TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 65, Issue Secial IV, December, 2022

IMPORTANCE OF THE BASIC REACTIONS IN THE MANUFACTURE OF SYNTHETIC RESINS

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Abstract: *In our days, natural resins have been totally replaced by synthetic resins. Synthetic resins are very important if we think about composite materials. Synthetic resins are divided into two classes, known as thermosetting and thermoplastic resins. This paper purpose is to clarify the importance of the basic reactions in the manufacture of synthetic resins: polymerization, polycondensation, polyaddition. The synthetic resins are produced by controlled chemical reaction, in the presence of the necessary solvent and catalysts under the proper conditions of temperature and time. Different polymerization, polycondensation and polyaddition techniques are known to obtain synthetic resins suitable for different uses. The main objective of the paper is to provide a clearer vision of how synthetic resins are formed. Synthetic resins are marketed or used in various forms and therefore their characterization and formation is very important. This work is a review of the literature on the basic reactions that occur in the production of synthetic resins and presents theoretical research about the importance of the basic reactions in the manufacture of synthetic resins.*

Key words: *synthetic resins, chemical reactions, polymerization, polycondensation, polyaddition.*

1. INTRODUCTION

Synthetic resin is a chemical organic compound mainly composed of atoms such as carbon, hydrogen and a little oxygen, nitrogen and sulfur combined with certain chemical-bond [1]. Synthetic resins commonly used in plastic composites are polymerization resins (vinyl, acrylic), polycondensation resins (polyester, amine, phenolic) and polyaddition resins (polyurethanes, epoxy) [2].

The chemistry of synthetic resins is part of organic chemistry and requires a thorough knowledge of molecular substances and manufacturing methods. The formation of macromolecular products takes place in three main ways: polymerization, polycondensation, polyaddition, differentiation between them based on the different reaction mechanism of the reactions that take place [3].

The desired property of a synthetic resin greatly depends on its method of preparation and its field of application [4]. One of the most important stages involved in the production of polymer products, from the synthesis of raw materials to the manufacturing of the finished product, is the polymer material processing [5].

This paper purpose is to clarify the importance of the basic reactions in the manufacture of synthetic resins: polymerization, polycondensation, polyaddition.

Composite materials are made up of a reinforcement or an additive, chosen according to the properties and field of use of the designed product, and a polymer matrix that serves as a support for the dispersed phase.

The matrix can be a thermoplastic polymer or a thermosetting polymer. The role of the matrix is to link the reinforcing fibres, distribute the constraints, provide the chemical resistance of the structure and give the desired shape to the final product [6]. The essential difference between a thermoplastic polymer and a thermoset polymer is how they respond to high temperatures.

The thermosetting polymer undergoes an irreversible transformation by heating, not being able to return to its initial state, and the thermoplastic polymer reaches the point of softening and melting, being able to return to its initial phase by cooling.

Thermosetting polymeric composites have cross-linked or network structures with covalent bonds with all molecules. They can be expose to repeated softening and melting, without being chemically transformed, then hardening, by cooling. They cannot be reshaped by cross-linking process. Representative for this are epoxies, polyesters, phenolics, urea's, melamine, silicone, and polyimides [7]. 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 moulding large parts with short, long or woven fibres.

The most frequently used thermosetting matrices are polyesters, phenoplasts, epoxy resins and polyimides [8]. Thermosetting plastics comprise large chains of repeated chemical molecules, which undergo an irreversible reaction to form close-networked structure with strong covalent bonds ("cross links"). This cross-linked structure provides the material with rigidity when cool but cannot be softened again by the application of heat, thus preventing flow. If excess heat is applied, thermoset materials will degrade. Consequently, they are not weldable [9].

Epoxy resins are among the best thermosetting materials used as polymer matrices for the formation of polymer composites [10]. Thanks to its manifold compositions, curing processes and resultant adhesion, chemical and heat resistance and mechanical behaviours, epoxy resin is one of the most eminent high-performance thermosetting polymers widely used in the fields of coatings, automobiles, electrical systems and electronics, adhesives, construction, aerospace composites and so on [11], [12].

Epoxy resins are prepared by condensation reaction between epoxy compounds with the multifunctional monomeric unit. Being soluble in a series of common organic solvents, they are often delivered in the form of a solution. The most common epoxy resin is synthesized by the condensation reaction of epichlorohydrin and bisphenol A.

The commonly used hardening agents are monoamine, diamine, polyamine, urea resin, phenolic resin, acids, and various acid anhydrides. Depending upon the property requirements, various types of hardening agents are employed [13].

Epoxy resins used for polymeric composite materials manufacturing are deliberately prepared with an excess of epoxy content balanced to hardener content. This is done to guarantee that the hardener is completely reacted during the cure time and is critical to remain in the network and become plastic [14].

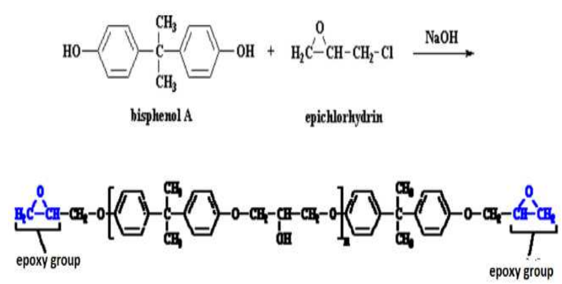

Fig.1. The relationship to obtain DGEBA [9].
(DGBA- diglycidyl ether bisphenol A)

The properties of DGEBA epoxy resin (Fig.1) depend strongly on the length of the polymer chains. Low-molecular-weight long polymer chains epoxy resins tend to be in the liquid state, and high- molecular-weight epoxy resins may be in the form of jelly or solid. DGEBA oligomers usually contain several certain hydroxyl groups that play an important role as catalysts in the kinetics of the curing process. In addition, two oxirane (ethylene oxide – C2H4O) function groups enable to create epoxy with a three-dimensional structure. The oxirane is highly reactive to nucleophilic compounds such as amines; thus, the highest cross-linked level of DGEBA epoxy resin is achieved through the addition of aliphatic or aromatic diamines [15].

The reinforcements must be chosen according to the demands of the technology. One of the crucial obstacles associated with polymeric composite materials manufacture is that of void formation during impregnation and cure time. As these gaseous voids become capture within the matrix, stress concentrations can be settled within the matrix.

These can derive in various ways: during the mixing of the resin with hardener or during the textile reinforcement filling of cavities.

The time between the polymeric composite chemical reactions which take place as the cure of thermosetting synthetic resins, as volatile gases are released and become capture in the crosslinked resin [14].

Recently, epoxy resins modified with different products have started to be used on a large scale.

The modification of these resins must be based on the reaction capacity of the epoxy and hydroxyl groups.

At present, epoxy resins are mainly prepared by the condensation of bisphenol A. However, the high production cost of bisphenol A epoxy resins and backward production process restricts its practical lead in the market.

Another limitation is its toxicity to the human body and the environment [16].

Thermoplastics polymers consists of linear or divided chain molecules having strong intramolecular bonds but weak intermolecular bonds.

They can be adjust by implement of heat and pressure and are either semi crystalline or amorphous in structure [17].

The article is structured on three concepts namely: manufacture of synthetic resins which includes the basic reactions in the manufacture of synthetic resins: polymerization, polycondensation and polyaddition.

Another idea is that of resins analysis with the determination of epoxy groups, a SWOT analysis of synthetic resin materials and finally the conclusions.

2. MANUFACTURE OF SYNTHETIC RESINS

The epoxy resins are distinguished by their chemical versatility and their expanding usefulness in a wide variety of applications. Their most attractive properties in general are the ability to "harden" (cross-link) with only very low shrinkage and without the formation of any volatile reaction products, and the excellent mechanical and electrical properties of the cross-linked resins.

The hardened products have excellent adhesion to many materials and possess good resistance to moisture and chemicals [18].

2.1 Polymerization

During polymerization, little molecules, called monomers, are synthesized to create big molecules or a macromolecule.

More of such macromolecules together form a polymer [19]. It is well established that the performance and quality of a polymeric material is determined by the manufacturing cycle which is accompanied by the exothermic polymerization of the thermoset resin.

Thermoplastic materials also comprise long chains of repeated chemical units called “mers” which when linked together form “polymers”. This reaction is known as “polymerization”; for example, polyethylene (known commercially as “polythene”) is produced when the ethylene monomer is polymerized.

The links between long chain molecules are essentially linear although branched molecules can also be formed by varying the polymerization process variables [20].

The gel time of the resin is the interval in which the polymerization reaction (started with the addition of the hardener) does not affect the entire volume and the prepolymer mixture. After the expiration of this interval the mixture becomes a consistent gel.

n – degree of polymerization is the number of monomer molecules that combine to form the polymer.

When $n < 50$, it is oligomers (lower polymers with $n = 2,3, 4, ...20$ and mesomeres with $n = 20$-50). When $n > 50$, we are talking about high polymers or polymers (consider true macromolecular compounds).

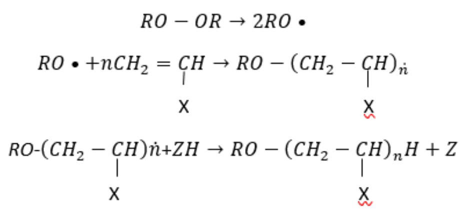

Fig.2. Polymerization reaction [3]
n – degree of polymerization

$$p = \frac{x}{N_0}, (1)$$

Where:
$p -$ the degree of conversion;
$N_0 -$ the number of molecules to be rearranged;
$x -$ the number of molecules of the product formed.
Then:

$$n = \frac{1}{1 - P}, (2)$$

Free-radical polymerization is applicable to a wide range of monomers and is widely applied for the commercial synthesis of polymers [21]. Characteristic of polymerization resins is the fact that the reaction does not proceed in stages, but the final product is obtained directly (Fig.2), which is why it is difficult to find a compromise between a low enough viscosity. This requires a low molecular weight and good mechanical properties, specific to a high molecular mass [3].

If the condensation products of phenol with formaldehyde (resoles or novolaks) are used as initial materials, when they react with epichlorohydrin, epoxy resins are formed and contain a large amount of epoxy groups, depending on the molecular weight of the novolak or solvent used. Encapsulation of organic particles with polymers can increase their stability and functionality.

Suspension polymerization, emulsion polymerization, and mini-emulsion polymerization are common methods of producing polymer-pigment composites. Such methods are often time consuming and result in the production of polydisperse polymer-pigment particle composite particles [22].

2.2 Polycondensation

There are many reactions underlying the polycondensation. Polycondensation is the term used to describe polymers formed as a result of reactions involving the condensation of organic materials (Fig.3) in which small molecules are split out [23]. Methylene derivatives or novolaks are formed in an acidic environment where the phenolic compound is in excess.

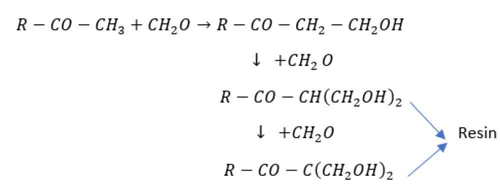

Fig.3. Condensation reaction of ketones with aldehydes [3].

In chain-growth polycondensation, the polymer end group is activated. This activation changes the reactivity of the substituents attached to the aromatic ring, so that a chain-growth polycondensation takes place [24].

Polyethylene terephthalate was obtained by the polycondensation reaction of ethylene glycol and terephthalic acid [8]. Polymers are much more commonly used, with unsaturated styrene-hardened polyesters having most low-to-medium performance applications and epoxy or more sophisticated thermosets having the higher end of the market [20].

2.3 Polyaddition

Polyaddition is based on obtaining a macromolecule by adding the reactive groups of bi- or oligofunctional reactants, without forming secondary products (Fig.4).

Ester polymers are easily obtained from cyclic esters with 6 carbon atoms which, under the influence of heat or a catalyst, can turn into polyester. Amide polymers are obtained in a similar way starting from amino acid lactams.

$$HO - R_1 - OH + OCH - R_2 - NCO \rightarrow$$
$$\rightarrow -O - R_1 - O - CO - NH - R_2 - NH - CO -$$

Fig.4. Polyaddition reaction

Urethane polymers are obtained by adding alcohols to isocyanates [3].

In polyaddition, the ratio between the reactants, the reaction environment, the reactivity of the components and the impurities contained by them play a very important role.

3. RESINS ANALYSIS

For the determination of epoxy groups, the reaction with hydrochloric acid or hydrobromic acid is used, which proceeds with the breaking of the ring and the formation of chlorohydrine.

The content of epoxy groups x, in %, is calculated using the formula [25]:

$$x = \frac{0.0043\,VK}{g} \bullet 100 = 0.43 \bullet \frac{VK}{g}, \quad (3)$$

where: V [ml] - is the volume of 0.1 n hydrobromic acid consumed for the titration of the resin solution;

K-the correction coefficient for bringing the concentration of the hydrobromic acid solution up to 0.1n;

g [g]- the amount of resin;

0.0043- the amount of epoxy groups, corresponding to 1ml of 0.1n hydrobromic acid solution.

Linear polymers are obtained from monomers that correlated, in simple and long chains.

Divided polymers result from complex reactions that attach to the main chain usually shorter segments, similar or different from its structure. The divided structure decreases the degree of compaction of the polymer, a fact highlighted by the decrease in the density of the polymer as the division is more intense.

Polymers with side bonds are obtained either during the synthesis process or by irreversible chemical reactions, which usually take place at high temperature. Often these side bonds between molecular chains involve atoms or radicals that are attached by covalent bonds to the long chains.

Polymers with a network structure are the result of the synthesis of monomers with three active covalent bonds

4. SWOT analysis of synthetic resin materials.

4.1. Strengths

Many synthetic resins have a relatively simple structure because they consist of identical repeating constitutional units (structural units or monomers). Therefore, they are called polymers. Some polymer properties, including tensile and impact strength, are specifically regulated by its short molecules. A great advantage of polymer materials is that they can be easily processed to give them the desired shape.

Polymers are involved in all important new technologies such as: construction industry, transports, naval industry, aeronautical industries, aerospace industries, chemical, pharmaceutical, dyes and paper industries, food industry, electrotechnical and electronic industries, telecommunications and agriculture. The texture and behaviour of articles made of polymers depend on the nature of the bonds between atoms and molecules, as well as on the type of atom or molecule from which it starts. Thus, polymers such as plastic have a major advantage over other materials, because they can be designed according to the requirements of each application. Given the diversity of needs in the different fields, synthetic polymer materials (simple or composite) are a very current and dynamic subject.

As advantages of polycondensation we can say that there are many possible reaction sites and the reaction speed is high. Also, there is good thermal control.

4.2. Weaknesses

A weaknesses line in polymeric composite materials and synthetic resin manufacture is considered the possibility of recovery and recycling of these materials to protect the ecosystem. So, current trends in polymer processing science are oriented toward this actual problem. As a disadvantage of the polycondensation reaction, we can say that the reaction speed is weak. The temperature rises in the middle, which causes degradation problems. There is a need for a reaction control and a solvent that is the same for both monomer and polymer.

4.3. Opportunities

The advantages of thermosets are that they do not release volatile substances during the creation of lateral chemical bonds and can be injected using low pressures, at room temperature. Also, in many cases, conventional plastics processing techniques can be used to produce injected or molded composite elements.

In the construction materials industry, organic and small polymers are used, because during the manufacturing process only these go through a plastic phase, which makes their processing easier.

The mechanical resistances are dependent on the strength of the bonds within the molecular chains and between the chains, but especially on the degree of polymerization or polycondensation.

Currently, the rapid spread of polymer materials in new markets requires not only the innovation of technological processes but, equally, the modernization of existing polymer processing technologies, which allow them to expand into new areas of social life.

4.4. Threats

During the polymerization process, not all molecular chains will grow to the same length, resulting in chains with different lengths, characterized by different molecular masses. In the description of a polymer, an average value of the molecular mass determined by measuring the physical properties influenced by it, such as viscosity and osmotic pressure, is usually used.

Continuous global competition due to the low specific weight and impact resistance impose pressure on profit margins and time to market for new products, forcing manufacturers to find innovative solutions for polymeric composite materials and synthetic resins performance and manufacturing process efficiency.

The physical and mechanical characteristics are affected by the size of the molecular mass: melting or softening temperature and mechanical strength, increase with the increase of the average molecular mass.

5. CONCLUSIONS

The paper presents theoretical research about the importance of the basic reactions in the manufacture of synthetic resins. Synthetic resins are polymers, which are built up from simple molecules or monomers and can be manufactured by: polymerization, polycondensation or polyaddition. The degree of hardening can be characterized by the amount of epoxy groups transformed in the hardening process.

The basic reactions in the manufacture of synthetic resins are a difficult field which has features of increasing composite materials industry. Today there are many types of synthetic resins with a wide range of interesting properties. They can be flexible as rubber or rigid as metal or transparent and can be used in many products manufacture.

The rapid increase in the production of synthetic resins is due to the unlimited diversification of manufacture types and aplication fields. That is why the importance of the basic reactions in the manufacture of synthetic resins is vital.

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IMPORTANȚA REACȚILOR DE BAZĂ ÎN FABRICAREA RĂȘINILOR SINTETICE

În zilele noastre, rășinile naturale au fost total înlocuite cu rășini sintetice. Rășinile sintetice sunt foarte importante dacă ne gândim la materialele compozite. Rășinile sintetice sunt împărțite în două clase, cunoscute sub denumirea de rășini termorezistente și termoplastice. Scopul acestei lucrări este de a clarifica importanța reacțiilor de bază în fabricarea rășinilor sintetice: polimerizare, policondensare, poliadiție. Rășinile sintetice sunt produse prin reacție chimică controlată, în prezența solventului și a catalizatorilor necesari în condiții adecvate de temperatură și timp. Obiectivul principal al lucrării este de a oferi o viziune mai clară asupra modului în care se formează rășinile sintetice. Rășinile sintetice sunt comercializate sau utilizate sub diferite forme și de aceea caracterizarea și formarea lor este foarte importantă. Lucrarea este o trecere în revistă a literaturii de specialitate privind reacțiile de bază care apar în producția de rășini sintetice.

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