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REVIEW ON EPOXY POLYMERS COMPOSITES WITH IMPROVED PROPERTIES

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ABSTRACT

An overview of recent developments in the chemistry of synthesized multifunctional epoxy polymers and their composites is presented in this paper. The resins or different reactive precursors are flame retardant, thanks to the presence of phosphorus, sulfur and nitrogen. They can be used alone or be added in bulk to the polymers, to increase their properties (thermal, mechanical, flame retardant, electrical, dielectric, anticorrosive, viscosimetric, viscoelastic, rheological, etc.).In this review, we present synthetic strategies that have been put in place to functionalize the different spacer arms.

Keywords: polymer, resin, precursor, multifunctional polymers, flame retardant, thermal and rheological properties.

INTRODUCTION

Currently, epoxy polymers have very interesting physicochemical properties, but they are not always the same with regard to their properties for fire resistance. Among the different approaches that can be considered to improve the fire properties of a polymeric resin, there are two strategies that attract the attention of the scientific and industrial community: on the one hand, the synthesis of new spacer arms of composite materials with good thermal stability and good fire behavior [1 - 2] and on the other hand, to intervene at the level of the macromolecular matrix itself, by grafting functions to improve its thermal stability [3 - 4].

This review concerns the synthesis of polymers that can be used as precursors, hardeners and additives in conventional resins. So, the choice fell on the chemical modification of various precursors, namely: bisphenol A, phosphorus trichloride, trichlorethylene and hexachloro cyclotriphosphazene to prepare new materials with thermal, mechanical, viscosimetric, rheological, high behavior. The different spacer arms can be incorporated in the macromolecular chains during the homopolymerization reaction by modifying the surface of the polymeric material. The chemical transformations of phosphorus-containing compounds and their participation in all stages of the polymer combustion process are not yet fully understood. Phosphorus-nitrogen derivatives are known for their good thermal properties and are part of a new generation of non-halogenated flame retardants [5]. They are considered as ecological fireproof [6].

In this review, we present synthesis strategies that have been put in place to functionalize the different precursors. These strategies are based on the chemical modification of the spacer arms by reactive functional groups leading to multifunctional epoxy polymers used in applications such as polymer materials, inhibitions, coatings, etc.

Thermal and flame retardant properties

Traditionally, brominated reactive compounds [7] are used as monomers with epoxy resins to obtain flame retardant materials. However, flame retardant epoxy resins containing bromine can produce corrosive smoke as well as toxic halogenated products with deleterious effects on the environment and on human health. Recently, research on halogen-free flame retardant epoxy architectures has received a lot of attention [8 - 9]. Phosphorylation is considered one of the most effective methods for conferring flame retardancy on epoxy resins [10]. The phosphate-based epoxy resins can exhibit excellent flame retardancy only by the use of curing agents. Some studies have indicated that the effectiveness of the flame retardant is improved significantly when phosphorus and nitrogen simultaneously existed in the epoxy curing system. Therefore, the synergistic phosphorus-nitrogen effect on flame retardancy is very interesting [5]. Indeed, the thermosetting epoxy resins can be flame retarded either by incorporating flame retardant additives, or by co-polymerizing with reactive flame retardants, because they have not only a wide range of thermal stabilities, but can also improve the flame retardant properties of polymers and their composites.

The different polymers studied are respectively the diglycidyl ether of bisphenol A (DGEBA) [11], diglycidyl ether diphenyl (DGEDP) [12], diglycidyl N-(3-triethoxy-silane propyl) (DGTESP) [13], diglycidyl ether diphenyl sulfone (DGEDPS) [14], triglycidyl ether triphenyl methane (TGETPM), tetraglycidyl ether terephthalydene bis-para phosphoric ester (TGETPEP)and hexaglycidyl ether terephthalydene bis-para phosphoric ether (HGETPEP) [15]. The semi-developed formulas of these polymers are shown in Fig. 1.These chemical

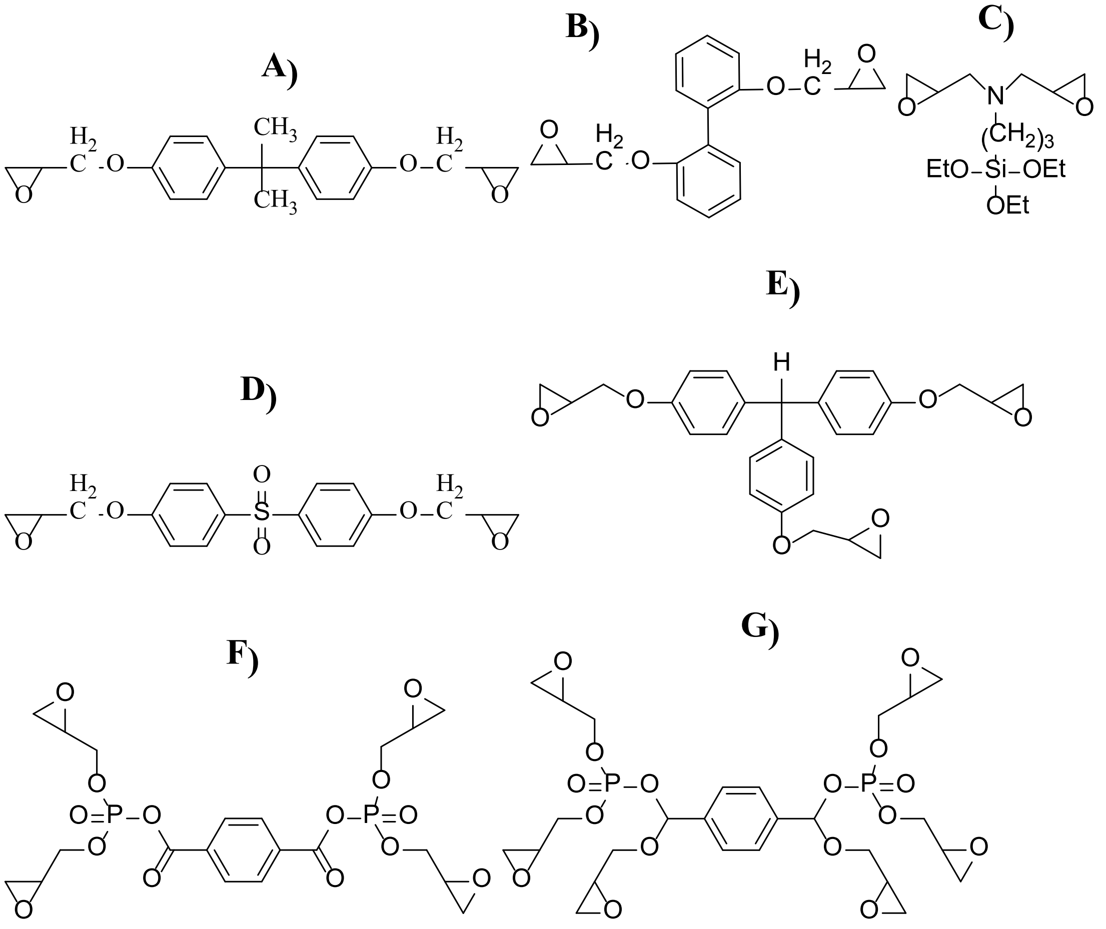

Fig. 1.A) Diglycidyl ether of bisphenol A (DGEBA); B) diglycidyl ether diphenyl (DGEDP); C) diglycidyl N-(3-triethoxy-silane propyl) (DGTESP); D) diglycidyl ether diphenyl sulfone (DGEDPS); E) triglycidyl ether triphenyl methane (TGETPM); F) tetraglycidyl ether terephthalydene bis-para phosphoric ester (TGETPEP); G) hexaglycidyl ether terephthalydene bis-para phosphoric ether (HGETPEP).

structures have aromatic rings and epoxide groups which improve their thermal and flame retardant properties

Cyclotriphosphazenes with nitrogen and phosphorus atoms have common thermal properties, such as flame retardancy. These are inorgano-organic materials of oligomeric or polymeric nature [16].When cyclotriphosphazenes are incorporated in the matrix of thermosetting polymers, they can improve the thermal behavior and flame resistance of the polymers. Due to the novelty in their structure, functionality and versatility in chemical processing, its structure is shown in Fig. 2-A). Liu and Wang [2] used hexakis (4-hydroxy methylene phenoxy) cyclotriphosphazene (PN-OH) as the intermediate compound to synthesize the cyclotriphosphazene epoxy resin. This resin has very interesting thermal and flame retardant properties (Fig. 2-B).

Containment of radioactive waste

Radioactive waste has a solid, liquid or metallic form. To be handled easy and safely, they are often used as waste packages. The packaging could ensure that the radioactive elements present in the waste do not migrate. The latter forms a barrier between the radioactive elements and the storage medium [17].The conditioning of solid and liquid radioactive wastes such as Ion Exchange Resins (REI) is used, after their characterization, in cement matrices because of its good mechanical, physical and chemical properties [18]. Cementing has led to a first ratification, which encourages researchers in the field of radioactive waste management to focus more on the cementing process optimizing [19]. They studied the performance of the confinement matrix while introducing the epoxy novolac polymer called diglycidyl 4-(para-chlorophenyl)-5-ethoxycarbonyl-6-methyl-2-thiol-1,5-dihydropyrimidine (DGCPEMTDHP) [20] to the formulation of the containment matrix. Its semi-developed formula is shown in Fig. 3.

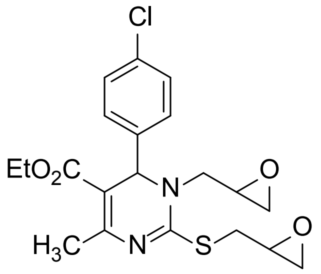

Fig. 3. Diglycidyl 4-(para-chlorophenyl)-5-ethoxycarbonyl-6-methyl-2-thiol -1,5-dihydropyrimidine (DGCPEMTDHP).

Mechanical properties

Several authors have described the synthesis of the tetrafunctional resin -tetraglycidylof ethylene dianiline (TGEDA) (Fig. 11) [21].The method described by N. R. Jagannathan and F. G. Herring gives the best results [22].These authors recommend the use of a large excess of epichlorohydrin relatively to the diamine.Bibenzyl (ethylene dianiline), of the methylene dianiline family, the presence of a methylene bridge more than TGMDA could bring additional physicochemical properties. Such

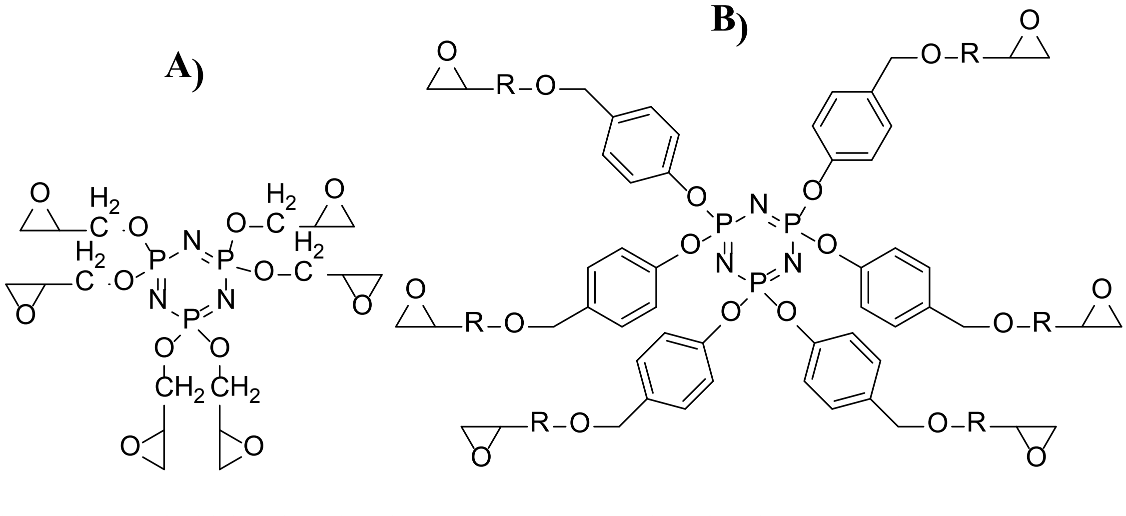

Fig. 2. A) Hexaglycidyl cyclotriphosphazene (HGCP); B) Cyclotriphosphazene containing an epoxide group.

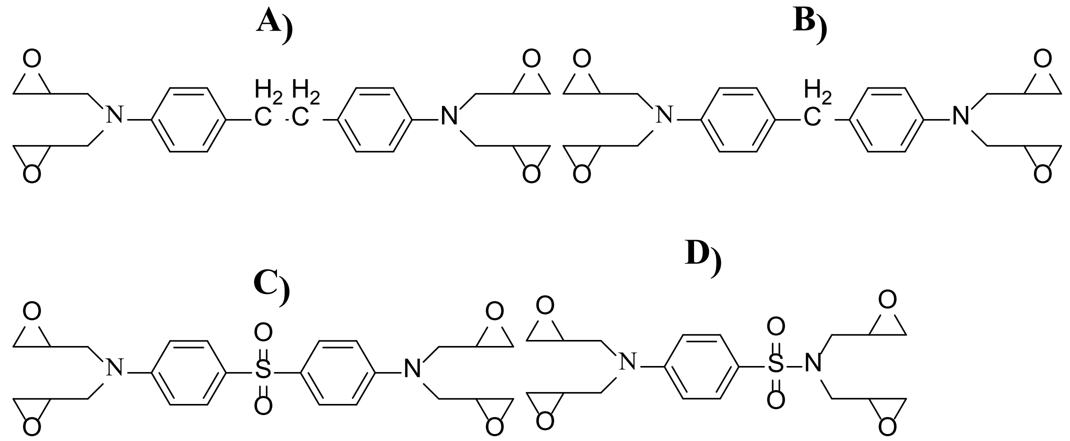

Fig. 4. A) Tetraglycidyl of ethylene dianiline (TGEDA); B) Tetraglycidyl of methylene dianiline (TGMDA); C) Tetraglycidyl of sulfone dianiline (TGSDA); D) Tetraglycidyl of 4-amino benzene sulfonamide (TGABSA).

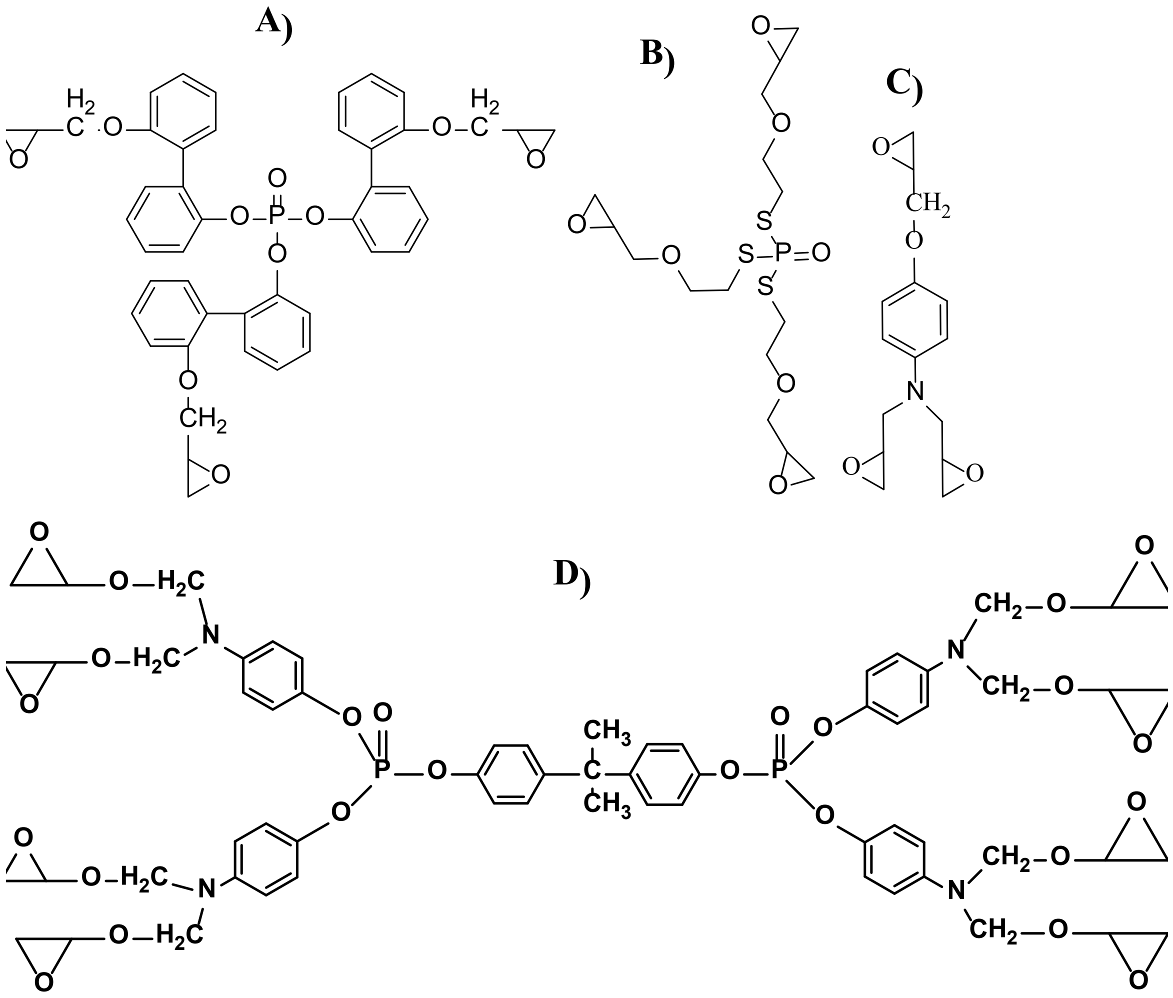

Fig. 5. A) Triglycidyl ether tri-diphenyl of phosphoric ester (TGETDPEP), B) Triglycidyl tri-ethyl ether of phosphorus tri-thioate (TGETP), C) Triglycidyl para-aminophenol (TGPAP); D) Octaglycidyl tetra para amino phenol of bisphenol A (Bis-para phosphoric ester).

tetrafunctional epoxy polymers are: tetraglycidyl of methylene dianiline (TGMDA), tetraglycidyl sulfone dianiline (TGSDA) [23] and tetraglycidyl of 4-amino benzene sulfonamide (TGABSA) [21]. These polymers were synthesized via aromatic diamines, where the active hydrogens of their amine functions react with an excess of epichlorohydrin to give four epoxide groups. They showed very good mechanical properties, (Fig. 4.).

Viscosimetric properties

Viscosity represents the deformation of bodies under the effect of constraints applied taking into account time. Generally, it studies the relation between stress and strain as a function of the velocity gradient [24].The viscosity was defined by Newton as the coefficient of proportionality between the shear stress and the velocity gradient.

Phosphorus epoxy resins: triglycidyl ether tri-

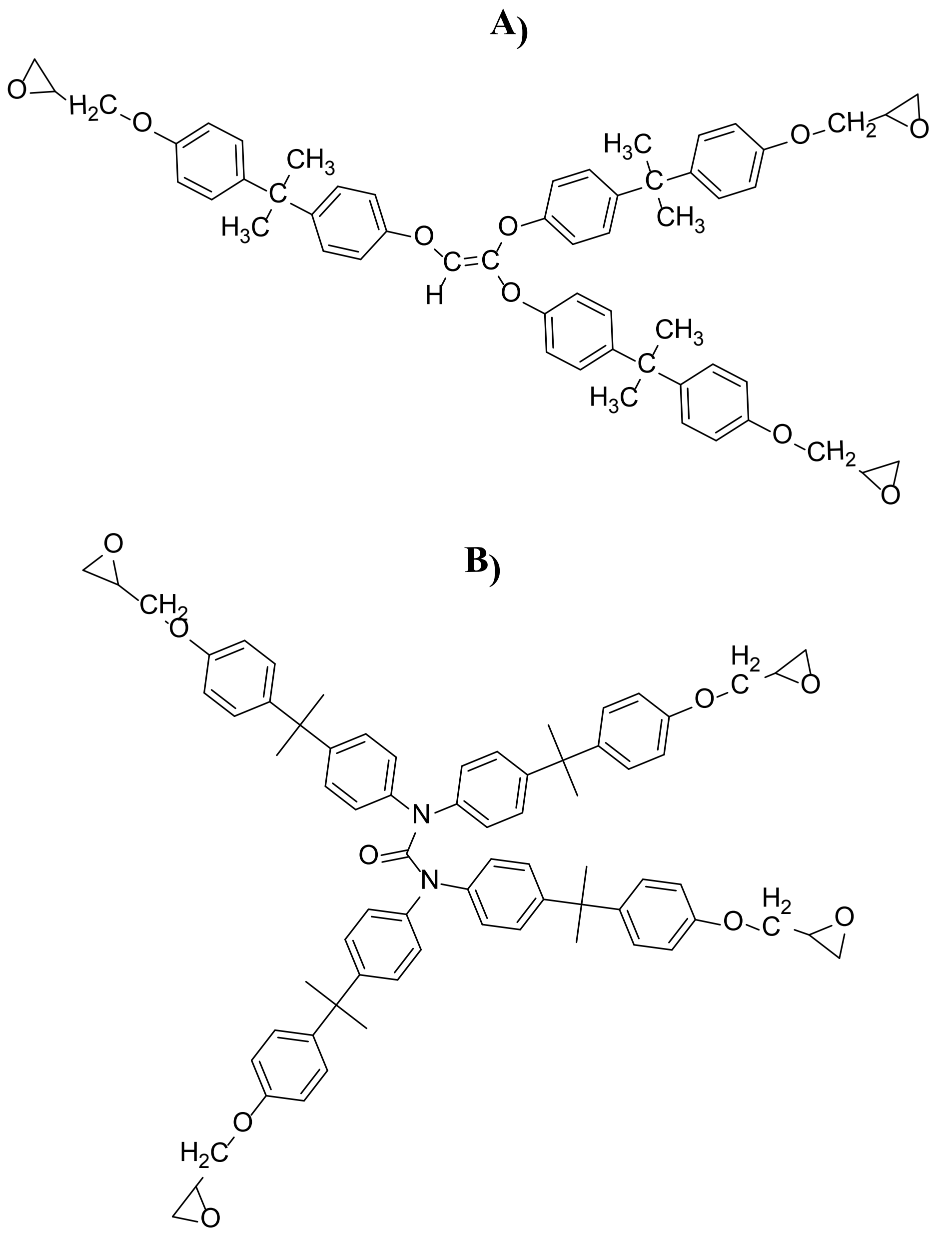

Fig. 6. A) Triglycidyl ether ethylene of tri-bisphenol A (TGEEBA); B) Tetraglycidyl ether urea of tetrabisphenol A (TGEUTBA).

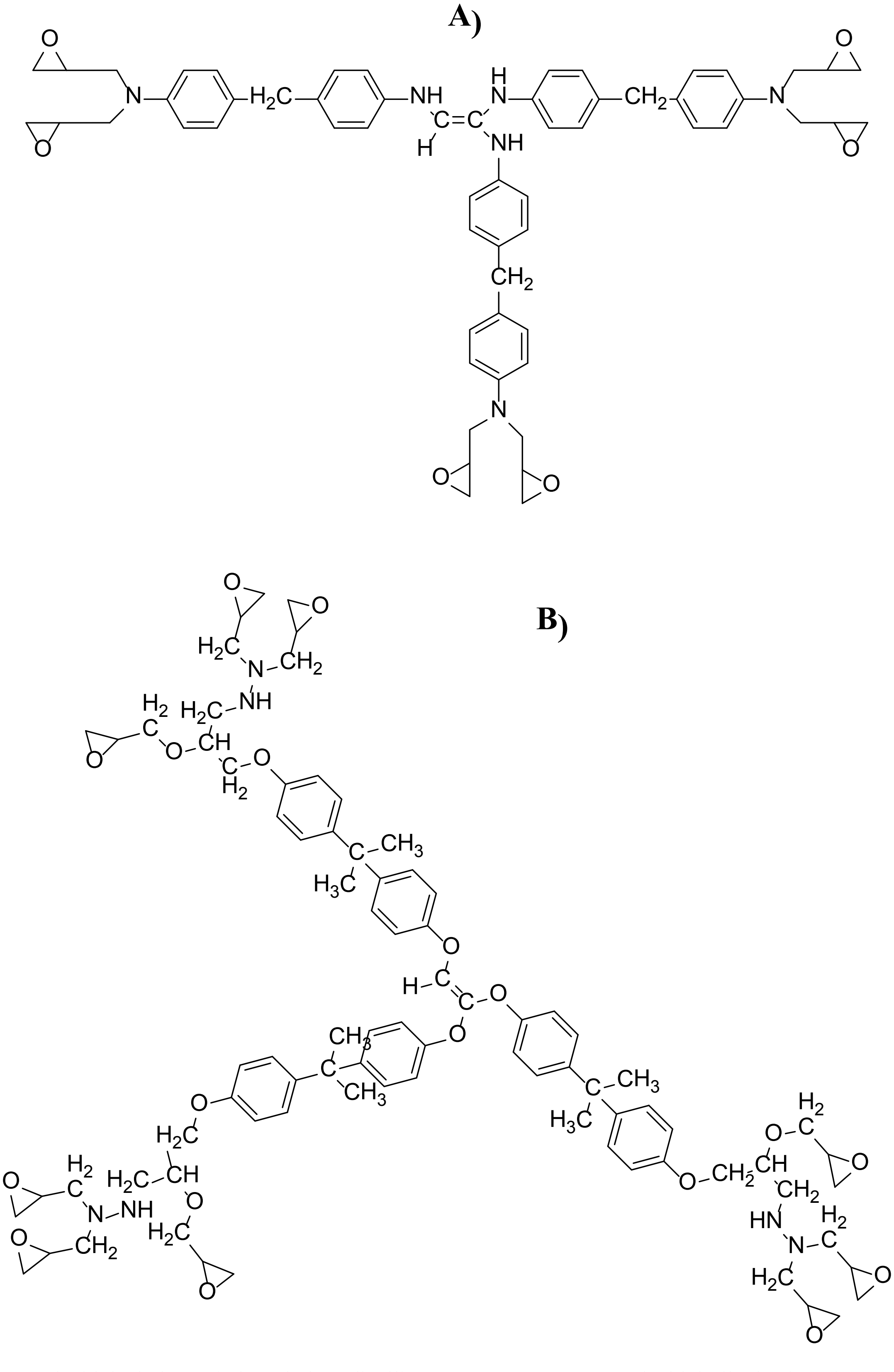

Fig. 7. A) Hexaglycidyl ethylene of tri-methylene dianiline (HGEMDA); B) Nanoglycidyl trihydrazine tripropoxy tribisphenol A of ethylene (NGTHTPTBAE).

diphenyl phosphoric ester (TGETDPEP) [25], triglycidyl triethyl ether of phosphorus tri-thioate (TGETP) [26], octaglycidyl tetra p-aminophenol of bisphenol A (Bis-para ester phosphoric) (OGTPAPBABPEP) [27] and triglycidyl para-aminophenol (TGPAP) [28-29], have viscosimetric properties superior to that of the difunctional resin diglycidyl ether of bisphenol A (DGEBA). These semi-developed formulas are mentioned in Fig. 5.

Rheological properties

The multifunctional epoxy polymers, respectively the triglycidyl ether ethylene of tri-bisphenol A (TGEEBA) (Fig. 6-A) [30] and the tetrafunctional tetraglycidyl ether urea of tetra-bisphenol A (TGEUTBA) (Fig. 6-B) [31] have very important rheological properties compared to difunctional resins. This is explained by the number of epoxide groups formed in the macromolecular matrix.

Bekhta et al. [32] and Hsissou et al. [30] studied the rheological properties respectively the elastic behavior and the vitreous behavior as a function of the angular velocity of the composites (TGEUBS/MDA/TSP) and (TGEEBA/MDA/NP).The results showed that the rheological behaviors increase with the addition of loading trisodium phosphate (TSP) and natural phosphate (NP) incorporated into the prepared composites. Several authors have shown that the addition of inorganic fillers in composites gives very interesting rheological properties [33].

Coating behavior

Polymers are the most used materials in the chemical industry because of its various advantages of being lightweight, have better fire resistance and show resistance to chemicals. The composite handles widely used in the chemical industry are used in the manufacture of structural supports, storage tanks, exhaust stacks and blowers, columns, pumps, reactors. The hexaglycidyl ethylene of tri-methylene dianiline (HGEMDA) (Fig. 7-A) [34] and the nanoglycidyl trihydrazine tripropoxy tribisphenol A of ethylene (NGTHTPETBA) (Fig. 7-B) [35 - 36] show that these deniers have very interesting anticorrosive properties. This is explained by the presence of epoxy groups and aromatic rings. In addition, the more the number of free doublets increases, the better the corrosion resistance will be, which implies that the free doublet is adsorbed on the metal surface by Van der Waals bonds [37].

CONCLUSIONS

This bibliographic review allowed us to appreciate the various efforts made in recent years by different researchers to try to shed light on all the phenomena that occur in composite materials based on different precursors. There is currently a very wide variety of polymeric materials on the market. However, research continues to develop new resins that would give much more interesting performance. In this context, we noticed that research is focused on different spacer arms for the synthesis of multifunctional polymers for the development of ecological materials. This review describes a certain number of approaches adopted in order to improve thermal, flame retardant, mechanical, viscosimetric, rheological and anticorrosive behaviors of the multifunctional polymers.

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