

POLYMER MATRIX COMPOSITES – ROUTES AND PROPERTIES

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Abstract: This paper is a continuation of the article “Composite Materials-A Review” and it presents an overview of polymer matrix composites. Its main aim is to assess the development of these materials and their need. The subject is treated in five sections. The first section presents an itinerary of polymer matrix composites. The second part is devoted to the classification of these materials. The classification depends on the number of components, on their nature and on the system of macromolecular interactions. The justification for the applicability of polymeric materials in various fields is analyzed in the third section. Processing techniques of polymer matrix composites are covered in section four. The paper ends with conclusions.

Key words: composite, cast, polymer, matrix, technology

1. INTRODUCTION

After metal melting and ceramics modeling, industrial-scale manufacture of the first synthetic polymer represented another landmark in the evolution of human society. Since then, polymers have witnessed an exponential development. It can be said that these materials have been integrated into all sectors of human activity.

The emergence of this new class of materials as a result of human curiosity and ingenuity was based on economic considerations and performance.

In this context, research has gained momentum, during the past few years, on the blends of natural and synthetic polymers which have found applications in ecology and biomaterials.

By the 1980s the term polymer composite referred exclusively to the systems consisting of a polymer matrix in which inorganic fillers or reinforcing textile materials were incorporated.

Such a combination was made at first due to economic reasons and later on, after the two-phase compatibility, out of performance reasons.

In the 90s the term polymer composite material was extended to all systems with at least two components, one of which was organic.

2. CLASSIFICATION OF POLYMERIC COMPOSITE MATERIALS

In our days there are no few economic domains in which are used nonmetallic materials. Of these materials, polymeric materials play a major role. With very diverse properties (from good machinability and easy implementation to specific weight, very low thermal conductivity and electrical) polymeric materials have become indispensable and irreplaceable.

The high diversity of polymer composites makes it impossible to treat these materials in a uniform manner. However, according to the literature, the main criteria for the classification of polymer composites are (Carcea, 2008; Nedelcu et al., 2008; Asthana et al., 2006):

- the number of components

Composite materials presuppose, in their structure, the existence of at least two components. Usually, the synthesis of composite materials is limited to the use of 2-3 components. In composite structure, besides polymers, micro molecular substances can be included.

- nature of components

Depending on the nature of components, polymer composites can be systems of: polymer-polymer (synthetic polymer-synthetic polymer, natural polymer-synthetic polymer, and natural polymer-natural polymer); polymer-inorganic compounds; polymer-organic compounds; polymer-metal.

- macromolecular interactions system

In terms of interactions between components, polymer composites can be: natural composites (interpolymeric complex) characterized by the fact that physical links (ionic, hydrogen, van der Waals, etc.) between components occur; chemical composites characterized by the fact that covalent bonds are established between compounds; physicochemical composites or interpenetrated networks (IPN) (Tang et al., 2008), partially interpenetrated (semi-IPN) or totally interpenetrated (full-IPN). In full-IPN polymer composites, the chains of one component (cross-linked or not by covalent bonds) are "fixed" in the reticular structure

of the second component.

- according to the state of the composite in its functional form: solid, quasi-solid (gel), liquid (composite solutions).

- according to the methods and processes for achieving mixtures

At the molecular level, the mixing of two macromolecular compounds can be achieved through the following methods: melt mixing; solutions mixing; solution mixing and drying; solution mixing followed by freeze-drying, coprecipitation.

The polymer materials class is very large and these materials can be classified in:

- plastic materials (polyethylene, polypropylene, polyvinyl chloride, polystyrene, phenolics, polyester etc.);

- elastomers (natural rubber, butadiene styrene, silicone etc.);

- polymeric fibres (fabric polymeric fibres, aramid fibres);

- coating materials (paints, lacquers, enamels etc.);

- adhesives (polymeric adhesives, natural-glu adhesive, casein, rosin);

- films (polypropylene, polyethylene, cellophane, cellulose acetate films);

- sponge or foam (polyurethane, rubber, polystyrene, sponge polyvinyl chloride).

2.1. Matrix

Fiber-reinforced polymers are widely used as structural materials for relatively low-temperature use. Usually, polymers have lower strength and modulus than metals or ceramic but they are more resistant to chemical attack than metals. Figure 1 displays a schematic comparison of the strength characteristics of ceramic, metals, polymers, and elastomers.

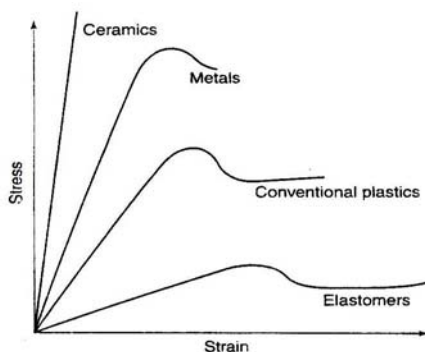


Fig. 1. Comparison of idealized stress-strain diagram for metals, amorphous polymers, and elastomers (Mitchell, 2004)

Polymers are giant, chainlike molecules or macromolecules, with covalently bonded carbon atoms as the backbone of the chain. Small-chain, low

molecular-weight organic molecules (monomers) are joined together via the process of polymerization; which converts monomers to polymers (Dang et al., 2011). Polymerization occurs either through additions of a catalyst. In addition to polymerization, monomers can be joined to form a polymer with the help of a catalyst without producing any by-products. For example, the linear addition of ethylene molecules (CH_2) results in polyethylene, with the final mass of polymer being the sum of monomer masses. Linear polymers consist of a long chain, often coiled or bent, of atoms with attached side groups (e.g. polyethylene, polyvinyl chloride, polymethyl methacrylate or PPMA). Branched polymers consist of side-branching of atomic chains. In cross-linked polymers, molecules of one chain are bonded with those of another, thus making the polymer strong and rigid. Ladder polymers form by linking linear polymers in a regular manner; ladder polymers are more rigid than linear polymers. Figure 2 illustrates these different types of polymers.

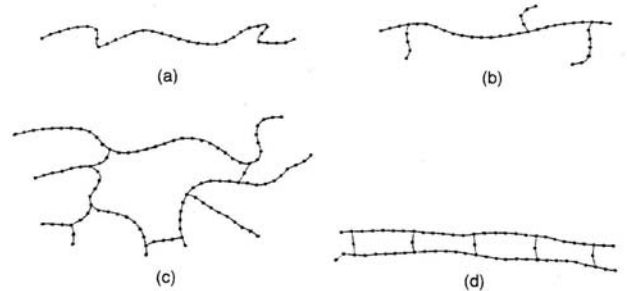


Fig. 2. Molecular chain configuration in polymers: a) linear; b) branched; c) cross-linked; d) ladder (Asthana et al., 2006)

Based on the type of repeating unit there is another type of polymer materials classification (Jiang et al., 2010). It is called homopolymer if one type of repeating unit forms a polymer chain. In contrast, polymer chains having two different monomers form co-polymers. If the two different monomers are distributed randomly along the chain, then the polymer is called a regular or random co-polymer. If, however, a long sequence of one monomer is followed by a long sequence of another monomer, the polymer is called a block co-polymer. If a chain of one type of monomer has branches of another type, then a graft co-polymer is said to form. Figure 3 schematically illustrates these various polymer structures.

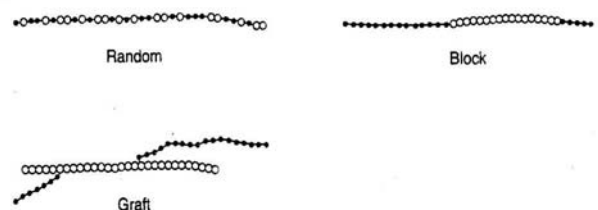


Fig. 3. Schematic representation of random, block and graft co-polymers (Asthana et al., 2006).

2.2. Properties of polymeric matrices

Glassy polymers follow Hooke's law and exhibit a linear elastic response to applied stress. The elastic strain in glassy polymers is less than 1%. Elastomers (rubbery polymers) show a nonlinear elastic behavior with a large elastic range as shown in figure 1 presented above.

Table 1 presents selected mechanical property data on some polymer composites. The mechanical properties of polymer composites often degrade because of

temperature and humidity effects. Moisture diffusion into a polymer matrix causes swelling, a decrease in the glass transition temperature of the matrix, and weakening of the interface. Besides humidity and temperature, electromagnetic radiation primarily ultraviolet radiation, can also degrade the polymer composite because the UV radiation breaks the C-C bond in the polymer. Resistance to UV radiation is enhanced by adding carbon black to the polymer matrix (Shokrieh and Omid, 2009).

Table 1. Mechanical properties of polymer and metal matrix composite

Composite	E, [GPa]		Strength, [MPa]	
	value parallel to the fiber axis	value perpendicular to the fiber axis	value parallel to the fiber axis	value perpendicular to the fiber axis
B-Al (50% fibre)	210	150	1500	140
SiC-Al (50% fibre)	310	-	250	105
Fiber FP-Al-Li (60% fibre)	262	152	690	172-207
C-Al (30% fibre)	160	160	690	690
E-Glassy-Epoxy (60% fibre)	45	12	1020	40
C-Epoxy (60% HS fiber)	145	10	1240	41
Aramid (Kevlar 49) – Epoxy (60% fibre)	76	5.5	1380	30

3. FIELDS OF USE

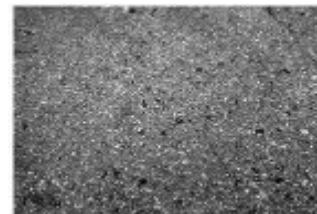
Polymeric materials are currently being used on a very large scale, the annual global production reaching over 130 million tones (in a big variety and more than 1700 trade names). Although substantially less than the consumption of metal materials (notably steel), in the U.S. the polymer turnover is over 100 billion dollars (about 26% of the total for all materials, while 38% is related to metal materials) (Domsa, 2006).

Current medical practice is using a wide range of polymer composite implants and instruments. The use of composite biomaterials in conducting medical implants is increasing. Composite biomaterials are more and more used for the total or partial replacement of tissue functions, of traumatized or damaged organs, to correct deformations etc. (Raduta, 2002; Hill, 1998).

From this point of view an interesting example to note, is the use of composites materials in dentistry. If the first resins composite (e.g. methacrylate) were used after 1930, with auto curing resin dental fillings were used in the next decade.

According to the statements of Rafael L. Bowen (Gregory et al., 1992) from 1962, resin composites reinforced with inorganic particles treated with silane gives good adhesion to the wall of the tooth, minimum polymerization shrinkage, increased hardness and mechanical load borne. A real breakthrough occurred in 1970 when were introduced

the dental composites which polymerize under the action of light. Posterior dental treatments with modern hybrid composites are currently recognized by the German Association for Dental, Oral and Maxilla-facial and German Dental Association that continuous treatment (Willems et al., 1993).



Dental composites reinforcing macro-particles can degrade easily and are more difficult to polishing.



Dental composite reinforced with micro-particles in excess are viscous and difficult to model

Fig. 4. Composites used in dentistry (Willems et al., 1993).

Polymer matrix composite materials are widely used in biotechnology and medicine. Polymeric biomaterials have several advantages (Deligkaris et al., 2010): elasticity, resilience and ease of manufacturing. Also these materials have a number of disadvantages: reduced strength, deformation and degradation over time. Table 2 shows polymer

biomaterials with their multiple applications. Table 3 summarizes the uses of hydrogels.

Table 2. Polymeric biomaterials (Domsa, 2006)

Material	Polyethylene	Polypropylene	Polymethyl methacrylate	Polyurethane	Hydrogel
Abbreviation name	PE	PP	PPMA	PU	PHEMA
Physical-mechanical properties	yield strength, hardness, opacity, resilience	hardness, yield strength, tensile strength, resiliency	yield strength, resilience, hardness	hardness, tensile strength	elasticity, shock resistance, amorphous
Modulus (GPa)	95-150	70-150	270-320	60-200	180-480
Density (g/cm³)	0,945-0,906	0,900-0,906	1,18	1,18-1,24	1,15
Processing	Injection Extrusion Thermal Training	Injection Extrusion	Injection Extrusion	Injection Extrusion Casting	Extrusion
Cost	accessible	accessible	accessible	expensive	expensive
Applications	pharmaceutical bottles, flexible containers, bags, tubes	membranes, surgical thread, artificial vascular grafts	dental materials, membranes, intraocular lenses, contact lenses, bone cement	tubes, surgical implants, maxillofacial prostheses	Contact lenses, artificial skin, controlled drug dosing systems, membranes for biosensors

Table 3. Hydrogel-filesds of use

Ophthalmology	<ul style="list-style-type: none"> - in eye surgery most important applications of hydrogels are: vitreous implants, devices glaucoma drainage, sclerotic swelling agents etc - in 1961 the process of obtaining soft contact lenses based on poly (hydroxyetylmethacrylat) was initiated (Guillon ed al., 2007) - soft intraocular lenses have the advantage of folding which allows the surgeon to make a tiny incision when introducing them; they have an increased permeability to oxygen preventing proteins adsorption on the lens surface - for vitreous implants, in some cases of retinal detachments, hydrogels are used to supplement, extend or replace the eye vitreous humor; for the replacement of vitreous humor are used more types of biodegradable hydrogels: collagen-based, cellulose derivatives, or acrylic gel.
Plastic and Reconstructive Surgery	<ul style="list-style-type: none"> - some hydrogels can be used as: bandages, absorbent, tissue adhesives etc. - an example is cross-linked gelatin-based hydrogel with dextran-dialdehyde used as tissue dressing.
Orthopedics	- hydrogel is used as a surgical system for the self-reconstruction of the cranium.
Bandages and coatings for sutures	- it is used in various forms as bandages for wounds, especially burns, ulcers and skin grafts
Pharmaceutical Applications	- hydrogels allow, under perfectly reproducible conditions, controlled loading and release of various physiologically active substances: antibiotics, vaccines, anticoagulants, antitumor substances, microorganisms, enzymes, contraceptives and antibacterials.

Interpolymeric complexes (CIP) are another form of polymer matrix composites. These complexes have applications such as: immobilization of enzymes, gene carriers, biodegradable materials, stabilization of milk casein, emulsions and suspensions stabilizer, to obtain ultrafine polymer layers, mechanical and chemical systems able to convert chemical energy into mechanical energy.

4. PROCESSING TECHNIQUES OF POLYMER MATRIX COMPOSITES

Manufacturing process of these materials is composed mainly of operations like: polymer matrix obtaining, reinforcing components preparation, impregnation or treatment of fibers, fibers cutting, reinforcement achieving (network, knitting, fabric etc.), blending components by injection, extrusion, pressing and stamping.

The most important manufacturing methods of polymer-based composites are described below (Nedelcu et al., 2008; Asthana et al., 2006; Mares, 2002; Florea and Carcea, 2011):

a) *Gravity casting* – consists in free fall casting of resins-particles (short fibers) to obtain large parts of thermosetting composites.

This procedure is applicable to thermosetting systems, reinforced with particles or short fibers (typically glass). The method is simple and can be applied for large pieces. It also has some disadvantages such as: reduced compactness of the final material, lengthy training processes and impossibility of using long fibers like forming elements.

b) Under pressure casting - consists in injecting liquid matrix over fiber or particle premoulds placed in a metal mould.

Although in terms of composite quality the method presents undeniable advantages, it is difficult to be applied in practice.

c) Contact moulding - consists in use of open lasts, on which successive layers of polymeric material and reinforcing elements are enforced.

The technological simplicity, the possibility of manufacturing oversized parts and the use of cheap materials for lasts are the most important advantages of this method. It also has some disadvantages, such as: low productivity, parts with reduced compactness, poor quality surfaces and uneven thickness, high labor consumption.

d) Simultaneous spray forming- this process uses a device like a spray gun, wherein the matrix material is mixed with particles or fibers chopped to the desired length.

The method presents some advantages: high productivity, thorough control over the constituents and the possibility of obtaining small parts or complex configurations. The disadvantages of the process are: impossibility of using fiber

reinforcement fabrics, high labor consumption, and the toxicity of the working environment.

e) Bag moulding - consists in placing successive layers of fibers and resins layers on the model after which an elastic and durable film (bag) is fixed tightly around the edges, through a pressure box or a metal frame. After pressure, or, respectively, depression is applied, the material is heated to be polymerized. The advantages of this method are strict control over the content of composite reinforcement elements and good surface quality of the manufactured parts. In contrast, among the disadvantages one can mention low productivity and expensive equipment.

f) Vacuum injection forming (moulding) - two metal moulds perfectly calibrated are used in the process; in between them the reinforcing material is placed; the interior space is then evacuated, that so that the resin (matrix) is brought forcibly to fill in the intervals between the reinforcing elements. The pores are thus removed from the polymer matrix, and this is the main advantage of the method, because it leads to the creation of composite materials with good physical and mechanical characteristics and with reduced surface roughness. The disadvantages of this process are: low productivity, precise and expensive moulds and the creation of parts that have only simple configurations.

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h) Cold pressing - two metal moulds are used for this process. The mixture of constituents is maintained under pressure until its strengthening is complete.

The process is advantageous because it can be applied to large series production, it minimizes loss of material and the manufactured parts have both sides finished. On the other hand, there is an important disadvantage: the need for expensive equipment.

i) Hot pressing - the materials are reticulated under heat in closed moulds, and the final thickness of the manufactured part is adjusted by the number of impregnated layers of fabric that are introduced. After the heat treatment the material is left to cool in the mould under pressure.

Among the advantages of this method we can

mention: high productivity, the possibility of obtaining accurate complicated parts, which are used, for example, in aeronautics and in military technology, as well as obtaining a material with outstanding physical and mechanical characteristics.

j) Forming by continuous stratification – this method uses a furnace in which the matrix is reticulated and the material is specialized and cut at the desired sizes.

k) Forming of thermoplastic materials – the thermoplastic polymer has to be mixed with reinforcing elements (particles or short fibers). This mixture is granulated by methods characteristic of plastics, most often by injection. The method has high productivity and ensures parts with complex shapes. On the other hand, there are some disadvantages: high energy consumption, the need for strong and expensive moulds, because the injection equipment is subject to intense fatigue through erosion. l) Formation of honeycomb core panels – these are panels consisting of several layers joined together and secured in the form of honeycomb. The process involves two steps: placing components cut to the desired size and the thermal formation of the panel itself, on hot press platens at (170÷190)°C and pressures of (2÷4)Mpa. Usually plated with metal sides (these structures have densities ranging between 80 and 500 kg/m³), these structures are called hybrid sandwich structures. These hybrid sandwich structures present essential materials for many leading technologies in the military and aerospace fields. It should be noted that if the cladding of panels is made with non-metallic sides (for example carbon or glass fiber hybrid fabric with polymeric material prepregs), then the sandwich structures have even lower densities than those cited.

5. CONCLUSIONS

Composites are currently recognized as the class of materials with the highest performance.

The possibilities of manufacturing composite materials, both in terms of composition and technology are virtually limitless. In this context they have been used in all fields of advanced technology (aerospace, robotics, machine building). Polymeric matrix composites are plausible solutions to environmental problems (biodegradable materials, superabsorbent hydrogels able to retain water in dry soils). These materials are successfully used for prostheses or body organs replacement.

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