### The Epoxy Resin - History and Perspectives

#### CATALIN NEGOITA<sup>1</sup>, NICOLETA CRISTACHE<sup>1</sup>, MARIUS BODOR<sup>1,2\*</sup>

<sup>1</sup>Dunarea de Jos University of Galati, 47 Domneasca Str., 800201, Galaļi, Romania

Since its discovery, more than eight decades ago, the epoxy resin grew quickly to be largely used in all-day activities around the world. This paper presents the evolution of utilization of the epoxy resin around the world, since its discovery until our times. Also, being such a familiar material in all industries, an analyses of its impact on the economy is also addressed in the second part of this study, revealing its importance on the economy of the countries on the both sides of the Atlantic Ocean. The research involving the utilization of the epoxy resin is still underway at this time, an interesting path being taken in Romania at the Research and Development Center for Thermoset Matrix Composites that is part of the Dunãrea de Jos University of Galati. Some of the ideas, already partially put in practice are presented in the last part of this article, the utilization of this resin as part of a composite being the main focus of obtaining some materials needed in greenenergy production.

Keywords: epoxy resin, composites, special properties polymers

Epoxy phenomenon reflected in the press - from chemical formulae to common usage

When in the year 1934, the German researcher Paul Schlack obtained a patent invention for creating a new, revolutionary product and four years later, the Swiss Pierre Castan and the American Sylvan Greenlee finalized successfully the researches in this domain, nobody suspected that only a few decades later, the epoxy resins will be an integrant part of the daily life, becoming an indispensable element of the modern civilization.

Of course, for the people in our times, not too concerned by formulas, but by their practical applications in domains of interest, epoxy raisins term or epoxy, as they are more known inwardly in the scientific world, does not say too much. In a succinct and scientifically vulgarized formulation, epoxy resins represent a group of rigid polymers, with high mechanical properties, with resistance to temperature and corrosion. What was related almost exclusively to the abstract science (chemistry) domain in the inter-war years, is found today everywhere, through the practical applications. The epoxy resins are used at metallic roofs, at anti-corrosive treatment, at manufacturing the electric insulating materials, at manufacturing the dyes, the electronic components, but also the decorative floors. The applications go to areas absolutely unimaginable, from manufacturing the components for ships, planes and cars or vehicles of high tonnage, up to plastic pieces which replace the metal or wood pieces. But the epoxy resins have entered also in other domains in which one might hardly believe they are used: in art (painting, sculpture, reconditioning the artifacts) or in medicine (artificial organs, stomatology). Even the indispensable mobile phones contain epoxy resins which cover the essential components of the device.

The huge success of the invention of the XX-th century which exploded on the market in the 1960s was due, equally, to perfecting the methods for obtaining the epoxy resins, but also to the publicity made to the new products by the *civil* media, which gave it special attention, as more and more domains of activity were circumscribed to this subject.

In the next pages we will try, without laying claim for an exhaustive research, to review the way in which the media

has been reflecting this subject. Since today it is unconceivable that the subject does not appear either in articles or in the commercials from the newspapers pages, our analysis will direct towards the press from the first post-war decades, i.e. the moment when *epoxy* phenomenon exploded in the daily life of the citizen, of the consumer of publicity and of information. We have analyzed the articles appeared in different countries from the world regarding this subject, trying to demonstrate how different the applications of the epoxy resins had been in the society of those times.

As usual, the U.S.A. had leaded the way in the post-war world to the explosion of the epoxy phenomenon. The press across the Ocean abounded in materials on the revolutionary product, which was constantly improved. On July 3<sup>rd</sup>, 1956, in *New York Times*, under the title *Epoxy resins licensed*, it appeared the information according to which Epoxy Resins Licensed Ciba Limited from Basel, Switzerland and Devoe Raynolds Company (New York) had signed a non-exclusive understanding of usage of the patent for epoxy and laminated resins [1].

A year later, also in the American press, it appeared the news according to which professor James Kriegh from Tucson, Arizona, was awarded a prize for using the epoxy in the re-establishment of the historic ruins from this federal state [2].

Accordingly, quite quickly, the new product, meant for the chemical industry, had found applicability in various domains. *Desert Sun*, newspaper which appeared in Palm Springs, published in the edition from March 3<sup>rd</sup>, 1961, an article where it was brought to knowledge the fact that the American Railroads Company intended to use a revolutionary process, replacing the traditional systems of attaching the sleepers to the steel railroads, by their soldering with an extremely powerful epoxy product. The first experiment of this sort was supposed to be done in Chicago [3].

On March 16<sup>th</sup>, 1961, in *Palos Verdes Peninsula News* an article is published regarding the varnishing day of the sculptor Ken Stuttgart and of the painter Glenn Dodendorff, at Cooperative Gallery from Redondo Beach, a satellite of Los Angeles, California. Those two used in their works epoxy resins [4].

<sup>&</sup>lt;sup>2</sup> Diagnose and Measurements Group, 41 Rosiori Str., 800055, Galaļi, Romania

<sup>\*</sup> email: marius.bodor@ugal.ro; Phone.: 0040746070322

In the year 1964, news about the new usage of epoxy appeared in the American press. Entering into the textile industry, the epoxy resins brought a plus of comfort into the American families: the shirts which do need ironing [5].

Another news published on January 4th, 1966, in *Desert Sun*, with the title *Glue Replaces Nuts and Bolts*, taken over from United Press International (UPI) agency, reminded about the *miraculous product of modern chemistry* used in the anticorrosive protection of the water tanks, of airplanes and in manufacturing the friction pads of cars, as well as at many more applications [6]. On March 4th, 1966, in the same newspaper, under the title Epoxy Mortar Made for Tile, it was mentioned a new mortar based on epoxy, resistant to acids, which glued perfectly the tiles [7].

Also in Canada the epoxy technology invaded the daily life. *The Hanna Herald and East Central Alberta News* from April 15<sup>th</sup>, 1965, presented the new technology used in domestic purposes. On April 14<sup>th</sup>, 1971, St. Albert & Sturgeon Gazette, published under the title From old empties to attractive glass or vase, an article on using epoxy resins in handmade interior decorations [8].

The Gazette St Albert Alta, published on December 20th, 1968, the article with the title Sky Cross Country, where it talked about the treatment of snow shoes with epoxy resins, which gave them assuredness and resistance [9].

The Gateway, publication which appeared in Alberta province, published on September 5<sup>th</sup>, 1984, under the title The Canadian Shuttle mission, an article about using the epoxy in alloys with carbon, for the spatial components which had an extremely small weight [10]. In the same publication from September 29<sup>th</sup>, 1987, the article Surgical super glue announces the fact that the *Walter Mackenzie* Health Sciences Centre of the University from Alberta was chosen as a testing place of a product based on epoxy, which stopped bleeding and which lead to tissues *sealing* in case of surgical interventions [11].

Epoxy resins had entered in Great Britain at the same speed. In Illustrated London News from April 25th, 1959, Shell Company made known the fact that it sold anticorrosive products based on epoxy, applicable in any domain [12]. The articles published in the British press had been, almost entirely, the themes of the American press regarding using the epoxy; consequently, we shall not insist on them. As domain, it is interesting the usage of epoxy in the reflectors *covering* systems, allowing them to use eight color filters (Illustrated London News, March 10th, 1987) [13].

The first mention of the epoxy resins appeared in Ireland in The Irish Times, in the year 1962, regarding the usage of the new technologies at boats and yachts [14]. The epoxy subject follows closely the British line in the Irish press.

In Switzerland, one of the epoxy's origin countries, Grigione italiano, on September 3<sup>rd</sup>, 1970, presented a commercial to the cars from Opel series, underlying the fact that they had the carriage body treated with an anticorrosive layer from epoxy resins [15]. Nouvelliste publication announced on December 5<sup>th</sup>, 1977, a Cours de perfectionement pour platriers et peintres, where there were presented the new series of epoxy resins [16].

Spain is one of the countries where the epoxy subject had been treated widely by the national media. The daily paper La Vanguardia Española, which appeared in Barcelona, had dedicated tens of pages in the 1970s to the subject of polymers and epoxy resins. On March 16<sup>th</sup>, 1972, under the title El Mundo de los Plasticos, it was presented a history of the plastic materials and of their usage in

different domains, from the artificial grass court to the components of the space stations [17]. In the number from February 5<sup>th</sup>, 1976, the same publication used the term plasticulture in order to underline the way the contemporary society had reported to the products which grew favor with them [18]. Among epoxy's magnitude applications, we note the re-establishment and consolidation of the roman aqueduct of Segovia, through injecting epoxy resins. (Spania entera, October 21<sup>st</sup>, 1975) [19].

The interest for epoxy resins were more than obvious in Holland. It was only natural for an over-industrialized country, epoxy being used in various domains, especially in the naval one. Besides the well-known domains, epoxy had entered also in the domestic life. *Epoxy paints eliminate mould stains* announced De Locomotief, commercial and publicity magazine, on May 7th, 1955 [20]. *Royal Dutch Shell was among the first large corporations which bought epoxy licenses of CIBA Swiss Company* announced Algemeen Handelsblad in October 17th, 1956 [21].

The interest for epoxy was also high in Italy. Since the '60s, the new technologies have been presented to the large public and especially their applications in domains related to the daily life [22].

In what concerns the epoxy's applications into art, we consider as interesting an article published in La Stampa, from March 15<sup>th</sup>, 1990, on the exhibition of Ferdi Giardini in the Altair gallery from Rome, the artist using epoxy resins, PVC pipes and lamps in achieving his works. Giardini declared he tried to achieve a *chemical war* [23].

The epoxy resins entered into the media's attention in Sweden also in the '60s of the last century. Dagens Nyheter, one of the largest daily papers from the country, published on September 30th, 1966, an announcement: We hire the director of the new polyurethane and epoxy department, meant for the construction industry [24]. In its turn, Expressen, Swedish tabloid newspaper, in the issue from November 28th, 1969, explained the novelty elements of the epoxy resins in terms accessible to the public [25]. Aftonbladet, evening Swedish newspaper, advertised the hardeners based on epoxy on April 20th, 1972 [26].

The epoxy phenomenon had the same intensity in Germany like in the other western countries. An article from Der Spiegel, from October 25th, 1968, presented the advantages of epoxy, as a method of glu-ing the materials, eliminating the welding. In the same newspaper, on September 6th, 1970, it was published an article regarding the sterilization of surfaces with the help of epoxy. Der Spiegel, from July 30th, 1973, published an article regarding re-establishing the mosaic windows of the cathedral from Augsburg, deteriorated by rains, pollution and scratches. It recovered its initial characteristics with the help of the epoxy resins [27]. Also in Die Zeit from March 21st, 1975, there were presented the new epoxy technologies which, in combination with the concrete, could make that the bridges weight less than one fifth from their initial weight [28]

In the Hungarian magazine *Szcenográfia*, issue 3/1960, the wood's epoxy treatment was presented [29]. As far as we know, it was the first serious reference on this subject. Hét Hungarian magazine, in issue 37 from May 18th, 1976, made a wide presentation of the materials from epoxy series, making known the qualities of the new products, as well as their applicability, in wide domains [30]. In the next issues of the magazine (38 and 39), the benefits of the products based on epoxy resins are explained to the large public. Their explosion on the Hungarian market had been described by frequent articles from the newspapers

from this country, especially after the year 1980: Heves Megyei Hirlap (issues 21-24/1990), Pest Megyei Hirlap issue 33 from July 1984, Tolnai Népújság, issues 34-36 from 1994 or 24 Ora, issues 27-29 from February 1994 [31].

In the former Soviet Union, the press concerns for the epoxy resins appeared quite at the same time with the other states. Unfortunately, we could not obtain any information from this space. The only references come from Latvia, there appearing many articles regarding the new technology. It is true that most of them were translations of some articles which were published in the occidental press, but they had been appearing since 1965 [32].

At Antipodes, Australia Beverley Times, from July 4th, 1963, contained an article entitled Painting under water. It was mentioned the accidental discovery of the American engineer Robert Jordan from Shell company (epoxy compound which hardens with difficulty in wet surfaces). Besides the *artistic* application, the article mentioned the anticorrosive properties of the new compound [33]. Another article refers to the paint used for marking the pedestrian crossings. Since on rainy weather, the drivers had reported sideslips of the cars on the marked lane, there had been used epoxy paints which reduce sensibly the phenomenon of side-slipping, having a longer life and a better visibility (*Canberra Times*, June 1st, 1979) [34].

In Brasil, *Suplemento tehnico industrial reclama Folha de Sao Paulo* from January 1<sup>st</sup> and 15<sup>th</sup>, 1964, published articles in which there were offered explanations on the way the epoxy resins acted [35]. Brasil has a digital data base very well organized. Accordingly, when consulting it, we note the existence of no less than 1076 results when searching for *epoxy* in the period 1964-2016. Their number is increasing from one year to another, the peak being the year 1989 (more than 100).

The first articles on anticorrosive treatment of steel, by using epoxy, appeared in Singapore, in the year 1962 (Preservatives for Industry Equipment, in Straits Times, January 26th, 1962) [36]. In the same newspaper, on June 16th, 1965, under the title Reflective paint now made here, the occurrence of a new reflective paint for the vehicles traffic was made known [37]. Finally, in the New Nation from January 30th, 1971, under the title Travelling to fame, it was reminded the fact that the artist Gerard Dalton Henderson had made the façade of Hilton hotel from Singapore, using epoxy technology [38].

The practical applications of the epoxy resins are unlimited, the art appealing to the achievements of the modern era. An article which appeared in the press from Cambodia informed on the re-establishment of the gigantic statue of Jayavarman the VII-th, the-leprous king. The statue from the XIII-th century was re-established after six months of conjugated efforts, the seven parts of the statue being glued with special epoxy resins and fixed with stainless steel bars. (Jayavarman VII set for Cultural Day tribute in The Phnom Penh Post, April 2<sup>nd</sup>, 1999 [39]. Epoxy art has had deep roots. No matter how impossible it would seem, the epoxy resins had entered onto the market in Faeroe Islands since 1959, when the first articles appeared in the plain language of citizens. In the year 1973, the epoxy paints commercials were a common thing in the press. Less common was Ragnar Kjantarsson, an artist who made sculptures and other objects of large dimensions from epoxy resins [40]

The epoxy applications do not stop here. After a cruise ship had entered into Cheeseburger coral reef from Grand Cayman Island, 140 divers and biologists descended into its depths, in order to reattach the still alive pieces of corals. During the re-establishment effort, which had lasted three

months, it was used an epoxy resin in order to glue more than 4000 pieces of coral [41].

As it can be noticed, epoxy has conquered the contemporary world, but it is important to know how to use the new technologies. It can happen that, due to lack of knowledge, one might produce almost irremediable damages due to epoxy. This is proven by the happening from the Museum of Egyptian Antiquities from Cairo, where the funeral mask of Tutankhamon was destroyed after the beard of the Pharaoh was glued with an epoxy resin. Noticing the beard was glued wrongly, the researches tried to detach it, using spatulas. But epoxy proved to be hard as a rock, and the result was that the mask was seriously deteriorated [42].

Economic aspects on the epoxy resin

From the economic point of view the composite industry represents both a challenge and a continuously growing market due imperatives of the environmental protection (i.e. reduction of carbon dioxide emissions). There had been purposed many strategies regarding this issue but, in actual world, one seems to take advantage into the competition, increasing the efficiency of automotive devices by reducing their weight but keeping the security of transportation [43] together with other important strategic directions. In this regard the polymer composites are the competitors of metals (which are traditionally used) due to their price/ strength rate [44]. On this market the thermoset composites are leading more valuable than the thermoplastic composite even if the second category of materials is also used [44]. Thermoset polymer epoxy resins and polyester are the most important actors shearing the market with 66% for polyester and 23% for epoxy resins (2007) [44]. Polyester resins are unsaturated polyesters which are widely used in the composite industry holding 66% share. Construction is the largest market for the polyester resin followed by pipe and tank and transportation in 2007.

Global thermoset composite materials market had been estimated at \$24.4 billion in 2014 and it is expected to increase at \$34.4 billion in 2020 [45]. This market is traditionally shared by North America - 36%, Europe - 24% and Asia and Rest of World - 40% (2007) [46]. On this market the most important materials are glass-fibre reinforced thermosets and carbon-fibre reinforced thermosets with an increasing tendency for second ones due to lowering of fabrication costs of carbon-fibre and improvement of forming technologies.

There are two main types of polyester resin used as standard laminating systems in the composites industry. Orthophthalic polyester resin is the standard economic resin used by many, whereas Isophthalic polyester resin is the preferred material in industries such as marine, where its superior water resistance is desirable. Because of their premium variety of mechanical attributes, corrosion resistance and low weight, polyester resins are frequently used in a host of applications where it proves to be advantageous. While building of the polymer chains, polyesters can easily be customized or modified. The foremost advantage of these resins is a balance of properties (including mechanical, chemical and electrical) dimensional stability, low cost, easy processing and handling. For manufacturing polyester concrete, clear casting resins, coatings, body fillers, buttons, etc. unreinforced versions of polyester resins are most commonly used. However, for building and sanitary (bath tub, pipe, tank, cooling tower, ladder, door, window), automotive parts (deck lid, doors, hoods), electrical parts

(housing, fuse box etc.), boat parts (boat hulls, decks, etc.) polyester resins with glass fibres are used (composite materials). The construction industry is the largest user of polyester resin materials with almost 1/3 of total polyester resin shipments in the year 2007. The pipe and tank industry is the second largest user of polyester resin materials in the world followed by marine transportation [46].

The applications for epoxy resin are extensive and include coatings, adhesives and composite materials such as those using carbon fibre and fiberglass reinforcements. Epoxies are notably being used in many applications. For heavy duty service on metal substrates (rapid dry protective coating applications), two-part waterborne epoxy coatings are used, which are energy economic. The coating dries swiftly providing a strong, UV resistant, protective coating with good abrasion resistance. It is also used in corrosion protection of steel pipes and fittings used in the oil and gas industry. Although, they are more expensive than polyester resins and vinyl-ester resins, yet generally produce stronger and more temperature-resistant composite parts. Major applications of epoxy resin for the composites industry are: electronics market such as in PCB (printed circuit board) for computers, wind energy, pipes, tanks, aircraft parts, sporting goods and industrial applications [46].

Many important companies in automotive industry had started programs on composites and even changed their research policy to fit the future environmental friendly requirements [43]. In an analysis realized in 2014 [47] there had been presented the most attractive opportunities for composites in the American market with a special attention on limitations of composites and a forecast regarding the enlargement of composites market in the period 2015-2035 by their application in civil engineering, oil and gas

industry and medicine.

A growth of composite materials market is expected near future due to innovation imposed by environmental policies and the attractiveness of their industrial applications. The innovation, according to [45] fits some important trends: continued light weighting of automotive, aerospace, and industrial parts, enhanced mechanical, chemical, and conductive properties of fibre and resin systems, cost reduction in various composite parts, faster and more predictable infusion, reduction in number of part counts in many applications, environmentally friendly resin and fibre systems.

The American system is the most receptive to changes and always the American companies and the American specialists analyse all the aspects of an imminent political decision. In the case of environmental policy and the connected of industrial opportunities with probable large benefits, a great attention was paid to composites and there are some documents that are emphasising the economic and social importance of composites in the next years [48-52]. The US Department of Energy Quadrennial Technology Review [53] chapter 8 - Increasing Efficiency and Effectiveness of Industry and Manufacturing is including analyses regarding many aspects of composites and their relations with other industries.

Regarding European market an annual analysis is being done by PlasticsEurope [54-56] and is containing the economic evolution of plastics (thermoplastic polymers) market with Germany as the greater demander, followed by Italy, France and UK and with Romania on 15<sup>th</sup> place during the 2012-2014 period. On all the studies, both thermoset and thermoplastic polymers are called plastics and that could generate a lack of attention from the part of the ones interested only in thermoset polymers or

thermoset matrix composites. Other aspect is connected with the fact that the epoxy resins are not separately mentioned in this study for the analysed period but there is (on all charts) an entrance called other plastics and this entrance has a significant share of the market. As economic aspects the mentioned analyses are referring to the main industries that are using plastics and their shares from the plastic market. A very important aspect is the one that the European studies are emphasising the importance of plastic waste management (with Romania in one of the last places) and the economic and business opportunities generated by the necessity of plastic and polymer waste management.

Another interesting study is realised annually by AVK Industrievereinigung Verstärkte Kunststoffe e.V. (Federation of Reinforced Plastics) [57-60] – for the period 2012-2015 and is taking into account GRP (Glass-fibre reinforced Polymers) and CRP (Carbon-fibre Reinforced Polymers). The mentioned studies are including composites market information and forecasts offering both an image of composites applications in Europe (comparing to the whole world) and ways for sustainable development and ideas for sustainable businesses [61-63].

3. Perspectives regarding the epoxy composites

The application area of composite materials is larger and larger due to their use into new fields along with traditional fields as military, marine industry, air and spacecraft, sports equipment and so on. Also it must be said that the definition of composites covers a very large area from, concrete to nano-composites, including reinforced and filled matrix, fact which leads to real challenges when a certain material has to be assigned into a class or another [64, 65]. The nowadays technologies allow practically any combination of two or more phases in order to form a composite structure but generally such structures are designed to maximize just a property of the material, other aspects being neglected.

Taking into account the DIRECTIVE 2009/28/EC it becomes necessary to change the actual point of view of composites' applications, to solve more efficiently and cheaper the use of such materials to build consumer-producer wind power stations, to solve the problem of composites usage in automotive industry not only for tuning, interior design and aerodynamic aspects but also for use, some parts of the body car, to recover or to generate energy in order to increase the efficiency of cars, especially

the future electric ones.

The studies discussed further on started with the idea to improve the electro-magnetic properties of a polymer (epoxy resin) using various powders such as carbon black, CNT or ferrite [66]. This attempt is generated by the necessity of avoiding the electrical charge for various parts of a structure which may be exposed accidentally or permanently to external actions [67].

First of all, filling the polymer is the cheapest method to alter its basic properties then, using a bi-component epoxy system with a long enough gel time is possible to obtain good dispersions of filler's particles into the polymer volume. This polymer preparation may be performed, at the beginning, with basic equipment which is not very expensive and is not involving the use of some

sophisticated apparatus [64].

It is well known and very clear that the problem of electrical conductivity of some polymers had been solved by using some expensive methods involving high technology, that is why this study is oriented toward finding cheaper solutions to solve the problem. Using the above mentioned powders and the epoxy system EPIPHEN RE 4020 – DE4020 particulate composites had been formed

and their electro-magnetic properties were studied. The methods used to disperse the electro-magnetic active powders (CNT and ferrite) had failed because some particles aggregated leading to bulk deficiencies into the polymer with secondary effects in mechanical properties of formed composite [66-68].

Using small amounts of clay or talc it was possible to obtain a better dispersion of larger amounts of active powders into the polymer volume. So, using two or more fillers it was possible to improve the electro-magnetic properties and mean time, to preserving the mechanical properties almost at the same level. The polymer composite usage is restricted also by their thermal properties due to the thermal stability of the matrix, using the above mentioned powders it might be noticed an improvement regarding the thermal behavior of formed particulate composites [68-70].

Taking into account the possibility to obtain particulate composites with some degrees of control over the electromagnetic and thermal properties the next step was to realize reinforced materials having as matrix not a polymer but a filled polymer [64, 65]. The literature regarding the mathematic description of composites mechanical properties is very rich and is based on the analysis of laminated composites starting with the basic element of the laminated material the lamina or the ply. Also it might be said that majority of the studies in this regard is oriented to orthotropic lamina's properties. It is extremely difficult to describe the properties of a multi-component composite in terms of its components properties. Generally, the final properties of a composite depend, not only on the components properties but also on the nature and quality of interfaces and on the forming technique [68].

Realizing laminated composites using individual plies involves the study of bonding properties and the properties of the laminated material, depending on the quality of bonding the ply being seen as an entity surrounded by matrix. The effects on the mechanical properties are represented by delamination, ply fracture and matrix fracture in the zone between two plies.

In laboratory conditions is difficult to obtain orthotropic arrangements of individual fibers to obtain a very regular displacement of reinforcement, to be placed inside a polymer matrix but, fortunately fabrics which are keeping the space distribution of fibers due to their structure exist. For this study the fiber fabrics were chosen to be used as reinforcement despite their relative lowered mechanical properties induced by the local deformation of fibers in the vicinity of warp and weft superposition [71].

The idea is to realize a laminated-like material with the same matrix all over the material and fabrics as reinforcement. Such material will better respond at mechanical solicitation because the efforts will load the entire matrix together with the reinforcement's layers unlike the laminated materials where the main causes of failure are given by the efforts in bonds [71].

To reach this goal it is necessary to stabilize the fabric which easily might be destroyed due the reciprocal slip of weft fibers with warp fibers. The spatial arrangement of fibers was disturbed at any attempt to cut the fabric in pieces to be molded so a method was set to stabilize the fabric by spraying a rubber solution on its surfaces. Starting with this point arises the idea to solve more than one problem by performing one operation and in this regard the rubber solution was added with carbon black and/or clay, and/or talc and so on, to ensure not only the fabric stability but also to increase de specific area of fibers, to ensure an interface with a better electrical conductivity and with better elastic properties allowing a smooth

loading transfer between matrix and reinforcement [67, 69, 71].

The adopted forming technique is a hybrid one consisting in layer by layer adding of pre-polymer imbued pieces of fabric into a glass mold followed by gas extraction through the vacuum bag method. Using pieces of stabilized fabrics, it is possible to obtain various orientations of fibers inside the material to gain a relative homogeneity of mechanical properties. The imbued prepolymer imbued pieces of material are placed into the mold inside the interval corresponding to the gel time of the polymer and the polymer chains are established not only between the reinforcement layers but also through them, due to the existence of spaces between fibers and between tows [71].

Two types of fabrics were used to investigate the opportunities of forming materials both of them are simple type fabrics, one realized from untwisted tows of carbon fibers as weft and warp, while the second one consists in alternately disposed untwisted tows of carbon fibers and aramide fibers as weft and warp. The two fabrics were chosen not only due to their low specific weight but also for their mechanical properties in both cases and more, for the electrical conductivity of carbon fibers and high strength of aramide fibers [67, 71].

Since the method was tested and worked, the next step was to form fabric reinforced materials with filled polymer matrix. The fillers were again used to change the electromagnetic and thermal properties of the composite but the matrix is the same in all the material volume. From this point it was clear that it is possible to form materials with different fillers in different layers, having the advantage of the same polymer structure of matrix in any point but with different electro-magnetic and thermal properties at different depths in material [64, 65, 71].

Fact is that electrical conductivity of a composite structure has to be higher at the surface of the material, not inside the material to avoid electrical charge, also better tribological properties has to be placed at the external layers the mechanical strength may be obtained from inside the material together with the magnetic properties [67, 72, 73].

Thus, the way in which the composites are thought, has to be changed from solving on property to solve more properties. The dimensional thermal stability may be reached by using appropriate volume fraction of carbon and aramide fibers or filling the polymer matrix not only with above mentioned fillers but also with carbon or aramide micro-fibers due to their known negative value of transverse coefficient of thermal expansion. Fillers might be used also inside the material to convert deformation energy into electric energy the carbon fiber might be used not only as reinforcement but also as an electric network to get information about material integrity and to transport electric energy [68, 74].

Starting with this point, it is possible to take into discussion even the design of fabrics to be used as reinforcement in multifunctional materials with glass fibers, to ensure mechanical strength on the main loading directions, protected by aramide fibers because they are so fragile at shocks and so on [71].

Mainly, this study is to identify ways to adapt the composites 'ingredients' to gain more and more and to make them valuable even if at the beginning they might be considered expensive. Another step of this study was to fill the epoxy with starch because its known ability to form networks when it is put in a liquid, various concentrations of starch were used in three ways of dispersing: into the first component of the epoxy system, into the second one

and directly into the pre-polymer [75, 76]. The analysis of these materials is continued at this moment but already some changes had been observed. In fact, during this study more than 200 materials were formed and some analysis were not yet performed on all of them. The results are encouraging the continuation of testing and forming new materials [77].

Improving the forming technique in order to directly form a structure such as a propeller blade for wind energy station is possible to reach better properties. Till this moment just plates of composites had been obtained to get information about general properties of materials. A wind station consists in a very high inactive structure (ensuring just the stability and height generator to be placed) using multifunctional composites it is possible to obtain electric energy also from temperature gradient and vertical currents (especially in the case of small wing stations to be used for consumer-producer citizen). Also from the automotive point of view is possible to obtain energy not only from recovering the breaking energy but also due to the movement itself. At least, it is possible to use not only a polymer but two or more if the final properties of materials are improved but in this case some studies must be performed to get information about polymers compatibility. In the case of two or more polymers, one of them - selfhealing - might be used at surface to chemically protect the entire structure. The energy is nearby but the ways in which is taken are poor, re-thinking the composites might be a starting point to try to take everything from everywhere.

A very important aspect is related to the high stability of epoxy resins which is making them almost indestructible and very difficult to neutralize. This study was started with poor funds and is still carried out with poor financial resources, the named epoxy system was chosen for its price and for its gel time long enough to allow all the molding maneuvers but that does not mean epoxy is the most suitable and valuable polymer to be used. Anyway, if the epoxy will be proved as the most valuable, its properties are recommending it for long life applications.

Studying the above mentioned materials it becomes more and more clearly that it will be very difficult to describe their properties in terms of ingredients properties or forming technique and so on, that is way the next step is connected with the use of neuronal networks to manage, describe and design a composite material or a composite structure.

#### **Conclusions**

Being used for almost a century in different applications, the epoxy resin is one of the modern materials that revolutionized the way we live. From simple use in day-by-day activities, as part of kitchen tools, for example, and up to utilization in space related research, this material seems to be omnipresent. This paper starts by presenting the spreading of epoxy resin utilization, from its discovery in Germany up until our times. For this, the first part of the article is a mix of information published all around the world, regarding the utilization of this material, highlighting thus its fast and global utilization.

The same global impact of the epoxy resin utilization seems even greater when the economic part is addressed. The second part of this study reveals the market share of the epoxy resin related activities around the world. Representing already a big part of the global market, the epoxy resin market, mainly shared between USA and Europe, is expected to grow even bigger in the future.

Being a very often used material in the research involving polymers and composites, the epoxy resin also became very utilized in research activities in Romania. The last part of this paper is presenting some research directions that the Research and Development Center for Thermoset Matrix Composites (part of the "Dunarea de Jos" University of Galati), took in the last few years. The research started by using this resin in different combinations, one final goal being to use it as part of a composite needed as material in construction of a light wind mill.

The long story of epoxy resin utilization, that started a long time ago seems to continue at an ever growing pace, especially taking into account its use in composites formation. The properties of this material have already helped the humanity to reduce the impact on the environment, to some extent, and the future utilizations will hopefully continue to do so.

#### Acknowledgements

Marius BODOR would like to acknowledge the financial contribution of the Project 12 P01 024 21 (C11) /31.08.2012 (code SMIS 50414).

#### References

- 1.\*\*\*,http://query.nytimes.com/search/sitesearch/?action=click&contentCollection®ion=TopBar&WT.nav=searchWidget&module=SearchSubmit&pgtype=Homepage#/epoxy/since1851/allresults/2/, Retrieved on 2016-08-03.
- 2. \*\*\*, http://casagrandepl.newspaperarchive.com/casa-grande-dispatch/1957-05-23/page-10/pageno-113334688?tag= epoxy&rtserp =tags/epoxy?psb=dateasc, Retrieved on 2016-08-03.
- 3.\*\*\*,http://cdnc.ucr.edu/cgi-bin/cdnc?a=d&d=DS19610303.2.58 &srpos=5&e=...en...20...1-byDA-txt-txIN-epoxy...1, Retrieved on 2016-08-03
- 4. \*\*\*, http://cdnc.ucr.edu/cgi-bin/cdnc?a=d&d=PVPN19610316.2.117& srpos=6&e=...en...20...1-byDA-txt-txIN-epoxy...1, Retrieved on 2016-08-03.
- 5. \*\*\*, http://casagrandepl.newspaperarchive.com/casa-grande-dispatch/1964-01-13/page-5/pageno-113341969?tag=epoxy&rtserp=tags/epoxy?psb=dateasc, Retrieved on 2016-08-03.
- 6.\*\*\*, http://cdnc.ucr.edu/cgi-bin/cdnc?a=d&d=DS19660104.2.45&srpos =34&e=...en...20...21-byDA-txt-txIN-epoxy...1, Retrieved on 2016-08-03.
- $7.^{***}, \ http://cdnc.ucr.edu/cgi-bin/cdnc?a=d\&d=DS19660304.\\ 2.38\&srpos=18\&e=...en...20...1-byDA-txt-txIN-epoxy-ARTICLE...1, Retrieved on 2016-08-03.$
- 8. \*\*\*, peel.library.ualberta.ca/newspapers/SGD/1971/04/14/3/Ar00303.html?query=newspapers%7Cepoxy%7C%7Cscore, Retrieved on 2016-08-03.
- 9. \*\*\*, peel.library.ualberta.ca/newspapers/SGE/1978/12/20/63/ Ar06307.html?query=newspapers%7Cepoxy%7C%7Cscore, Retrieved on 2016-08-03
- $10.\ ^{***},\ peel.library.ualberta.ca/newspapers/GAT/1984/09/05/10/Ar01000.html?query=newspapers%7Cepoxy%7C%7Cscore, Retrieved on 2016-08-03.$
- 11.\*\*\*,peel.library.ualberta.ca/newspapers/GAT/1987/09/29/1/Ar00100. html?query=newspapers%7Cepoxy%7C%7Cscore, Retrieved on 2016-08-03
- 12. \*\*\*, http://www.britishnewspaperarchive.co.uk/search/results?basicsearch=epoxy&page=2, Retrieved on 2016-08-03.
- 13. \*\*\*, http://www.britishnewspaperarchive.co.uk/search/results?basicsearch=epoxy&page=2, Retrieved on 2016-08-03.
- 14.\*\*\*, http://www.irishtimes.com/search/archive.html?q=epoxy&fromDate=&toDate=&sortOrder=oldest&rm=listresults&start=30, Retrieved on 2016-08-03.
- 15.\*\*\*, newspaper.archives.rero.ch/Olive/APA/SNL\_EN/#panel=search&search=3, Retrieved on 2016-08-03.
- 16.\*\*\*, newspaper.archives.rero.ch/Olive/APA/SNL\_EN/#panel=search&search=3, Retrieved on 2016-08-03.
- 17. \*\*\*,http://hemeroteca.lavanguardia.com/preview/1976/03/07/pagina 23/34291699/pdf.html?search=Resina%20epoxi, Retrieved on 2016-08-03

- 18. \*\*\*, http://hemeroteca.lavanguardia.com/preview/1976/03/07/pagina-38/33772687/pdf.html?search=Resina%20epoxi, Retrieved on 2016-08-03.
- 19. \*\*\*, http://hemeroteca.abc.es/nav/Navigate.exe/hemeroteca/madrid/abc/1988/02/17/054.html, Retrieved on 2016-08-03.
- 20. \*\*\*, http://www.delpher.nl/nl/kranten/view?query=epoxy&page =70&maxperpage=50&sortfield=datedesc&coll=ddd&identifier=ddd%3A011178546%3A mpeg21%3Aa0075&resultsidentifier=ddd%3A011178546%3Ampeg21%3Aa0075, Retrieved on 2016-08-03.
- 21.\*\*\*,http://www.delpher.nl/nl/kranten/view?query=epoxy&page=70&maxperpage=50&sortfield=datedesc&coll=ddd&identifier=KBNRC01%3A0000413 17%3Ampeg21%3Aa0013&resultsidentifier=KBNRC01%3A000041317%3Ampeg21%3Aa0013, Retrieved on 2016-08-03
- $22.***, http://archiviostorico.laprovinciacr.it/storico/index\_ricerca.jsp \#ricerca=Resina+epossidica&giorno\_dal=01\&mese\_dal=01\&anno\_dal=1967\&giorno\_al=01\&mese\_al=12\&anno\_al=2009\&type=and, Retrieved on 2016-08-03.$
- 23.\*\*\*, http://www.archiviolastampa.it/component/option, com\_lastampa/task,search/Itemid,3/action,detail/id,1301\_02\_1990\_0071\_0012\_18955319/, Retrieved on 2016-08-03.
- 24. \*\*\*, http://tidningar.kb.se/?q=epoxy&sort=asc&page=1, Retrieved on 2016-08-03.
- 25. \*\*\*, http://tidningar.kb.se/?q=epoxy&sort=asc&page=1, Retrieved on 2016-08-03.
- $26.\ ^{***}, http://tidningar.kb.se/?q=epoxy&sort=asc&page=2, Retrieved on 2016-08-03.$
- $27.^{***}, http://www.spiegel.de/spiegel/print/d-41955206.html, Retrieved on 2016-08-03.$
- $28.\ ^{***},\ http://www.zeit.de/1975/13/faeden-fester-als-stahl,\ Retrieved on 2016-08-03.$
- 29. \*\*\*, http://library.hungaricana.hu/hu/view/SZAK\_SZIN\_Mk\_04/?pg=0&layout=s, Retrieved on 2016-08-03.
- 30.\*\*\*, http://library.hungaricana.hu/hu/search/results/?query=epoxy&page=8&per\_page=20&simple=1, Retrieved on 2016-08-03.
- 31.\*\*\*, http://library.hungaricana.hu/hu/search/results/?query=epoxy&page=8&per\_page=20&simple=1, Retrieved on 2016-
- 32. \*\*\*, http://www.periodika.lv/#searchResults;simpleQuery=epoxy, Retrieved on 2016-08-03.
- 33.\*\*\*,trove.nla.gov.au/newspaper/article/202720512?searchTerm=epoxy&searchLimits=, Retrieved on 2016-08-03.
- 34. \*\*\*, http://trove.nla.gov.au/newspaper/rendition/nla.news-article110949352.txt, Retrieved on 2016-08-03.
- 35.\*\*\*,http://acervo.folha.uol.com.br/resultados/?q=epoxi&site=&periodo=acervo&x=0&y=0, Retrieved on 2016-08-03.
- 36. \*\*\*, http://eresources.nlb.gov.sg/newspapers/Digitised/Article/straitstimes19620126-1.2.113.13.aspx?q=epoxy&mode=advanced&f\_ct=ARTICLE&page=1&sort=oldest&token=epoxy&sessionid=c1cdc309bf4146219debcd 9469a1ec82, Retrieved on 2016-08-03.
- $37. ****, http://eresources.nlb.gov.sg/newspapers/Digitised/Article/straitstimes19650616-1.2.90.9.aspx?q=epoxy&mode=advanced&f_ct=ARTICLE&page=1&sort=oldest&token=epoxy&sessionid=c1cdc309bf4146219debcd9469a1ec82, Retrieved on 2016-08-03.$
- 38. \*\*\*, http://eresources.nlb.gov.sg/newspapers/Digitised/Article/newnation19710130-1.2.38.8.aspx?q=epoxy&mode=advanced&f\_ct=ARTICLE&page=1&sort=oldest&token=epoxy&sessionid=c1cdc309bf4146219debcd9469a1ec82, Retrieved on 2016-08-03
- 39. \*\*\*, http://www.phnompenhpost.com/national/jayavarman-vii-set-cultural-day-tribute, Retrieved on 2016-08-03.
- 40.\*\*\*, http://timarit.is/view\_page\_init.jsp?issId=82920&pageId=1181706&lang=4&q=epoxy, Retrieved on 2016-08-03.
- 41. \*\*\*, http://www.dloc.com/CA01300699/00085/search?search=epoxy, Retrieved on 2016-08-03.

- 42. \*\*\*, http://www.mediafax.ro/stiinta-sanatate/masca-funerara-din-aur-a-lui-tutankhamon-a-fost-distrus a-foto-13783910, Retrieved on 2016-08-03.
- 43. \*\*\*, http://www.lucintel.com/LucintelBrief/Lucintel-brief-Opportunity-and-Challenges-in-Automotive-Composites-Industry.pdf, Retrieved on 2016-08-13.
- 44. \*\*\*. https://www.trfa.org/erc/docretrieval/uploadedfiles/Technical%20Papers/2008%20Meeting/Maz
- umdar-Lucintel\_ppt-Composites\_industry.pdf, Retrieved on 2016-08-13.
- 45.\*\*\*,http://www.easyfairs.com/fileadmin/groups/8/Advanced\_Engineering/Advanced\_Engineering\_2016/AE\_2015\_presentations/Weds\_forum\_3\_-Nigel\_O\_Dea\_-Emerging\_Innovations\_in\_Composites-Lucintel\_UK\_Adv\_Eng\_Show\_15\_N\_ODea\_ver\_Final.pdf, Retrieved on 2016-08-13.
- 46. \*\*\*, https://www.trfa.org/erc/docretrieval/uploadedfiles/Technical%20Papers/2008%20Meeting/Mazumdar-Lucintel\_paper-Composites\_industry.pdf, Retrieved on 2016-08-13.
- 47. \*\*\*, http://www.lucintel.com/ACMA-Strategic-Growth-Opportunity-in-Composites-Industry.pdf, Retrieved on 2016-08-13.
- 48. \*\*\*, http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20%20Next%20Gen%20Materials%20TA%20Feb-18-2015.pdf, Retrieved on 2016-08-13.
- $49.\ ^{***}, http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20%20Composite%20Materials%20and%20Manufacture%20Feb-13-2015.pdf, Retrieved on 2016-08-13.$
- 50. \*\*\*, http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20%20Critical%20Materials%20TA%20Feb-13-2015.pdf, Retrieved on 2016-08-13.
- $51.\ ^{***}, http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20%20Additive%20Manufacturing%20TA%20Feb-13-2015_0.pdf, Retrieved on 2016-08-13.$
- 52. \*\*\*, http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20%20Smart%20Manufacturing%20TA%20Feb-13-2015.pdf, Retrieved on 2016-08-13.
- $53.\ ^{***},\ http://energy.gov/sites/prod/files/2015/02/f19/QTR\%20Chapter\%208\%20Webinar-\%20Industry\%20\%20Manufacturing\%20Feb\%20\%2011\%202015_v2.pdf,\ Retrieved\ on\ 2016-08-13.$
- 54. \*\*\*, http://www.plasticseurope.org/documents/document/20150227150049-final\_plastics\_the\_facts\_2014\_2015\_260215.pdf, Retrieved on 2016-08-13.
- 55. \*\*\*, http://www.plasticseurope.org/documents/document/20131014095824-final\_plastics\_the\_facts \_\_2013\_published\_october2013.pdf, Retrieved on 2016-08-13.
- 56. \*\*\*, http://www.corepla.it/documenti/5f2fa32a-7081-416f-8bac-2efff3ff2fbd/Plastics+TheFacts+2015.pdf, Retrieved on 2016-08-13.
- 57. \*\*\*, http://www.eucia.eu/userfiles/files/20141008\_market\_report\_grpcrp.pdf, Retrieved on 2016-08-13.
- $58.\ ^{***}, http://www.avk-tv.de/files/20130917\_market\_report\_2013\_2.pdf, Retrieved on 2016-08-13.$
- 59.\*\*\*,http://www.eucia.eu/userfiles/files/Composites\_Market %20Report\_2015.pdf, Retrieved on 2016-08-13.
- 60. \*\*\*,http://www.komposittforbundet.no/admin/common/getimg.asp?FileID=1200, Retrieved on 2016-08-13.
- 61.\*\*\*,http://www.easyfairs.com/fileadmin/groups/8/Advanced\_ Engineering/Advanced\_Engineering\_2016/AE\_2015\_presentations/ Weds\_\_forum\_3\_-\_Nigel\_O\_Dea\_-\_Emerging\_Innovations\_in\_Com posites-Lucintel\_\_UK\_Adv\_Eng\_Show\_15\_N\_ODea\_ver\_Final.pdf, Retrieved on 2016-08-13.
- 62. \*\*\*, http://cdn.intechweb.org/pdfs/13343.pdf, Retrieved on 2016-08-13.
- 63. \*\*\*\*, http://www.swananys.org/pdf/bigpicture.pdf, Retrieved on 2016-08-13.
- 64. CIRCIUMARU, A., BRIA, V., ROMAN, I., ANDREI, G., DIMA, D., BIRSAN, L-G., Annals of DAAAM, 2011, p. 0059.
- 65. CIRCIUMARU, A., BIRSAN, I.-G., ANDREI, G., BRIA, V., POSTOLACHE I., Academic Journal of Manufacturing Engineering, **8**, 2010, p. 30.

- 66. ANDREI, G., DIMA, D., BIRSAN, I., ANDREI, L., CIRCIUMARU, A., Mat. Plast., **46**, no. 3, 2009, p. 284.
- 67. MURARESCU, M., DIMA, D., ANDREI, G., CIRCIUMARU, A., Annals of DAAAM, 2011, p. 0925.
- 68. CIRCIUMARU, A., ANDREI, G., DIMA, D., BIRSAN, I,-G., BRIA, V., Annals of DAAAM & Proceedings, 2010, ISSN: 1726-9679.
- 69. CIRCIUMARU, A., BIRSAN, I.-G., BRIA, V., POSTOLACHE, I., Annals of UDJG, 2, 2009, p. 149.
- 70. DIMA, D., MURARESCU, M., ANDREI, G., CIRCIUMARU, A., Annals of DAAAM & Proceedings, 2010, ISSN: 1726-9679.
- 71. CIRCIUMARU, A., ANDREI, G., BIRSAN, L-G., SEMENESCU, A., Mat. Plast., **46**, no. 2, 2009, p. 211.
- 72. BIRSAN, L-G., CÎRCIUMARU, A., BRIA, V., UNGUREANU, V., Tribology in industry, **31**, 2009, p. 33.

- 73. BRIA, V., DIMA, D., ANDREI, G., BIRSAN, I.-G., CIRCIUMARU, A., Tribology in industry, **33**, no. 2, 2011, p. 104.
- 74. MURARESCU, M., DIMA, D., ANDREI, G., CIRCIUMARU, A., Dig J Nanomater Biostruct, **9**, 2014, p. 653.
- 75. BRIA, V., CIRCIUMARU, A., BIRSAN, I.-G., Mat. Plast., **48**, no. 2, 2011, p. 189.
- 76. BIRSAN, I.-G., ROMAN, I., BRIA, V., UNGUREANU, V., CIRCIUMARU, A., Annals of DAAAM, 2011, p. 0285.
- 77. BRIA, V., CIRCIUMARU, A., BIRSAN, I.-G., ANDREI, G., DIMA, D., ROMAN, I., Annals of DAAAM & Proceedings, 2011, ISSN: 1726-9679

Manuscris received: 10.01.2016

# Reinnoiti-va abonamentele la REVISTA DE CHIMIE si revista MATERIALE PLASTICE pe anul 2016

Pretul unui abonament la REVISTA DE CHIMIE este de: 200 lei pentru persoana fizica 400 lei pentru universitati 500 lei pentru societati comerciale

## si la revista

MATERIALE PLASTICE este de: 150 lei pentru persoană fizica 200 lei pentru universitati 300 lei pentru societati comerciale Conturi: S.C. BIBLIOTECA CHIMIEI SA

RO20 RNCB 0072049700600001 BCR sector 1 RO51 TREZ 7065069XXX002561 Trez. sect. 6

C.U.I. RO 13751581