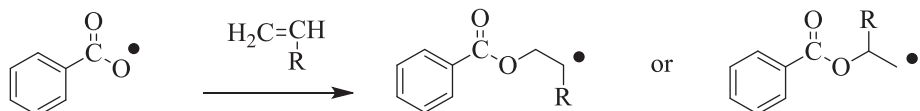


Fig. 2. Formation of the activated monomer.

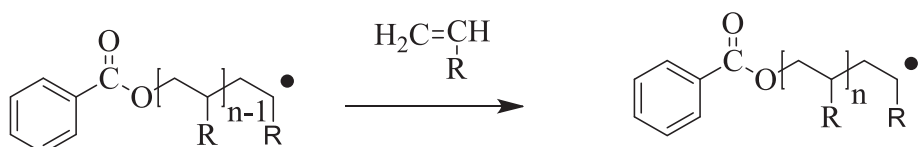


Fig. 3. Synthesis of radical polymer.

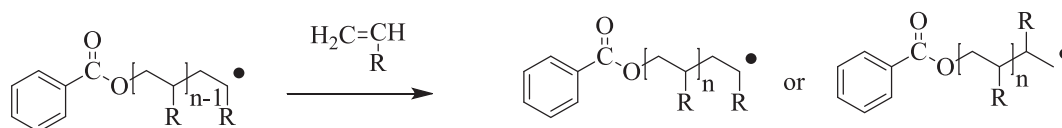


Fig. 4. Propagation of the activated monomer.

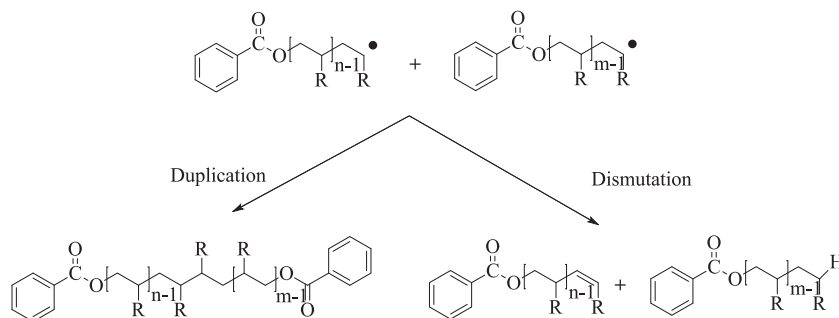


Fig. 5. Synthesis of the final polymer.

stitute more than 95% of production and the most important demanders are the transport industry (automobile, railway) and electrical construction.

2.2. High performance composites

The constituents are mainly epoxy resins reinforced with long glass fibers, but especially carbon or aramid. The applicants interested in their high mechanical and thermal characteristics. However, in very low production series are the aeronautical and space industry.

3. Composite materials formulation

The main components of the composite materials formulation are matrices, fibers and additives or fillers (Scheme 1), respectively.

4. Matrix

The matrix can be of the thermoplastic, thermosetting and/or elastomer type. The role of the matrix is to linked the reinforcing fibers, distribute the constraints, provide the chemical resistance of the structure and give the desired shape to the final product [40,68]. The choice of matrix depends on the use for which the composite material is intended. Composite materials, as defined in the context of this study, have been deliberately limited to those formed by organic matrices.

4.1. Thermoplastic matrices

The thermoplastic matrices are in the form of linear chains which can be transformed in the molten state. In most manufacturing processes, the thermoplastic matrices are heated, then formed by molding, injection, extrusion or thermoforming, before being cooled so that the finished product retains its shape. This operation is reversible. Today there are many types of thermoplastics with a wide range of interesting properties. They can be made as flexible as rubber, as rigid as metal and concrete, or as transparent as glass, for use in many products. They do not oxidize, have high corrosion resistance and are excellent thermal and electrical insulators. Due to their lightness, high mechanical strength and resistance to the effects of the environment, thermoplastics are an ideal material for many applications.

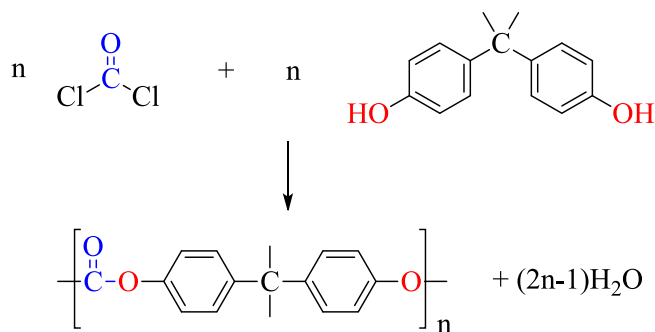


Fig. 6. Synthesis of PC.

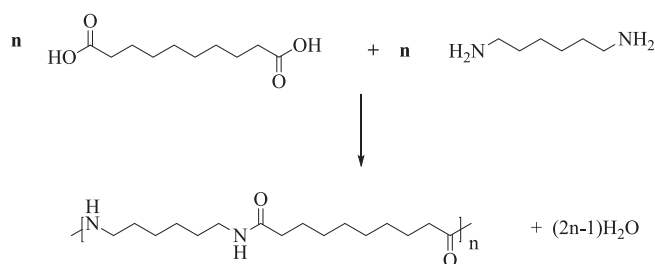


Fig. 7. Synthesis of nylon (6, 10).

4.1.1. Radical polymerization

The following polymers are obtained by the radical polymerization of vinyl monomers in the presence of a radical initiator (low and high density polyethylene, polypropylene, polyvinyl chloride, methyl polyacrylates and polystyrene) in three steps (priming, propagation and termination) [69].

• Priming phase

A polymerization initiator is a substance which has at least one labile chemical bond capable of generating, by homolytic rupture, free radicals. There are two main families of polymerization initiators (peroxides and azo derivatives). In the case of peroxides, the formation of radicals results from the breaking of the O—O bonds. Under the action

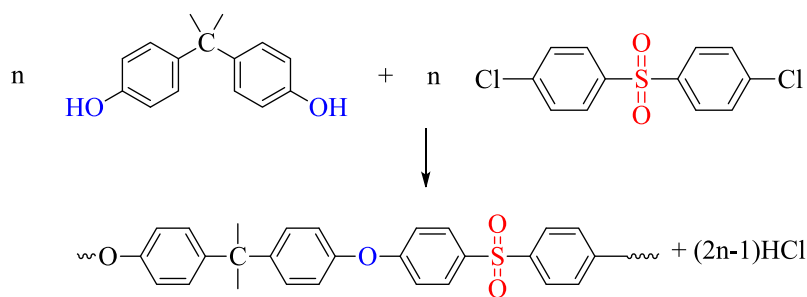


Fig. 8. Synthesis of PES.

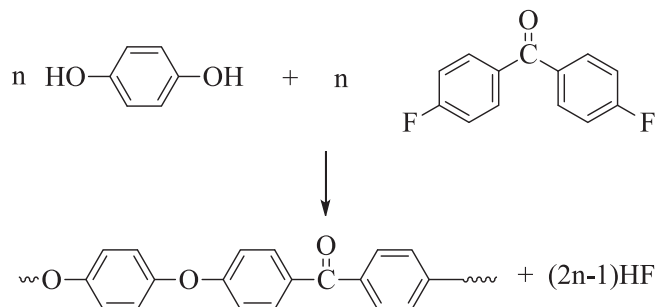


Fig. 9. Synthesis of PEEK.

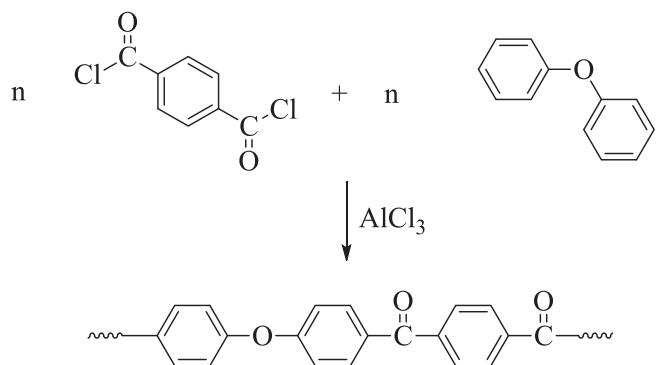


Fig. 10. Synthesis of PEKK.

of heat, benzoyl peroxide breaks down into free radicals according to the mechanism presented in Fig. 1.

There are two types of radicals; benzoyloxy radicals which by β elimination, form phenyl radicals and CO_2 . These two types of radicals are capable of initiating polymerization (Fig. 2).

• Propagation phase

The main stage of radical polymerization during which the macromolecule is built up; the propagation stage is 10^3 – 10^4 times more frequent than the initiation or the termination. It corresponds to the propagation of the active center to other monomers (Fig. 3).

At the level of propagation, a new possibility of isomerism is manifested, analogous to that observed at the level of the addition of initiator radicals to a first molecule of monomer. There may be head–tail or head–head addition (Fig. 4).

The head–tail addition is generally favored. Several factors influence the regioselectivity of addition, the following three factors are generally considered such as stabilization by resonance of the radicals formed and the steric effect and the polarity.

• Termination phase

The radical polymerization ends by meeting and deactivating two by two of the propagating radicals. This termination occurs either by duplication or by disproportionation (Fig. 5).

During the duplication reaction, a bond σ is formed by collision between two propagating radicals. A single chain is thus formed with a head–head placement in the middle. For the dismutation reaction, there is capture by a growing polymer radical of a hydrogen atom attached to a penultimate carbon of another growing radical polymer. Two macromolecules are formed, one of which has an unsaturated terminal unit.

4.1.2. Polycarbonate

Polycarbonate (PC) is an amorphous thermoplastic polymer most employed in many industrial application fields such as aeronautics, astronautics, automotive and others. Polycarbonates have excellent properties such as mechanical, thermal, electrical, workability, optical, toughness, flame retardancy and high impact resistance [42,70,71]. Polycarbonates present low cost and delicate processing. Polycarbonates were obtained by the polycondensation reaction of phosgene and bisphenol A (Fig. 6).

4.1.3. Polyamide (Polyhexamethylene sebacic)

Polyamides (polyhexamethylene sebacic) have good mechanical properties, resistance to friction and good fire behavior. Their temperature resistance is considerably increased with the presence of fiber glass [72–74]. Polyhexamethylene sebacic (Nylon 6–10) was obtained by the polycondensation reaction of hexamethylene diamine and sebacic acid (Fig. 7).

4.1.4. Polyether sulfone

Polyether sulfone (PES) is a high-performance thermoplastic polymer and the most used in several fields of applications namely automotive, aerospace and others. PES has very good mechanical properties, combined with excellent temperature resistance and remarkable fire behavior, which make it a material reserved for highly technical parts. Its uses are limited by its sensitivity to solvents and ultraviolet radiation, its difficulties of implementation and are very high price [75–78]. Polyether sulfone was obtained by the polycondensation reaction of bisphenol A with 4,4'-dichloro diphenyl sulfone (Fig. 8).

4.1.5. Polyether ether ketone (PEEK)

Polyether ether ketone (PEEK) is a thermoplastic polymer and a high performance polymer which has been widely realized in several applications such as medicine, electronics, telecommunication and also aerospace. Polyether ether ketone has a very high thermal resistance in association with fiber glass which characterizes this material. PEEK showed the excellent mechanical performances and the high chemical resistance. PEEK is a thermoplastic material reassuring material because of their great resistance against deformation and a lower creep rate [79–82]. Polyether ether ketone was obtained by

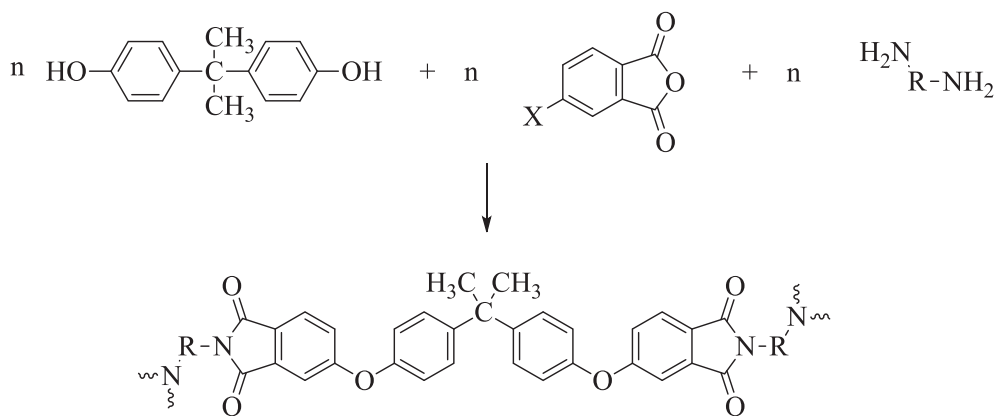


Fig. 11. Synthesis of PEI.

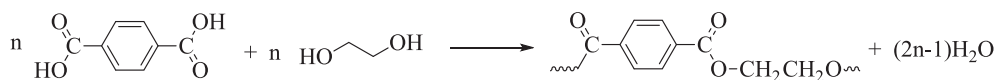


Fig. 12. Synthesis of PET.

the polycondensation reaction of 4,4-fluorobenzophenone with hydroquinone (Fig. 9).

4.1.6. Polyether ketone ketone (PEKK)

The use and the development of macromolecular thermoplastic polymers based on aromatic matrices have the potential to meet all industrial needs. Polyether ketone ketone (PEKK) is a thermoplastic material and is currently investigated with a higher interest in the aeronautic industries as macromolecular matrices for carbon fiber reinforced structural composites. PEKK is a higher performance material, showed exceptional thermal properties at higher temperatures and also, good impact resistance. The viscosity of PEKK composite materials at high temperature decreases, which evacuates all porosities under employed pressure [79,80,83,84]. PEKK prepared and synthesized from diphenyl ether and terephthalic acid in presence of aluminum trichloride as catalyst (Fig. 10).

4.1.7. Polyether imide (PEI)

Polyether imide is a thermoplastic material which having high characteristics that are practically constant up to 175 °C. PEI showed excellent chemical and thermal resistance and their remarkable fire resistances make it a material increasingly used despite its high price. PEI presents several industrial applications, namely higher-level offices, submarines and airplanes [57,85]. Polyether imide was obtained by the polycondensation reaction in presence of three monomers such as the bisphenol A, the phthalimide anhydride halogen and diamine (Fig. 11).

4.2. Thermosetting matrices

Generally liquid at room temperature, they solidify during their implementation under the influence of heat and an additive called hardener. They are thus transformed by cooking which is a chemical modification consisting of a very strong bond between the molecules in three dimensions. This process is irreversible and the material thus treated becomes infusible and insoluble in most solvents (alcohols, ketones and hydrocarbons). In general, they are more rigid than thermoplastic matrices, resist creep better and are suitable for molding large parts with short, long or woven fibers [86]. The most frequently used thermosetting matrices are polyesters, phenoplasts, epoxy resins, polyurethanes and polyimides.

4.2.1. Polyesters (Polyethylene terephthalate)

Polyethylene terephthalate (PET) is a thermosetting material with various applications such as one dimensional fiber, two dimensional layer and network three dimensional. PET is high performance thermosetting polymer and a low cost, is widely employed as packaging materials, owing to hardness, abrasion resistance, solvent resistance, electric insulation and good rigidity [87,88]. They represent 85% to 95% of the use of thermosetting matrices. Polyethylene terephthalate are characterized by the average mechanical and thermal resistance, the ease of implementation (implementation without solvent), the possibility of manufacturing materials stable over time and with rapid implementation and the transparent, colorless (ease of coloring in all shades) [89,90]. Polyethylene terephthalate was obtained by the polycondensation reaction of ethylene glycol and terephthalic acid (Fig. 12).

4.2.2. Phenoplasts

Phenoplasts are thermosetting materials having many applications thanks to its excellent fire behavior and are characterized by average mechanical properties, good temperature resistance, implementation in a solvent medium, possibility of making stable preregs and impossible coloring in light shades [18,91]. They are obtained by polycondensation of formaldehyde on phenol. This reaction can be carried out either in an acid medium or in a basic medium (Fig. 13).

4.2.3. Epoxy resins

Epoxy resins are thermosetting materials reserved for the manufacture of elements having to undergo high mechanical and thermal stresses. Epoxy resins are characterized by good mechanical and thermal resistance superior to those of polyesters, implementation possible without solvent, good resistance to chemical agents, very low uptake of humidity in immersion and excellent adhesion to fibers and metals [11,45,92–94]. Diglycidyl ether of bisphenol A (DGEBA) was obtained by the condensation reaction of bisphenol A with epichlorohydrin in the presence of a base (Fig. 14).

4.2.4. Polyurethane

Polyurethanes (PU) belongs to the family of thermosetting polymers, which their structure property relationships having pinched more attention. Polyurethane owning ability and excellent thermal mechanical and adhesion properties and also have high potential

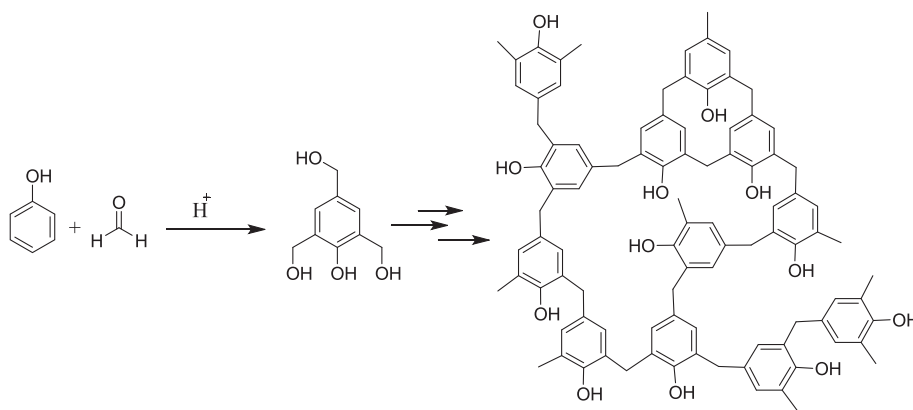


Fig. 13. Synthesis of phenoplasts.

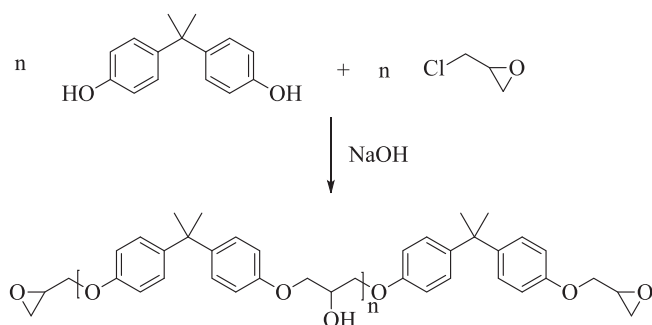


Fig. 14. Synthesis of polymer DGEBA.

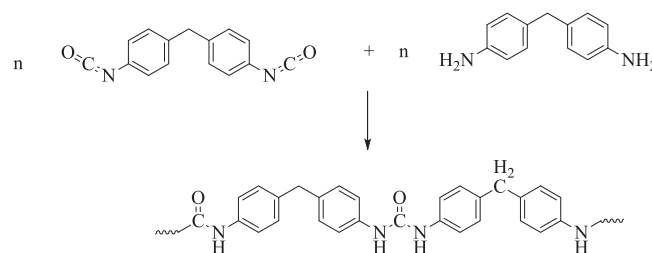


Fig. 15. Synthesis of PU.

applications in different fields namely coatings, adhesives, foams, marine antifouling and packaging materials [94–96]. Polyurethane was obtained by the polycondensation reaction between diisocyanate and mobile hydrogen compounds (diol or diamine). For example polyurethane was synthesized from methylene diphenyl diisocyanate (MDI) and methylene dianiline (MDA) (Fig. 15).

4.3. Elastomers

Elastomers polymers have the same elastic qualities as rubber. A resting elastomer consists of long molecular chains folded back on themselves. Under the action of a constraint, the molecules can slide relative to each other and deform. In order for the base material to have good elasticity, it undergoes vulcanization. It is a hardening process that creates a more or less rigid three-dimensional network without removing the flexibility of the molecular chains. Sulfur, carbon and various chemical agents are introduced into the elastomer during vulcanization [41,97,98]. Different formulations allow the production of synthetic rubbers for specific uses. Elastomers are used in the manufacture of cushions, certain insulators, shoe soles or tires. Styrene butadiene is a thermoplastic material which is obtained using polymerization of styrene in the presence of butadiene (Fig. 16) [99,100].

5. Reinforcement

The reinforcement constitutes the reinforcement or the skeleton which provides the mechanical strength (tensile strength and rigidity). It is, by definition, of filamentary nature (organic or inorganic fiber) going from the elongated particle to the continuous fiber [39,75]. The most used is E glass fiber which represents more than 95% of applications. In addition, aramid fiber (Kevlar) is also of great interest [101,102]. In general, in a composite structure (anisotropic), the fibers

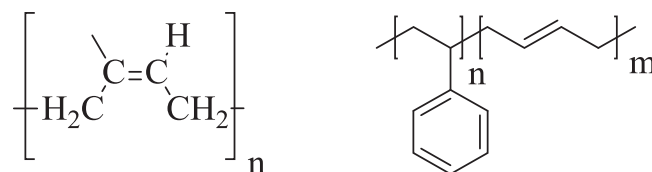


Fig. 16. Natural rubber (polyisoprene) (left) and synthetic rubber (styrene-butadiene) (right).

work well in traction, but in comparison with metallic structures (isotropic), the performance in compression is less good and the resistance to shearing remains weak. Further, the most used reinforcements are in the form of fibers or derived forms (Scheme 2).

5.1. Glass fibers

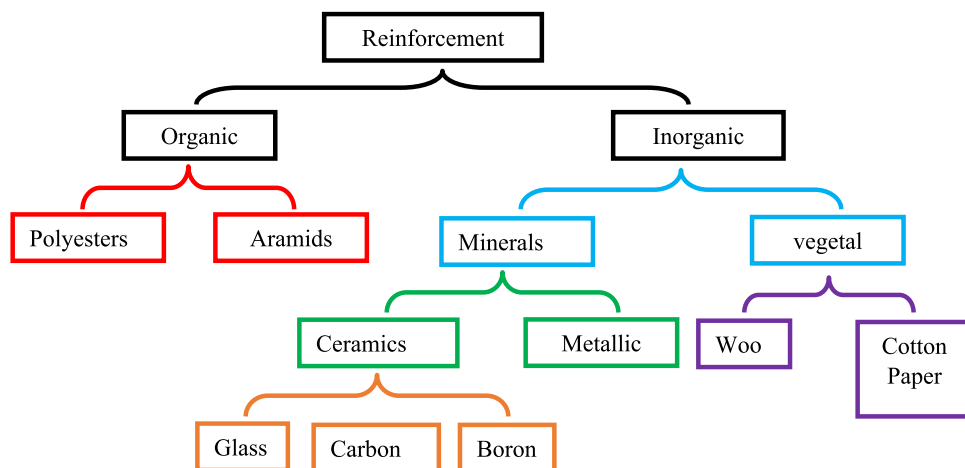
Currently, the glass fibers represent the majority of the reinforcements most employed for the reinforcement of advanced composite materials in various application fields industrial [82]. Glass fibers constitute the essential reinforcement of diffusion large and high performance composite materials (Table 1).

5.2. Phenolic fiber

Industrial fiber manufactured under the KYNOL brand (excellent thermal performance and good dimensional stability) (Fig. 17).

5.3. Polybenzimidazole fiber

Polybenzimidazole (PBI) is a very effective fiber and has excellent new and advanced properties in composite materials employed in the aerospace, automotive and wind power sectors [103]. Known as PBI



Scheme 2. Main reinforcement materials.

Table 1

Main glass fibers.

Main constituents in %	Types of glasses		
	E	D	R
Silica oxide (SiO ₂)	53–54	70	60
Alumina oxide (Al ₂ O ₃)	14–15	–	25
Magnesia oxide (MgO)	20–24	0.5	9
Boron oxide (B ₂ O ₃)	6–9	22	6
Boron oxide (B ₂ O ₃)	6–9	22	6

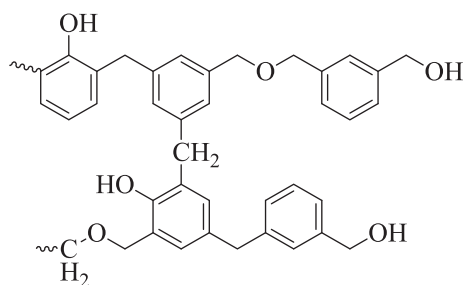


Fig. 17. Structure of phenolic fiber.

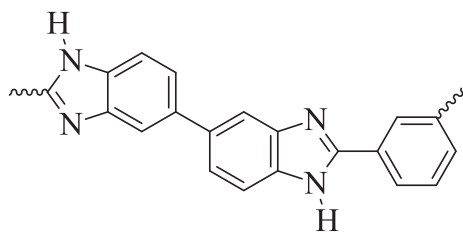


Fig. 18. Structure of PBI fiber.

fiber, obtained by spinning a solution of poly 2,2'-(m-phenylene)-5,5'-bibenzimidazole in dimethylacetamide (Fig. 18).

5.4. Aramid fibers

Currently, advanced thermosetting composite materials reinforced with aramid fibers have significant economic performance in the industrial field. These advanced materials have excellent toughness, excellent impact resistance, low density and a longer life

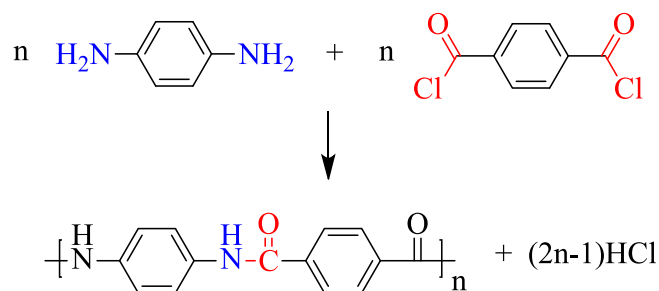


Fig. 19. Synthesis of aramid fiber.

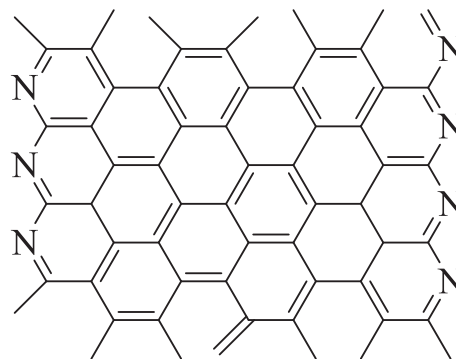


Fig. 20. Structure of carbon fiber of high strength.

[39,73,104]. Aromatic polyamide fibers, the best known is KEVLAR fiber, obtained by polycondensation reaction of terephthalic diacid chloride with para-phenylene diamine in the medium (hexamethyl phosphoramide and N-methylpyrrolidone) (Fig. 19).

5.5. Carbon fiber of high strength (CFHS)

Carbon fibers are widely employed in the elaboration of the thermosetting composite materials. They are employed in several industrial fields such as space construction, aeronautics, aircraft, automobile, [43,105–107]. Carbon fibers offer exceptional mechanical and thermal resistance characteristics, extremely high tensile and compressive strength and superior rigidity. Carbon fiber known as the best fiber, it was prepared from polyacrylonitrile (PAN) carbonization followed by graphitization (Fig. 20).

6. Filler

Under the general name of filler is designated any inert substance which, added to the base polymer, makes it possible to appreciably modify the mechanical, electrical or thermal properties, to improve the surface appearance or else, simply, to reduce the price of the transformed material [64,65,108]. Thermosetting materials are always contained fillers of various kinds and shapes, at often high rates of up to 60% by mass. For a given polymer, the choice of filler is determined according to the modifications sought for the finished object. However, the substances which can be used as plastics fillers must first satisfy a certain number of requirements:

- **Compatibility with the basis resin:** non-toxicity, absence of coloring, chemical inertness and neutrality, heat and light stability, low water absorption, no influence on the stability of the polymer or its color.
- **Wettability:** good distribution of powders in the polymer matrix or adhesion of the fibers to the basis polymer.
- Uniformity of quality and grain size.
- Low abrasive action.

6.1. Organic fillers

- **Cellulose fillers:** cellulose fillers are used as fillers for thermosetting resins (phenoplasts and aminoplasts). The advantages of these cellulosic materials are their low cost and their low density.
- **Wood flour:** wood flour are used with phenolic and aminoplast resins, to increase impact resistance, lower shrinkage during molding and give better dimensional stability to molded parts.
- **Fruit bark flour:** fruit bark flour is used in thermoplastics matrices such polypropylene (PP) and copolymer (acrylonitrile–butadienestyrene) (ABS) with an incorporation rate of between 9 and 23%, as well as in phenolic resins.
- **Vegetable fibers:** vegetable fibers are made of cellulose, entirely for cotton fiber, partly for wood fiber [109]. Their density is low and they are very sensitive to humidity. Their mechanical characteristics are low, they have good wear resistance and provide thermal and electrical insulation.
- **Starches:** starches are carbohydrates contained in plants, in particular polysaccharides having the general formula $(C_6H_{12}O_5)_n$. The starches are very different in size and configuration: the smallest are those of rice (3–7 μm), those of corn are 15–20 μm , those of wheat are 20–30 μm . Starches are used as filler to obtain plastics with controlled biodegradability.

6.2. Mineral fillers

6.2.1. Carbonates

Calcium carbonates (CaCO_3) exist in two crystalline forms: calcite (rhombohedral) and aragonite (orthorhombic) [42].

- Chalk can contain up to 99% calcite, silica and other minerals. The average size of its particles varies from 1 to 3 μm .
- Limestone and marble contain 80–90% calcite and varying amounts of magnesium oxide and silica. The particle size is between 0.5 and 30 μm .
- Calcium carbonates are mainly used with polyvinyl chloride (PVC) and in thermosetting materials as well as polyurethanes because of its hydrophobic character.

6.2.2. Silica

Silica (SiO_2), in its pure state or combined with metal oxides, is used as filler in different forms, depending on its origin, its crystallinity, its

Table 2

Main mineral fillers with their interesting properties.

Mineral fillers	Interesting properties
Talcs	Thermal insulation and water resistance
Titanium dioxide	Resistance to water and heat
Carbonates	Hydrophobic character
Silica	Dielectric, mechanical, abrasion resistance and heat
Zinc and magnesium oxide	Electrical conductivity and resistance to heat
Alumina	Electrical resistivity, thermal conductivity, rigidity, abrasion resistance and fire
Beryllium oxide	Electrical and thermal conductivities
Aluminum and magnesium hydroxide	Fire performance
carbon black	Thermal and electrical conductivity
Carbon nanotubes	Rigid, thermal conductivity

hardness and the size of the particles. Its incorporation into the composite material improves the fuel efficiency, the dielectric properties, wet traction, the mechanical properties, the abrasion resistance and the resistance to heat and humidity of molded objects. There is also an increase in the glass transition temperature and compressive strength, as well as a reduction in swelling in the solvents [99,110–112]. Silica is the main filler of silicones, it is found either in its natural state: silica sands, quartz, or in synthesized form.

6.2.3. Talcs

Talcs are generally hydrated silicates of magnesium ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) and sometimes aluminum ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) among their characteristics, we find the low hardness, the good inertia to chemical agents, the easy coloring, the good thermal stability up to 300 °C, the good resistance to thermal shock and the ease of distribution in the matrix. Talcs are used to improve thermal insulation and water resistance, and to facilitate the molding operation. It is the most widely used filler in thermoplastics [113,114]. It gives them better resistance to creep as well as greater rigidity.

6.2.4. Titanium dioxide

Titanium dioxide is a white pigment, UV barrier that improves resistance to aging, it also gives good resistance to water and heat. Titanium dioxide is mainly used in thermoplastics and in unsaturated polyesters [115].

6.2.5. Zinc and magnesium oxide

Zinc oxide is a white pigment, UV barrier, which gives the resins good electrical conductivity and high resistance to heat. Magnesium oxide provides the resins with rigidity, hardness, resistance to creep and improves thermal conductivity [116–118]. It is also used as a curing agent and increases the viscosity of polyester prepolymer.

6.2.6. Alumina

Alumina filler provides resins with better electrical resistivity as well as good thermal conductivity; it decreases the coefficient of linear thermal expansion, increases rigidity as well as resistance to abrasion and fire [119].

6.2.7. Beryllium oxide

Beryllium oxide was used in the form of microspheres in epoxy resins; it increases the electrical and thermal conductivities. These microspheres are also used in structural density foam (PUR), as well as for the manufacture of ultra-light polyester parts.

6.2.8. Antimony oxide

Antimony oxide (Sb_2O_3) was used alone in a polymer, it does not cause any delay in combustion effect. However, in the presence of halogenated additives, it reacts in situ with the halogenated acids

Table 3
Main metallic fillers with their interesting properties.

Metallic fillers	Interesting properties
Aluminum	Shock resistance, thermal and electrical conductivities
copper	Thermal and electrical conductivities, protection against radiation
zinc	Corrosion resistance, protective coatings

generated by the flame retardant to form antimony oxyhalides much heavier than hydrides, antimony trioxide and therefore widely used as a synergist in systems containing halogens.

6.2.9. Aluminum and magnesium hydroxide

Aluminium hydroxide is used as a flame retardant and smoke suppressor. It is one of the most widely used inorganic flame retardants [120]. It begins to decompose at 200 °C. Aluminum hydroxide is generally used in plastic formulations whose processing temperatures are around 190 °C. This is the case of polyolefin for electrical cables, polyvinyl chloride (PVC), polyurethane (PUR), thermosetting such as unsaturated polyester, phenolic, polyepoxide and rubber. Magnesium oxide decomposes at a higher temperature than aluminum hydroxide, between 250 °C and 300 °C. It exerts an endothermic effect, with a release of water vapor. The final surface of magnesium oxide helps to decrease the smoke rate. It can be used in plastics whose processing is carried out at a higher temperature such as polypropylene. To get attractive fire performance, a fairly high charge rate is required, which decreases the level of mechanical properties of the material.

6.2.10. Carbon black and nanotube

Carbon black has been used for a very long time in the plastics industry as a dye, pigment, UV barrier, antioxidant,... Carbon black improves the resistance polyethylene (PE) and that of the polyvinyl chloride (PVC). Composite materials formulated by the carbon black as a charge increase the thermal conductivity [45]. Also, the electrical conductivity of charged materials increases with the carbon content and with the fineness of the particles. Carbon nanotubes present a special structure of carbon. Carbon nanotubes are in the form of the tubes a few nanometers in diameter. Carbon nanotubes are generating interest in the research world because their properties are exceptional in many ways. They exhibit both excellent rigidity comparable to that of steel and very high thermal conductivity. Also, from an electrical point of view, single-wall nanotubes have the quite exceptional feature of being able to be either metallic or semiconductor depending on their geometry [30,42,82,104]. The main mineral fillers with their interesting properties are listed in Table 2.

6.3. Metallic charges

The introduction of metallic powders (aluminum, copper and zinc) is carried out to make the plastic materials used in aerospace and electronics conductive of electricity or heat. The addition of metallic powders (aluminum or bronze) in the polyamides made it possible to obtain conductive moldings, which could be plated with metals [64,65]. Polypropylene loaded with aluminum powder has excellent physical properties. Aluminum improves the shock resistance, the thermal and the electrical conductivities. Aluminium is used in tool parts, paints, synthetic paper, cold plastic welds. Further, copper improves the thermal and the electrical conductivities. Copper is used in tools, and in decoration (like bronze). Then, iron improves the resistance to abrasion. Moreover, lead provides protection against radiation and absorption of sound in high density materials. In addition, magnesium is used in pyrotechnic applications. Also, stainless steel is used as a tool and finally, zinc improves the corrosion resistance; it is used in protective coatings (Table 3).

6.4. Additive

Additives (adjuvants) are substances that are physically mixed with polymers. Additive is intended to modify or improve the rheological behavior of polymers in a processing machine, or the use properties of finished materials (physical properties, environmental stability) [117,121–123]. Additives are organic, organometallic compounds, often of low molecular weight compared to that of the polymer, used in low concentration. Additives are usually separated into categories based on their main effect such as plasticizers, stabilizers, lubricants, dyes and anti-shock agents whose main functions are theoretically known.

6.4.1. Lubricants

The forming of thermoplastics is only possible in the molten state or at temperatures above their glass transition temperature. Under these conditions, the increase in temperature is not enough to lower the viscosity sufficiently; that is why we must use processing aids, including lubricants. A lubricant can have an external behavior towards a polymer with which it is not compatible and an internal behavior in a polymer with which it is compatible [124]. This compatibility can be predicted using the solubility volumes of the polymer and the lubricant concerned. There are two types of lubricants:

- **External lubricant:** very slightly soluble in the polymer, forms a protective layer on the metal surface. This layer is more or less mobile depending on the nature of the metal, the chemical structure of the lubricant and the polymer concerned.
- **Internal lubricant:** improves the flow of molten polymer in the processing machine by lowering the viscosity. In the case of polyvinyl chloride (PVC), the internal lubricant plays a special role. Even in the presence of stabilizers, the gelation of PVC cannot be ensured without thermal decomposition by simple heating; homogeneity is only obtained by kneading to cause the interpenetration of grains and fine particles of polymer rubbing against each other. The main lubricants are saturated hydrocarbons, polymers, fatty alcohols, fatty acids, esters of fatty acids and alcohols, amides and silicones.

6.4.2. Plasticizers

Low or negligible volatility substance, incorporated into a polymer, intended to lower its softening interval, facilitates its implementation and increases its flexibility or extensibility [125,126]. Its action can also result in a reduction in viscosity in the molten state by a lowering of the glass transition temperature or a reduction in the modulus of elasticity of the plasticized object. Polyvinyl chloride (PVC) is the plastic that uses the largest amount of plasticizers of all kinds (85%), around 35 other polymers share the use of just over 10% of plasticizers (Fig. 21):

- Cellulose esters or ethers plasticized with phthalates (especially those of low molecular weight) which give them flexibility compatible with the end use.
- A large number of thermosetting resins (epoxides, phenolics and polyamides), in which plasticizers (melamines) are used as processing agents.
- Acrylic for example polymethyl methacrylate (PMMA) or styrenic resins (polystyrene (PS)) for paints in which the plasticizers facilitate application in the form of films.
- Alcohol phthalates can be considered the most common of the polyvinyl chloride (PVC) plasticizers because they most often have an acceptable set of required properties.
- Epoxides are most often epoxidic fatty acid derivatives, the best known of which are epoxidic soybean oil, octyl epoxy stearates and epoxy tallates (salt or ester of tall oil fatty acids, liquid resin obtained as a by-product of paper pulp).

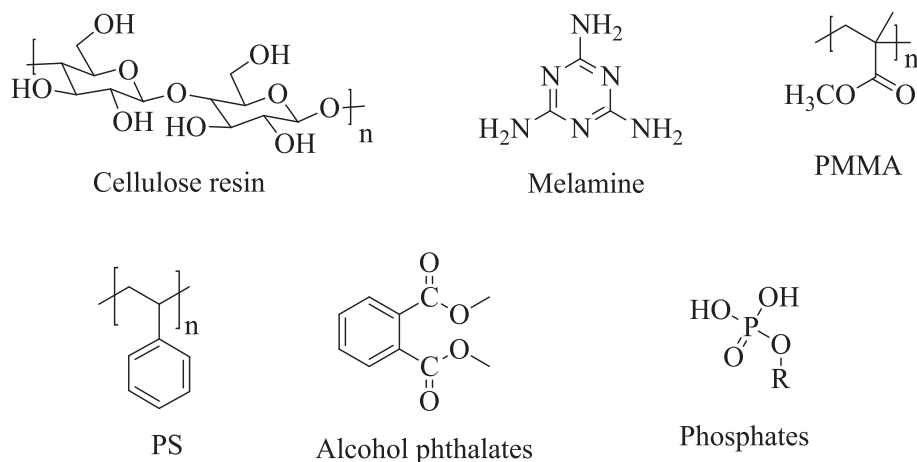


Fig. 21. Structure of cellulose resin, melamine, PMMA, PS and alcohol phthalates.

- Esters of aliphatic dicarboxylic acids (adipates, sebacates and azelates).
- Polyesters (polymeric plasticizers) are the products of the reaction of an aliphatic diacid with diol. The most common are polyadipates of glycol, of various molecular weights (from 800 to 10,000 g/mol).
- Phosphates are widely used in older formulations of polyvinyl chloride (PVC), alkyl and/or aryl orthophosphates are often mixed. The oldest is tricresyl phosphate, but diphenyl-octyl (or diphenyl-isodecyl) phosphates are generally preferred because they give good cold performance (Fig. 21).

6.4.3. Stabilizers

Large scale polymers are unstable; their instability manifests itself under the effect of thermomechanical constraints, under the action of thermal, light, or chemical aggressions, which alter the properties of materials. To inhibit or delay the reactions responsible for the degradation of polymers, they are incorporated with additives called stabilizers, classified according to their mode of action (antioxidants and anti UV agents) [126]. Unlike biopolymers (cellulose and starch), synthetic polymers are generally resistant to microorganisms. However, when they are combined with shorter molecules (plasticizers and lubricants), the biological attack causes undesirable effects. Poly-methyl methacrylate (PMMA), polyethylene (PE) and polyvinyl chloride (PVC) are resistant to microbial attacks. Biopolymers, polyamides, natural rubber and highly plasticized PVC are sensitive to microorganisms, especially in tropical climatic conditions.

6.4.4. Anti-Shocks

Under the effect of a shock, there are two modes of deformation of plastics such as the deformation by shear flow without decohesion and the deformation with formation of cracks and fractures [127]. Fragile materials mainly deform by shear flow. There are intermolecular shifts without variation in density. The flow is limited to specific areas called shear bands. In fragile materials, stresses cause the appearance of voids containing tearing areas called cracks which can spread and initiate fractures. These cracks contain polymer fibrils oriented in the direction of application of the stress. They are manifested by a bleaching of the polymers. In both cases, the cracks originate mainly from preexisting surface defects. Plastic deformation can be encouraged, for example by plasticizing PVC. However, in this case, other properties such as the softening temperature are modified. To improve the impact resistance without altering the other characteristics, shock-absorbing additives are used which disturb the distribution of impact energy. Following a shock on the plastic object, the resulting stresses can be dissipated and the impact energy absorbed by the presence, in the polymer, of microvoids or microcavities. However, the reinforcement

is notably greater by adding nodules of adjuvants which are not very compatible with the matrix and of different elastic modulus. The brittleness of a thermoplastic depends on the temperature at which the deformation takes place and on the speed of application of the stresses [128]. If the modulus of the reinforcing agent is greater than that of the polymer, the impact effect manifests itself on the contrary at the poles of the shockproof particles. The physical parameters which govern these phenomena are the respective elastic modulus of the reinforced polymer and the reinforcing agent (Young modulus), and also, the diameter of the nodules and the average distance which separates, corresponding, from a practical point of view, to the particle size and to the dispersed state. The shock absorbers used can be polymers with a glass transition temperature lower than that of the polymer to be reinforced and sufficiently compatible to adhere to it:

- Chlorinated polyethylenes (C-PE): They are widely used in opaque polyvinyl chloride (PVC) (Fig. 22). Contents of 20% by mass allow an impact resistance of more than 45 kJ/m² to be achieved for initial values (without shockproof) of less than 5 kJ/m². Their thermal and light stabilities are good. They do not affect the flammability of the finished products.

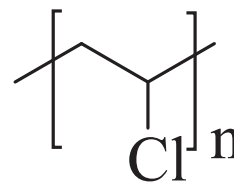


Fig. 22. Structure of PVC.

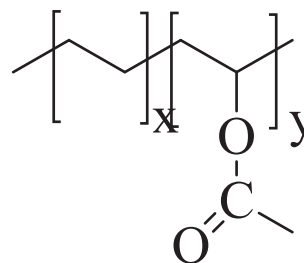


Fig. 23. Copolymer (E-VA).

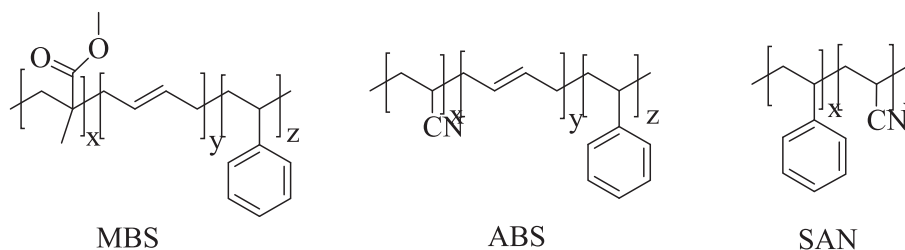


Fig. 24. Structures of three copolymers (MBS, ABS and SAN).

- Copolymers of ethylene and vinyl acetate (E-VA) (Fig. 23): These are copolymers used in rigid opaque polyvinyl chlorides (PVC), in high and low density polyethylenes and in polypropylenes. Their dispersion (and therefore their effectiveness) can be affected by too severe thermomechanical constraints or by other adjuvants (stabilizers and lubricants).
- acrylic copolymers (Fig. 24): copolymer (methacrylate/butadiene/styrene) MBS, copolymer (acrylonitrile/butadiene/styrene) ABS and copolymer (styrene/acrylonitrile) SAN, these acrylic copolymers are easily dispersible in opaque and transparent polyvinyl chlorides (PVC), the best transparency being obtained with MBS. However, the light sensitivity of these shock absorbers does not because the impact resistance of reinforced PVC to fall faster than if PE-copolymer-EVA is used.
- Elastomers: Elastomers based on copolymers (ethylene/propylene) are used to reinforce polypropylene and polyamides.
- Strengthening minerals: Mineral additives are frequently used to modify the physical properties of polymers. This increases the density, the rigidity; the costs are reduced. However, the shock resistance has not been improved under certain conditions of concentration, implementation and accounting. To play the role of shockproof, the particles of reinforcing agent must be independent of each other after dispersion. Otherwise, the embrittlement of the material is observed. For a given polymer, filler and particle size, the impact resistance increases with the concentration of reinforcing agent up to a limit beyond which it decreases suddenly. The dispersion of certain fillers can be obtained by coating them (for example with stearic acid or calcium stearate in the case of carbonates intended for reinforcing polyvinyl chloride). Also, coupling agents, in addition to the role already described, also facilitate the dispersion of the charges, the most used of the organosilane type.

6.4.5. Pigments and dyes

The great majority of the polymers are little or not colored. Their coloring must meet very diverse requirements as aesthetics (coated fabrics and furniture), technique (improvement of certain physical characteristics of the polymer or protection against visible light or ultraviolet radiation), safety (fluorescent signs for vehicles and road works), identification (cables) and camouflage (weaponry) [115,129,130]. The coloring matters fall into two main groups:

- **Pigments:** are dispersed in order to obtain a uniform coloring and to develop the coloring power of the pigments to the maximum. This is achieved by reducing the size of the aggregates and agglomerates to an optimal particle size ranging from 0.2 μm to 5 μm . The Van der Waals and electrostatic forces that cause agglomerates are often very high and the energy required to achieve good dispersion is considerable.
- **Dyes:** are very easily incorporated by simple dissolution in a solvent, a plasticizer or in the molten polymer, before transformation.

7. Conclusion

After studying a large number of literatures on thermoplastic polymers, elastomer polymers and thermosetting polymers reinforced by fibers and formulated by fillers we have recommended and concluded the following points:

- Composite materials thermosetting showed exceptional mechanical and thermal resistance at high temperature.
- Technological composite materials reinforced by glass fibers and carbon fibers present excellent high tensile and compressive strength.
- Advanced composite materials are currently investigated and employed with higher interest in the several industries.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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