

Chapter 8

Epoxidized Vegetable Oils for Thermosetting Resins and Their Potential Applications

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Abstract In the recent decades, bio-based polymers have gained increasing interest, especially for composite materials. These polymers and their respective monomers are derived from renewable resources, being thermoplastics or thermosetting resins which are biodegradable or non-biodegradable. Thermosettings are strong, rigid polymer materials and cannot be easily processed by melting after their hardening. At present, thermosetting resins are obtained using highly toxic and volatile petrochemicals, which require human and environmental safety monitoring. Considering the wide range of diverse renewable monomers available, vegetable oils (VOs) are especially well-suited when it comes to the synthesis of thermosetting resins due to their carbon-carbon double bonds, highly desirable for this type of application as these unsaturated bonds can be chemically modified in order to increase reactivity toward further polymerization. Thus, epoxidation, which consists of introducing a single oxygen atom to each non-saturated bond to yield in an epoxidic cycle, is a simple, effective method to modify these VOs. The resulted thermosetting resins exhibit improved toughness and environmental-friendly behavior. VOs, especially soybean oil which is abundant and cheap, are typically mixtures of unsaturated fatty acids with numerous bonds that can be easily converted into the more reactive oxirane rings through the reaction with peracids or

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peroxides. The present chapter focuses on composites obtained from epoxidized vegetable oils (EVOs) and epoxy resins and their properties in correlation with their envisaged applications.

Keywords Vegetable oils · Epoxidation · Thermosetting resins · Applications

1 Introduction

In recent decade, there has been noticed an increasing research interest for using vegetable oils in obtainment of valuable polymer materials (Gan and Jiang 2015; Paluvai et al. 2015a, b; Mustață et al. 2013; Stemmelen et al. 2011; Raquez et al. 2010; Guner et al. 2006). These bio-based polymer materials are usually designed for technical applications. Considering their different uses, for example, biomedical purposes, or surface coatings applications (such as paint and printing ink formulations), these materials should have specific features including good thermal stability and significant ability to resist damage by chemical reactivity or solvent reaction.

As these materials are biodegradable being resulted from renewable raw materials, they should be also biocompatible in terms of their physical and chemical properties, mainly when they are used for medical applications. Other technical usefulnesses should require electrical conductive, non-flammable, gas permeable properties, or materials with good adhesion to metallic substrates (Guner et al. 2006).

Vegetable oils derived from seeds of oil-type plants and separated through extraction procedures are natural, environmental friendly and renewable raw materials with large availability, low cost, and functionality readily to be significantly improved in order to obtain novel bio-based functional polymers and polymer materials (Gan and Jiang 2015; Quirino et al. 2014; Lligadas et al. 2013). The structural constituents of vegetable oils are triglycerides, resulted from glycerol and fatty acids by esterification reaction. Oils are in fact a complex mixture of such esters with different saturation levels. Fatty acids content is specific for each vegetable oil and they confer many reactive sites (e.g. double bonds, ester groups, epoxy groups) suitable for modification approaches in order to obtain new synthesized structures.

Most of the present literature data focused on the use of vegetable oils and their functionalized derivatives for either linear structures, three dimensional networks, or matrices for thermoplastic and thermosetting-based composites, biocomposites and hybrid materials (Paluvai et al. 2015a, b; Altuna et al. 2015; Quirino et al. 2014; Ding and Matharu 2014; Miao et al. 2014; Lligadas et al. 2013; Biermann et al. 2011; Raquez et al. 2010; Guner et al. 2006).

Among vegetable oils, the most used for tailoring oil-modified polymers with different potential applications include linseed (Pin et al. 2015a, b; Ding et al. 2015; Luo et al. 2013; Henna et al. 2008; Lligadas et al. 2006a Miyagawa et al. 2005a),

sunflower (Taghizadeh et al. 2008), castor (Echeverri et al. 2015; Rosu et al. 2015; Paluvai et al. 2015a, b; Ray et al. 2012; Sharmin et al. 2011; Mulazim et al. 2011), soybean (Roşu et al. 2016; Tsujimoto et al. 2015; Echeverri et al. 2015; Altuna et al. 2015; Hosoda et al. 2014; Pan and Webster 2011; Adekunle et al. 2010; Tsujimoto et al. 2003; Uyama et al. 2003; Gerbase et al. 2002), palm (Jusoh et al. 2012), pine (Abdelwahab et al. 2015), tall (Liu et al. 2015), corn (Mustață et al. 2013), rapeseed (Wu et al. 2000), grapeseed (Stemmelen et al. 2011), and tung (Meiorin et al. 2015; Luo et al. 2013) oils.

Thermosetting resins are valuable products for industrial applications (Raquez et al. 2010; Thakur et al. 2013a, b; Pappu et al. 2016) considering their versatile properties that can be tailored as desired, for example enhanced strength, and high modulus, improved stability (e.g. chemical, thermal) and durability. All these desirable properties are conferred by the high cross-linking density exhibited by thermosetting resins (Yousefi et al. 1997; Feldman 1996; Krawczak and Pabiot 1995; Singha and Thakur 2008a, b, c, 2009a, b, c, d), but there are also some inherent disadvantages including reduced impact properties and not being reshaping after curing/polymerization process (Carfagna et al. 1997). Fibers type fillers including glass, carbon, aramid or natural ones (intact or shredded), and clay type fillers are often used as additives in resin formulations to produce composite materials (Paluvai et al. 2014; Shibata et al. 2009; Miyagawa et al. 2005b; Uyama et al. 2003; Hayes and Seferis 2001).

2 Thermosetting Resins from Renewable Resources and Their Applications

The use of vegetable oils, an important class of renewable raw materials, readily available for the synthesis of different monomers and polymeric materials with many applications, was briefly presented as reviewed (Xia and Larock 2010). The resulted polymer materials, converting soft, flexible rubbers into hard, rigid plastics, display a large range of beneficial properties, the main important being the mechanical, and thermal ones, and constitute potential promising alternatives to classic oil-based materials. A thermosetting polymer material results as a solid state from liquid solution (comprising mainly a mixture of co-monomers) through curing process in an irreversible way, under heating or UV irradiation. It is essential that one or more of the monomers have at least three or more reactive groups in the molecular structure, which further generates tri-dimensional cross-linked networks with no ability to reshape after the reaction ending. Usually, thermosetting materials are obtained using a resin, a curing agent, a catalyst or initiator, and sometimes a solvent (Auvergne et al. 2014; Raquez et al. 2010).

Thermosetting polymer materials, representing less than 20% of plastic products, have many industrial applications. The most important examples are represented by phenolic resins, urea formaldehyde resins, unsaturated polyesters, and epoxy resins.

Epoxy resins are low molecular mass monomers containing at least two epoxide groups (glycidyl or oxirane group type). These epoxy monomers can interact with themselves through homo-polymerization reactions (anionic or cationic), or in the presence of a large range of co-reactants (polyfunctional amines, acids, anhydrides, phenols, alcohols, thiols) that are usually called hardeners. Blending with some additives and fillers is also applied when reduction of costs or achieving desirable processing and/or properties are envisaged (Auvergne et al. 2014). An effective approach to generate oxirane groups is represented by peroxidation of double bonds which, in the case of aliphatic chains, is a simple oxidation process by using hydrogen peroxide (e.g. epoxidation of vegetable oils). Vegetable oils comprise varied fatty acids structures which present naturally occurring functional groups (carbon-carbon double bonds, hydroxyl groups, even epoxy groups). The first mentioned ones, with reduced reactivity, can generate new functional groups capable to be easily polymerized. Some of the most significant applications of thermosetting resins from epoxidized vegetable oils will be further presented.

2.1 Coatings

Epoxidized vegetable oils (EVOs)-based polymers have been extensively used as coatings, given their superior mechanical properties, processing ability, and chemical resistance, in various applications: electrical engineering, electronics, automotive and even aeronautics, biomedical and food packaging (Auvergne et al. 2014). Thus, commercial products are readily available on various markets. Functionalized vegetable oils can be employed in coatings made of epoxidized linseed oil (ELO) and epoxidized soybean oil (ESO), the most common and widely used (Miyagawa et al. 2006). The synthesis approach may vary to a large extent. ESO is known to undergo both cationic and thermal processing (Raghavachar et al. 2000) while epoxidized palm oil (EPO) have been used for UV-curable coatings (Wan et al. 2003; Raghavachar et al. 2000), as well as the vernonia oil, which naturally contains epoxide groups that made it fit for such applications (Thames and Yu 1999). Since each type of application sets its own performance requirements, all formulations are target-oriented. As for the coatings, the processing techniques, along with the complex chemistry characteristic for a multi-component polymer system, are a key factor. Temperature, pressure, reaction rate and visco-elastic behaviour can influence the properties of the materials during each stage of processing, and even afterwards (delamination, debonding or even post-processing reactions (Pascault and Williams 2013)).

Complex coating formulations may also include additives of various types aimed to improve mechanical and thermal properties, specifying that they may also undesirably increase the viscosity. Initiators having cationic structure are inert under normal conditions (ambient temperature and illumination), but they exhibit activity under external stimulus (heating or photo-irradiation). They are used not only for epoxidized vegetable oils-based coatings, but also for adhesives, paintings,

inks and photoresists. The preparation of epoxy-modified cyclohexene-containing linseed oil (ECLo) was reported and the kinetics of photo-polymerization was studied in comparison with the corresponding compound without epoxy groups (Zou and Soucek 2005; Zong et al. 2003). The epoxy conversion and the polymerization reaction rate, as well as the mechanical properties of the coatings, were proven to depend on the reduced viscosity of the system.

Other kinetic studies were focused on the polymerization of EVOs bearing benzyl alcohols units (Ortiz et al. 2005). The effect of the both cationic and anionic initiators on the rate of the photo-polymerization of epoxidized triglycerides was evaluated. The raw material used was vernonia oil, known to naturally contain epoxy moieties, and the resulted coatings exhibited high flexibility and impact strength (Crivello and Narayan 1992). UV-curable coatings with an interesting supramolecular architecture were obtained using vernolic acid units grafted onto a functionalized hyperbranched polyether (Samuelsson et al. 2004).

Fundamental studies were also performed on different triglyceride-initiator systems aiming to optimize them. For ESO, which is considered a representative green monomer, it was found that silyl radical chemistry used for promoting the free-radical cationic polymerization was highly efficient, even in air and upon natural irradiation: after 1 h exposure, a tack-free uncolored coating yielded in with a conversion of 60% (Tehfe et al. 2010).

An epoxidized derivative of anacardic acid was reported to yield in thin films by cationic photo-polymerization (Pascualt and Williams 2010) in the presence of a solution of triaryl sulfonium hexafluoroantimonate salt in propylene carbonate. The coatings exhibited surface with enhanced hydrophobicity due to the achieved long, hydrophobic alkyl chain localized at the coating-air interface. (Chen et al. 2009; Huang et al. 2012). These epoxidized vegetable oils may be used as reactive additives in UV curable materials by cationic photo-polymerization (“humidity blockers”).

The use of hardeners, either from renewable resources or synthetic, is aimed to improve the properties of coatings. The literature is scarce concerning epoxidized vegetable oils formulated with bio-based hardeners. Still, data on the properties of ESO-based coatings cured in the presence of maleinated soybean oil (Warth et al. 1997) or terpene derived acid anhydride (Takahashi et al. 2008) were communicated. Resins obtained from epoxidized linseed oil using a vegetable oil polyamine prepared by thiol-ene chemistry as cross-linker (Stemmelen et al. 2011) were reported to exhibit elastomeric properties and low glass transition temperatures. Other coatings were obtained using bio-based hardeners formulated with synthetic commercially available epoxy ethers, namely glycerol polyglycidyl ether (GPE; epoxy functionality 2) and polyglycerol polyglycidyl ether (PGPE; epoxy functionality 4.1) (Shibata and Nakai 2010; Takada et al. 2009).

Coatings properties may be upgraded by applying different methods, one of them being the increase of the epoxydic precursor functionality. Such an example is the synthesis of new epoxy monomers, namely epoxidized sucrose esters of fatty acids (ESEFAs) (Pan et al. 2011), that reacted with a cycloaliphatic anhydride (4-methyl-1,2-cyclohexanedicarboxylic anhydride, MHHPA) in the presence of an

initiator (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU). Their properties as coatings for steel were studied in comparison with a commercially available ESO-based coating and the data collected from various measurements indicated these ESEFAs-based materials as high performance thermoset coatings in correlation with their high content (approx. 75%) of vegetable component. The high modulus values of these coatings, their hardness and ductility can be explained considering the structure of ESEFAs and their enhanced functionality. These monomers may be of further use for composites and adhesives, as well.

Other thermosetting coatings were obtained by substituting in a certain degree synthetic prepolymers (i.e., diglycidyl ether of bisphenol A DGEBA) with EVO commonly used as reactive diluents and/or agents for improved flexibility (Czub 2006). Thus, formulations containing DGEBA and ESO, including methyl tetrahydrophthalic anhydride (MTHPA) as hardener and 1-methylimidazole (1-MI) as an initiator (Altuna et al. 2011), yielded in coatings reported to have decreasing T_g values along with the increasing amount of ESO and a good balance between composition and properties was reached for a ratio DGEBA/ESO = 40/60 (wt%). When soybean (Miyagawa et al. 2005b) or linseed oil (Miyagawa et al. 2005c) was used in combination with diglycidyl ether of bisphenol F (DGEBF), employing the same hardener and initiator, the properties of the resulted coatings were comparable.

Another approach to enhance the properties of EVOs-based coatings consists of chemical modifications performed to the EVO precursors. In example, grafting phenol units (such as bisphenol A) onto EVOs (epoxidized soybean, rapeseed, linseed, and sunflower oils) yielded in prepolymers that may be further cross-linked in the presence of various hardeners (2-methylimidazole, dicyanodiamide, hexahydrophthalic anhydride, and triethylenetetramine) (Czub 2009).

The new materials were reported to have improved mechanical strength. When reagents bearing phosphorus moieties were employed to modify EVO, coatings with flame retardant properties were obtained. Thus, a diepoxy monomer was synthesized starting from 10-undecenoyl chloride and a diphenol resulted from the reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and benzoquinone; subsequently, the double bonds were oxidized (Lligadas et al. 2006b, c). Then methylene dianiline (MDA) or bis(m-aminophenyl)methylphosphine oxide (BAMPO) was used for the cross-linking reaction. It was proven the material achieved a diminished flammability.

Coatings with tailored properties, such as biocide, biocompatible, biodegradable, anti-corrosion, low emission of volatiles, were designed for special applications, namely decorative, protective and architectural layers, electrically insulations, films for paper packaging or having self-healing properties (Alam et al. 2014).

Coatings having paint properties were obtained from EVOs containing oxazoline units (Trumbo and Otto 2008). Pure vegetable oils and in blends with polymethylmethacrylate and polystyrene have been used as anticorrosive coatings with high flexibility (Ahmad et al. 2006a, b). Coatings obtained from EVOs blended with polyvinyl chloride and polyvinyl alcohol, respectively, have achieved biodegradable character and may be used as films for food packaging (Riaz et al.

2010, 2011). Naturally-containing epoxy moiety vernonia oil, as well as epoxidized vegetable oils (ESO and ELO) have been used as reactive diluents, the resulting coatings showing improved properties and zero emission of volatiles (Das and Karak 2009).

When employing epoxidized 10-undecenoic acid triglyceride, cured in the presence of amines, coatings with high UV-stability, good adhesion, solvent resistance and toughness were obtained (Earls et al. 2004).

2.2 *EVO Based Composites*

Fiber reinforced composites are materials that may be used in automotive and aircraft industry, as structural materials, with good results. Manufactured generally starting from natural (flax, hemp) and synthetic (glass, short carbon fibers, as well as mineral fibers, such as surface-modified wollastonite) fibers, they employ polymeric matrices which can be made also from renewable resources, as in the case of epoxidized vegetable oils. The growing interest in the use of such materials is a mark of the last decades, considering the global environmental movement and green policy.

The epoxidized soybean oil (ESO) based composites are an example of epoxidized vegetable oils successfully used as matrices (Meier et al. 2007; Kayode and Adekunle 2015; Petrovic et al. 2004). Reinforced with glass and carbon fibers (Liu et al. 2002, 2007), these composites proved thermal, mechanical and physical properties comparable to classic oil-based elastic polymeric materials. The formulations included some well-chosen curing agents and epoxy resins to enable the final composite to fit a wide range of end-user requirements. The method of manufacturing was also a new approach, as the solid free from fabrication (SFF—a method of producing objects without molds, best known from stereo lithography as a method to rapidly obtain prototypes) is not commonly used to produce fiber reinforced composites. Experimental results showed, as follows: glass and carbon fibers exerted a better reinforcing effect as compared to mineral fibers; the composite modulus depended on the fibers orientation, aspect ratio and volume fraction; the reinforcement effect is enhanced at higher temperature; it is possible to use the SFF method to obtain end products based on such composites when other manufacturing approaches cannot be employed.

Further functionalization of vegetable oils yielded in valuable compounds that were used as matrix for fiber-reinforced composites with either natural or synthetic fibers. This is the case of acrylated epoxidized soybean oil (AESO), maleinized soy oil monoglyceride (SOMG/MA) and maleinized hydroxylated oil (HO/MA) synthesized from the triglyceride oil, or even maleinated acrylated epoxidized soybean oil (MAESO) (Campanella et al. 2015).

When glass fibers (QM6408 E-Glass) were employed, AESO-based composites containing up to 50% fibers showed excellent mechanical properties (Khot et al. 2001). The addition of natural fibers (flax and hemp) in various ratios induced

improved elastic properties. These properties exhibited by composites with combined natural and synthetic fibers can be furthermore exploited, since they are combining advantages from the both classes of fiber composites (i.e., the low cost of natural fibers and the high performance of the synthetic ones).

Lignocellulosic materials (flax, cellulose, pulp, hemp, wheat straw fibers) were also used to produce AESO-based composites. For this purpose, flax fibers were mixed with butyrate kraft lignin (Thielemans and Wool 2004) which acted as compatibilizing agent between matrix (AESO and styrene) and fibers by improving the adhesion at the interface. This behaviour was evidenced by SEM images illustrating that fibers fractured along with the matrix, without pulling out. When short wheat straw fibers were employed, the effect of butyrate kraft lignin was most evident in the tensile strength improvement, as the system enabled a better interaction between matrix and fibers, given the enhanced fibers wettability. All these composites were made by the vacuum assisted transfer molding process which granted a good permeation of the matrix around and within the fibers.

Another approach in this field was the production of fiber-reinforced composites directly as end-products. Thus, panels for in-door applications (housing, structural materials, furniture, automotive parts, etc.) were made from AESO and natural fiber mats (flax, cellulose, pulp and recycled paper, hemp) up to 10–50% (O'Donnell et al. 2004). Vacuum-assisted resin transfer molding or resin vacuum infusion process were used to obtain such panels. All these materials showed good mechanical properties as compared to woven E-glass fibers reinforced AESO composites, with different values of the flexural modulus depending on the nature of fibers, but the production costs were lower.

The maleinated acrylated epoxidized soybean oil (MAESO) is another example of functionalized vegetable oil that can be used in fiber-reinforced composites production (Campanella et al. 2015).

Composites panels were made of both glass fibers and natural fibers (flax), and using MAESO along with wisely chosen reactive diluents (styrene, vinyl-toluene, divinyl-benzene, methyl methacrylate and methacrylated fatty acid—MFA) as matrices. The end-products proved to have good mechanical characteristics and physical properties close to those made of oil-based polymers. It was shown that tuning the amount of MFA versus MAESO, it was possible to increase the amount of natural fibers in the formulation, but given their lower density, the composites remained lighter as compared with glass fiber reinforced ones. At the same time, the flax containing composites displayed enhanced elastic properties, despite their lower strength, which makes them fit for lightweight applications in automotive industry. The experimental data confirmed that MAESO is a versatile compound fit for further processing in order to obtain multi-component systems with tailored properties. Since the presence of MFA in formulations reduced the modulus but increased the elongation for equivalent strength, it is beneficial to combine MAESO and MFA to obtain lightweight composite products with high content of natural fibers.

Other ESO-based resins were also tested to be further used in the production of fiber-reinforced composites. Thus, a combination of epoxidized soybean oil ESO

and diglycidyl ether of bisphenol A DGEBA was formulated and cured in the presence of *p*-aminobenzoic acid (*p*-ABA). The influence of ESO on the curing kinetics and thermal properties of the cured resin was investigated (Mustață et al. 2011). The results confirmed that ESO contributed to improve the resin toughness, as well as its biocompatibility. The morphology study of the cross-linked system showed a smooth fracture surface and cracks uniformly spread in the entire sample, indication of the enhanced toughness due to the reactive epoxidic groups of ESO and DGEBA cross-linked to yield larger network structures. This phenomenon was enabled by the good dispersion of ESO in the resin bulk.

Other inexpensive composites with glass fibers were made by using renewable resources, namely epoxidized allyl soyate (EAS), a soy-based resin produced starting from unsaturated soybean oil (Chandrashekhara et al. 2005). EAS consists of mixtures of epoxidized fatty acid esters and it was expected to yield a highly dense intermolecular cross-linking given its superior reactivity and, subsequently produce materials with better mechanical properties than those of materials resulted from unmodified ESO. Data collected for the pultruded glass fiber reinforced composites indicated good values for flexural strength, modulus and impact resistance, confirming the possibility to use these composites as structural materials. The decrease in the pull force during the pultrusion process was noticeable, as expected, given the unctuousity of the soybean oil. These results validated the potential of EAS to environmentally friendly and low cost structural applications.

Keratin fibers were also considered when it came to the development of novel bio-based composite materials with specific properties (Hong and Wool 2005). Keratin fibers originating from feathers are tough, despite their lightweight and hollow structure and, given their chemical proteic nature, are compatible with acrylated epoxidized soybean oil (AESO). Since the fibers are not filled with resin during the processing, the final composites contain a high amount of air inside the hollow structure of fibers and the density barely reach 1 g/cm^3 for 30% (volume fraction) keratin fibers content. Therefore, the values of the dielectric constant are lower than silicon dioxide or epoxy, or polymer dielectric insulators. At the same time, the value of the coefficient of thermal expansion is also low enough, and that makes these composites fit for electronics. Another property evaluated was the water sorption which is correlated with the amount of keratin fibers and their wettability by AESO. The mechanical properties (storage modulus, fracture toughness, flexural strength) were dramatically increased due to the presence of keratin fibers. Even more significant improvements may be achieved by wisely select the matrix in terms of compatibility with the reinforcement and strictly sort the fibers.

Particulate composites using EVO as matrices are found to be of high interest in structural materials, depending on the amount and type of particles, as well as mechanical level of performance of the considered resins. It is well known that the best mechanical properties in particulate composites are achieved when particles with different size, from coarse particles to fine particles, are mixed previously. This protocol enables an enhanced reinforcement of the final composite as each dimensional fraction of particles occupy a specific volume and contributes to the formation of a rigid “skeleton” inside the matrix. Under these circumstances, the

higher the compatibility between matrix and filler, the better the wettability, the better elasticity to strength ratio of the composite.

An interesting study on composites made of epoxidized castor oil (ECO) and mixtures of inorganic fillers in different ratios evidenced this assessment (Balo 2011). The filling materials (coal fly ash, clay, perlite and pumice) were selected due to their characteristics, mainly their pozzolanic effect, and local availability. The pozzolans are siliceous materials with no cementitious properties by themselves, but added in controlled ratios and in finely ground state to classic formulations may react with calcium hydroxide in the presence of water, at ambient temperature, to yield in compounds with remarkable cementitious properties. Thus, it is possible to estimate the pozzolanic activity (Snellings et al. 2012). The coal fly ash is currently a municipal waste commonly disposed of in landfill or ash deposits, with noticeable negative environmental impact. It is already used in low amounts in some applications, such as component in concrete used for grouting and other stabilizing operations in mining, as well as filling material in civil engineering (Horiuchi et al. 2000). The clay used in these formulations was commercially available. Pumice is a glassy volcanic rock (rhyolitic or dacitic magma) with high porosity which grants a specific density lower than 1 and enables it to float. In civil engineering applications as structural materials, pumice proved to be easy processable and to contribute to the heat and sound insulation, and fireproofing (Shrew and Brink 1977). Perlite is an amorphous volcanic glass which contains high amount of water and may be expanded to 7–16 times its original volume upon heating at 850–900 °C, when its density becomes 0.03–0.15 g/cm³ (Maxim et al. 2014). In natural state, perlite has a good pozzolanic effect and it is used in concrete formulations to improve their mechanical properties, mainly the compressive strength (Mo and Fournier 2007; Demirboğa et al. 2001).

The experimental results indicated that the fly ash and ECO contributed to the decrease of the compressive-tensile strength and thermal conductivity, but the lowest values were obtained in samples containing pumice and expanded perlite (5% each); same for the abrasive loss and water sorption. The thermal conductivity of samples increased along with the increasing density of materials, but decreased when the water sorption enhanced. It was also proven that the presence of clay caused an improved abrasion resistance. It is noticeable that these composites are able to incorporate high amounts of filler, while maintaining low density and high structural performance, which recommends them for lightweight applications.

2.3 Nanocomposites with EVO Matrices

Polymer nanocomposites are multi-component systems and basically consist of nanofillers (particles of different shape, platelets, fibers and fibrils, etc.) dispersed in a polymeric matrix made of one polymer or a mixture of polymers. The transition from micrometer to nanometer scale entails changes in both physical and chemical

properties of the materials. Since the nanofillers are affecting the behaviour of the nanocomposite, it is of interest to consider two structural aspects of the filler: the increased surface area:volume ratio, and the size of the particle. The smaller the particles, the higher the surface area:volume ratio, which shifts the interest from the atom interactions inside the particle to the ones at the exterior surface of the particle, or, more specifically, at the interface between matrix and particle.

Typical nanofillers are considered silica (SiO_2) nanoparticles, metal-oxo clusters ($-\text{O}-\text{Ti}-\text{O}-$, zirconia, etc.), clays in native state or organically modified, etc. Polymers reinforced with well-defined nanosized inorganic clusters, including ceramers (IUPAC 1997), have attracted a great interest due to their versatility in terms of properties and applications.

Polyhedral oligomeric silsesquioxane (POSS) compounds have a unique cage-like structure (1–3 nm in diameter) where the ratio between oxygen and silicon is $(\text{SiO}_{1.5})_n$, $n = 8, 10, \text{ or } 12$. Various POSS were used to obtain nanocomposites by copolymerization with different organic monomers (Kannan et al. 2005); even epoxidic resins were employed to prepare such nanocomposites (Abad et al. 2003).

Generally, the presence of POSS renders improved thermal and mechanical properties, as well as reduced flammability. When the structure contains POSS pendant on a network chain, the $(\text{SiO}_{1.5})_n$ clusters exhibit a trend to aggregate, depending on the nature of organic ligands, and the POSS-POSS interactions become the network structuring driving force. Even more, the extent of POSS aggregation increases along with the decrease of the POSS crosslinking functionality (Matějka et al. 2004).

An excellent example of biobased POSS-nanocomposites from plant oil derivatives is represented by the epoxidized linseed oil (ELO) and 3-glycidylpropylheptaisobutyl- T_8 -polyhedral oligomeric silsesquioxane (G-POSS) in different amounts (2, 5, and 10 wt%) that were cross-linked (Lligadas et al. 2006d). At low amounts of G-POSS (2 wt%), no aggregates were observed, but for higher contents clusters having several nanometers in diameter were noticed. The glass transition temperatures were higher and storage moduli of the networks in the glassy state were improved as compared to those of pure ELO network. A rubber plateau was also observed to be higher than that of the pure resin. These findings were attributed to the reinforcing effect of the G-POSS clusters.

Novel biobased hybrid organic-inorganic materials were obtained using several polyfunctional hydrosilylating agents, such as 1,4-bis(dimethylsilyl)benzene (DMSB), tetrakis(dimethylsilyloxy)silane (TKDS) and 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS) (Galià et al. 2010). Other several inorganic precursors, namely 3-glycidoxypropyl-trimethoxysilane (GPTMS), 2-(3,4-epoxycyclohexyl)-ethyl-trimethoxysilane (ECTMS), 3-aminopropyl-trimethoxysilane (APTEOS), and 2-aminoethyl-3-aminopropyltrimethoxysilane (AEPTEOS), were also employed in order to obtain hybrid materials (Tsujimoto et al. 2010).

Biodegradable nanocomposites were successfully prepared starting from epoxidized soybean and linseed oils (ESO and ELO) and 3-glycidoxypropyltrimethoxysilane (GPTMS) (Tsujimoto et al. 2003). The nanocomposites were obtained in situ by an

acid-catalyzed reaction and this allowed the simultaneous formation of both resin matrix and silica network. The covalently bonded organic and inorganic structures enabled a highly organized architecture that entailed improved film properties. Thus, the hardness and tensile strength were enhanced, as well as the flexibility of the nanocomposites. The reinforcing effect of the silica network was also substantiated by the rheologic behaviour of the novel materials, which were also tested for their biodegradation susceptibility with good results: after 2 months in an activated sludge, the samples degraded over 50%.

On the other hand, using the same ELO and ESO, and GPTMS, it was possible to obtain nanocomposites by an acid-catalyzed curing reaction, these being able to form highly glossy, transparent films, with good coating characteristics, while maintaining their biodegradability (Tsujiimoto et al. 2010). Besides the improvement of the mechanical strength and thermal stability, the reinforcing effect of the silica network was also confirmed by the dynamic visco-elasticity analysis.

Other ceramers were prepared by sol-gel processes using an inorganic precursor, namely tetraethoxysilane (TEOS), and epoxidized castor oil (ECO), in various ratios, aiming to reach an optimum between composition and properties (de Luca et al. 2006). The morphology of the materials was characteristic to homogeneous films when the inorganic component was in low amounts. Unlike simple castor oil-based nanocomposites, the ceramers made of ECO may include higher amounts of inorganic component without any occurrence of phase separation, which is an indication of the wettability of the inorganic network, hence, the compatibility of the two components. Mechanical properties (hardness and tensile strength) improved along with the increasing amount of TEOS, though the swelling in toluene diminished. All considered samples have showed good adhesive properties, which recommend them for coating applications.

Another inorganic precursor, namely 3-aminopropyltriethoxysilane (APTES), was employed for ceramers preparation due to its structural and functional features. This bifunctional precursor, containing an amine group supplemental to the silane moiety, is able to yield 3D silicon oxide networks where -NH_2 and -Si-OH groups can be crosslinked. Therefore, in a wisely chosen reaction system it may act as reagent, contributing to the inorganic network, as well as a coupling agent, linking the organic and inorganic components. Thus, hybrid homogeneous films were obtained using ECO and mixtures of APTES and TEOS in various ratios (Becchi et al. 2011). It was proven that additional APTES did not enhanced the thermal stability of the nanocomposites, as compared to ECO-TEOS ones, but contributed to the increase of the hardness and tensile strength values. Given the thermal data achieved for the ECO-APTES-TEOS systems, it was suggested that the conversion of the inorganic precursors into pure silica was not complete, as expected, but they also yielded in some amorphous silicon oxycarbide ($\text{SiC}_x\text{O}_{4-x}$). The samples studied have proved competitive adhesive properties toward aluminum surfaces and, consequently, these materials may be considered for anti-corrosive protection coatings.

Ceramers containing metal-oxo clusters were designed to yield materials with beneficial properties derived from both organic and inorganic phases; they may be

prepared through sol-gel processes, as the inorganic phase can generate self-assembled networks and, at the same time, react with the organic phase by cross-linking via hydrolysis and condensation reactions (Wold and Soucek 2000).

Thus, ceramer coatings intended for electronics applications were obtained with good results using linseed and sunflower oil, as the organic phase, and titanium (IV) *i*-propoxide (TIP), titanium (IV) di-*i*-propoxide bis-acetoacetate (TIA), and zirconium *n*-propoxide (ZRP), as the inorganic phase (Tuman and Soucek 1996; Tuman et al. 1996).

Given the reactivity of the EVO and considering the conditions of the sol-gel process, it was suggested that better results might be obtained by replacing blown or bodied vegetable oils with the epoxidized ones. Thus, the sol-gel precursors proved to be more reactive in the presence of EVO, bonding with both hydroxyl and epoxide groups in their structure. Even more, a certain catalytic effect of the inorganic precursor on the homo-polymerization of the epoxidized oil was assumed (Chen and Chen 1997). A significant improvement was noticed in terms of mechanical properties in the ceramers obtained from ESO and inorganic precursors, such as titanium (IV) *i*-propoxide (TIP), titanium (IV) di-*i*-propoxide bis-acetoacetate (TIA), and zirconium *n*-propoxide (ZRP) (Teng and Soucek 2000). The tensile modulus, strength, and hardness varied depending on the nature of the precursor, thus supporting the hypothesis of different interactions between organic and inorganic phases. The improvement in mechanical properties (tensile modulus and strength, and hardness) might be attributed to the formation of both inorganic rigid clusters and organic high density cross-linked network. At the same time, the higher the amount of inorganic component, the lower the elasticity of the ceramer films is.

The use of clays (either in native state or organically modified) as nanosized fillers for EVO-based nanocomposites was considered as an alternate pathway to achieve not only enhanced mechanical properties, but reduced flammability and significantly improved biodegradability, as well. Thus, starting from ESO and ELO as organic components, it was possible to obtain nanocomposites using an organically modified montmorillonite (containing an octadecylammonium tail, 30 wt%), by thermal curing in the presence of a benzylsulfonium hexafluoroantimonate derivative, as a thermally latent cationic catalyst (Uyama et al. 2003). The ESO containing nanocomposites yielded in homogeneous, resilient, highly elastic films, due to the decrease of the cross-linking density of ESO when the clay was dispersed in the matrix and the reinforcing effect of clay platelets. The ELO-based nanocomposites have showed a higher cross-linking density, given the greater number of epoxide moieties. These data suggested that these materials are expected to be used in applications as coatings and biodegradable plastics.

A mixture of ESO and diglycidyl ether of bisphenol-A (DGEBA) was also considered as matrix for bio-based nanocomposites with organically modified montmorillonite (OMM) (Aboobucker Sithique and Alagar 2010). The morphology analysis (wide angle X-ray diffraction WAXD and scanning electron microscopy SEM) proved that the clay tactoids exfoliated up to a high extent inside the matrix, which explained the significant improvement in tensile strength and modulus,

flexural strength and modulus (up to 24% for 7 wt% OMM content), and impact strength. The increased tortuosity of the system, granted by the clay platelets, restricted the chains mobility so that the diffusion of volatiles lowered, while the overall thermal stability increased.

Aiming to obtain green composites, different matrix formulations were designed, including further modified EVO, such as acrylated epoxidized soybean oil (AESO) (Thielemans et al. 2005) or acrylated epoxidized castor oil (AECO), or even mixed matrices, namely AECO-DGEBA (diglycidyl ether of bisphenol A) (Paluvai et al. 2015a, b). The organically modified clay used in this case was Cloisite 30B—montmorillonite functionalized with bis(2-hydroxyethyl) quaternary ammonium salt- and the transmission electron microscopy TEM and X-ray diffraction XRD analysis results confirmed exfoliated structure of the nanocomposites. The cross-linking density increased along with the amount of clay, because the alkylammonium groups reacted with the AECO-DGEBA system and contributed to the tensile and flexural properties. At the same time, a certain degree of ductility was noticed evidencing the plasticization effect of clay platelets, although higher amounts of clay entailed some brittleness.

The same Cloisite 30B was used for other mixed matrices, namely anhydride-cured epoxidized linseed oil (AELO) or octyl epoxide linseedate (OEL) and diglycidyl ether of bisphenol F (DGEBF) (Miyagawa et al. 2005a, b, c). The advisedly chosen curing agent and bio-based epoxies yielded in matrices displaying high values for elastic modulus, glass transition temperature, and heat distortion temperature. The addition under sonication of the functionalized clay produced nanocomposites with almost completely exfoliated structure, as evidenced through morphology studies. Thus, they achieved a higher storage modulus as compared to the initial resin. Given the value of the heat distortion temperature (100 °C) as well, it is possible to consider these materials as promising options for industrial applications.

Interesting result were achieved when the classic montmorillonites were replaced with other silicates, such as attapulgite (ATT—derived from the US town Attapulgis, in SW Georgia, where is abundant) or palygorskite (after the name of the first described deposit at Palygorskaya, in 1862, on the Popovka river, in Middle Urals, region Permskaya, Russia). This is a magnesium aluminium phyllosilicate that consists of bundles of acicular bristle-like crystals, having 2–3 µm in length and <3 nm in diameter (www.handbookofmineralogy.com), although other sources indicated 20 nm in diameter and few micrometers in length (Zhao et al. 2008), hence, a fiber-like morphology. The bundles are wetted by a slightly swellable smectite matrix. When added to metakaolin mortars, it may be used for period-correct restoration of mortars in heritage sites (Andrejkovičová et al. 2013).

Neat ATT was used as reinforcement in epoxy resins (Lu et al. 2005), but further modification of the clay surface was expected to improve the compatibility between matrix and filler, with beneficial effects on the mechanical, thermal and flame retardant properties of the nanocomposites (Shen et al. 2006; Xue et al. 2006). Thus, poly(ethylene oxide) (PEO) has been used to functionalize the surface of layered nanoparticles, due to its interactions with metal ions (Tunney and Detellier

1996), but another reagent, namely poly(ethylene glycol) diglycidyl ether (PEGDE), proved to be a better choice (Zhang et al. 2013). The clay surface functionalization was confirmed by FTIR spectroscopy: a novel absorption band was identified and attributed to the newly formed hydrogen bonds and chelation phenomena that occurred. This filler was further employed in different matrix formulations containing epoxidized soybean oil (ESO) and cyanate ester resin (CE) in order to obtain bio-based nanocomposites with enhanced properties. It was shown that a moderate degree of ATT functionalization had entailed the highest improvement in terms of storage modulus, as compared to neat or highly functionalized ATT.

When these nanocomposites are intended for applications that require higher levels of performance, such as structural applications, the clays are mixed with high-performance fillers, such as glass fibers or carbon fibers (CF). The processing of such multi-component systems must take into consideration the compatibility between partners, as well as the most suitable methods. Thus, new nanocomposites based on ELO, Cloisite 30B and carbon fibers were obtained in stages (Miyagawa et al. 2006), as follows. First, the ELO-Cloisite 30B nanocomposite was prepared by the sonication technique that allowed exfoliated structures, evidenced by the enhanced modulus and strength, and the homogeneous dispersion was confirmed by TEM. In the second stage, CF-reinforced materials were obtained through compression molding. The elastic modulus of unidirectional carbon fiber reinforced polymers (CFRP) made with different matrices (DGEBF, DGEBF-ELO, ELO-Cloisite 30B exfoliated or intercalated) was consistent regardless the matrix, due to the fact that the flexural test for the unidirectional CFRP is highly depending on the fibers characteristics. The inter-laminar shear strength tests indicated that the failure occurred in the ELO-Cloisite 30B phase (matrix) or at the matrix-fibers interface.

3 Conclusions and Future Perspective

In recent decade, there has been noticed an increasing research interest for using vegetable oils in obtainment of valuable polymer materials usually designed for technical applications. Considering their different uses, for example, biomedical purposes, or surface coatings applications, these polymer materials should have specific features including good thermal stability and significant ability to resist damage by chemical reactivity or solvent reaction. Vegetable oils are natural, environmental friendly and renewable raw materials with large availability, low cost, and functionality readily to be significantly improved for obtainment of bio-based functional polymers and polymeric materials (e.g. linear structures, three dimensional networks, and matrices for thermoplastic and thermosetting materials, biocomposites and organic-inorganic hybrid materials). An effective approach to generate epoxy resin moieties (e.g. with oxirane groups) is represented by epoxidation of vegetable oils (namely, peroxidation of double bonds which, in the case of

aliphatic chains, is a simple oxidation process by using hydrogen peroxide). Some of the most significant applications of thermosetting resins from epoxidized vegetable oils (EVOs) include coatings, fiber reinforced composites, and nanocomposites. As for the coatings, the processing techniques, along with the complex chemistry characteristic for a multi-component polymer system, are a key factor. Coatings properties may be improved by applying different methods, an effective one being the synthesis of new epoxy monomers by increasing functionality of the epoxy precursor. Further functionalization of vegetable oils (e.g. acrylated epoxidized soybean oil, maleinated acrylated epoxidized soybean oil) can generate valuable compounds to be employed as matrices for fiber-reinforced composites with either natural or synthetic fibers. Particulate composites using EVO as matrices are found to be of high interest in structural materials, depending on the amount and type of particles, as well as mechanical level of performance of the considered resins. Polymer nanocomposites are multi-component systems and basically consist of nanofillers (particles of different shape, platelets, fibers and fibrils, etc.) dispersed within a polymeric matrix made of one polymer or a mixture of polymers. Polymers reinforced with well-defined nanosized inorganic fillers (e.g. silica SiO_2 nanoparticles, metal-oxo clusters, clays in native state or organically modified) including ceramers have attracted a great interest given their versatility in terms of properties-application relationship. The resulted organic—inorganic hybrid materials may exhibit enhanced mechanical properties, but reduced flammability and significantly improved biodegradability, as well. Nevertheless, an increasing interest for bio-based, sustainable materials, with significant performance and endurance features, and not quite biodegradable, is observed. The future of bio-based polymers, including precursors for thermosetting epoxy resins, is strongly dependent on the future of different biorefinery strategies.

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