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## Feature Article

# A short review on novel biocomposites based on plant oil precursors



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## ABSTRACT

The last two decades have witnessed an exponential growth in the interest for using bio-derived products, which has been driven by the need for replacing petroleum based materials reducing the fuel consumption and, equally important, for producing materials with lower environmental impact. Vegetable oils constitute a rich source for many different polymers and polymer precursors and they are being considered for the production of “greener” composites. The wide range of possible combinations of vegetable oils, chemical modifications, polymerization routes, nature of the fillers and fibers used as reinforcement materials allows tailoring the composite properties to fit the requirements of structural or functional materials. Thus, a wide range of macro, micro and nanosized particles and fibers have been proposed as reinforcements/fillers, including organic and inorganic ones, natural or synthetic, in order to give adequate answers to specific requirements. Although, the role of oil-based products may seem modest in some cases (partial replacement of synthetic materials), there is a clear trend to increase the percentage of “green”-based raw materials in the formulations of commodities as well as specialty polymers/composites for high added value applications. Examples of different types of reinforced thermoset and elastomeric bio-composites are presented in this short review.

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## 1. Introduction

Besides their use in foods, vegetable oils have always found application in other areas such as lubricants, varnishes or paint solvents. In the last 20 years, plant oils began to receive a constant and growing attention from the academy and industry. This interest is accompanying the general revival of materials derived from renewable resources that resulted from the need to replace fossil resources and the growing compromise of using materials with lower environmental impact, a requirement for which bio-based products are generally better fitted than petroleum-based ones.

Vegetable oils, from edible to drying oils, are a rich source of polymer precursors that can be modified to exhibit various types of functionalities, leading to new materials with a wide range of properties from structural to functional. Reviews, dedicated chapters and books have already been published reflecting the international efforts to use these natural products to produce novel polymers and polymer precursors for increasing the number of its potential applications. Triglyceride molecules can be chemically modified through hydrolysis or transesterification or by reacting/modifying unsaturations present in the fatty acid chains. This last option leads to a large variety of functionalized molecules, with those containing epoxy or hydroxyl groups being probably the most popular choice. The interested reader may access exhaustive reviews on the chemical modification of vegetable oils for the production of polymeric materials [1–6].

To further contribute to this area, this review will concentrate on the use of vegetable oils as the base-materials for the production of polymer composites that incorporate inorganic and organic particles and fibers, both synthetic and natural in origin, and sized from the macro to the micro and nanoscale.

It is also interesting to notice that a literature search for vegetable oil-composite materials shows that the number of articles has grown exponentially since the end of the nineties to present (from one or two articles to hundreds per year), clearly illustrating the growing interest in the use of vegetable oils as part of the formulation for polymer composites, which in some cases have already reached industrial scale.

## 2. Monomers from chemical modification of triglycerides

As already mentioned in the introduction many exhaustive works have been published on the subject of vegetable oil modifications as source for the formulation of different polymers [1–6]. For that reason, only a very brief summary on that subject is included in this work, which is focused

on the use of these oil-based polymers for the production of composites.

Vegetable oils are composed of triglyceride molecules containing sites that can be chemically reacted in order to introduce new functional groups [5]: essentially, double bond and ester groups. Several of the synthetic pathways reported in the literature are illustrated in Fig. 1 [5]. The incorporation of new functional groups through chemical modification results in monomers or resins to be applied in polymerization reactions, just as polymer precursors derived from the petrochemical industry.

Triglyceride molecules are formed by three fatty acid chains joined to glycerol by ester groups. The fatty acids involved contain a varied number of carbon–carbon double bonds, but unless these double bonds are conjugated, they are not reactive enough to produce viable materials by free radical or cationic polymerization [3,4]. For that reason, the isomerization of different plant oils containing nonconjugated multiple unsaturations has been reported as a first step for carrying out crosslinking by cationic polymerization, for example conjugated linseed oil and low saturation soybean oil have been prepared using a rhodium-based catalysts [7]. On the other hand, the naturally conjugated triene structure of the tung oil makes it well fitted to polymerize by cationic polymerization [8,9] without any previous modification [10].

On the other hand, the modification of the double bonds can incorporate functionalities like maleates (Fig. 1(5)) [5], hydroxyl (Fig. 1(8)) [5,11,12] or epoxy (Fig. 1(7)) [5,13,14] groups making possible a further reaction via ring opening or polycondensation polymerization. After this reaction step, the product can be used without further modification in crosslinking reactions or it can be further modified through other chemical steps broadening the variety of functional molecules to be obtained. For example, the epoxidized triglycerides can be reacted to attach vinyl functionalities (Fig. 1(6)). Acrylates have been incorporated by reaction of the epoxy groups with acrylic acid, and as an example the acrylated epoxidized soybean oil (AESO) has been frequently reported in the preparation of bio-based polymers and composites [15]. On the other hand, maleate half esters and esters can be prepared by the reaction of hydroxylated triglycerides with maleic anhydride (Fig. 1(11)). Further on, these monomers can be blended with reactive diluents and cured by free radical polymerization to obtain thermoset polymers [16].

Another method for synthesizing more reactive monomers from triglycerides is the chemical modification of the ester groups to convert the triglyceride to monoglycerides through a transesterification reaction with molecules, such as glycerol (Fig. 1(3A)). The amidation reaction is illustrated in Fig. 1(2) and (3B). The hydroxyl groups of the glycerol moieties can be later reacted to incorporate new useful groups such as a diacid, epoxy, or anhydride (for example, Fig. 1(9) and (10)). Specifically, different

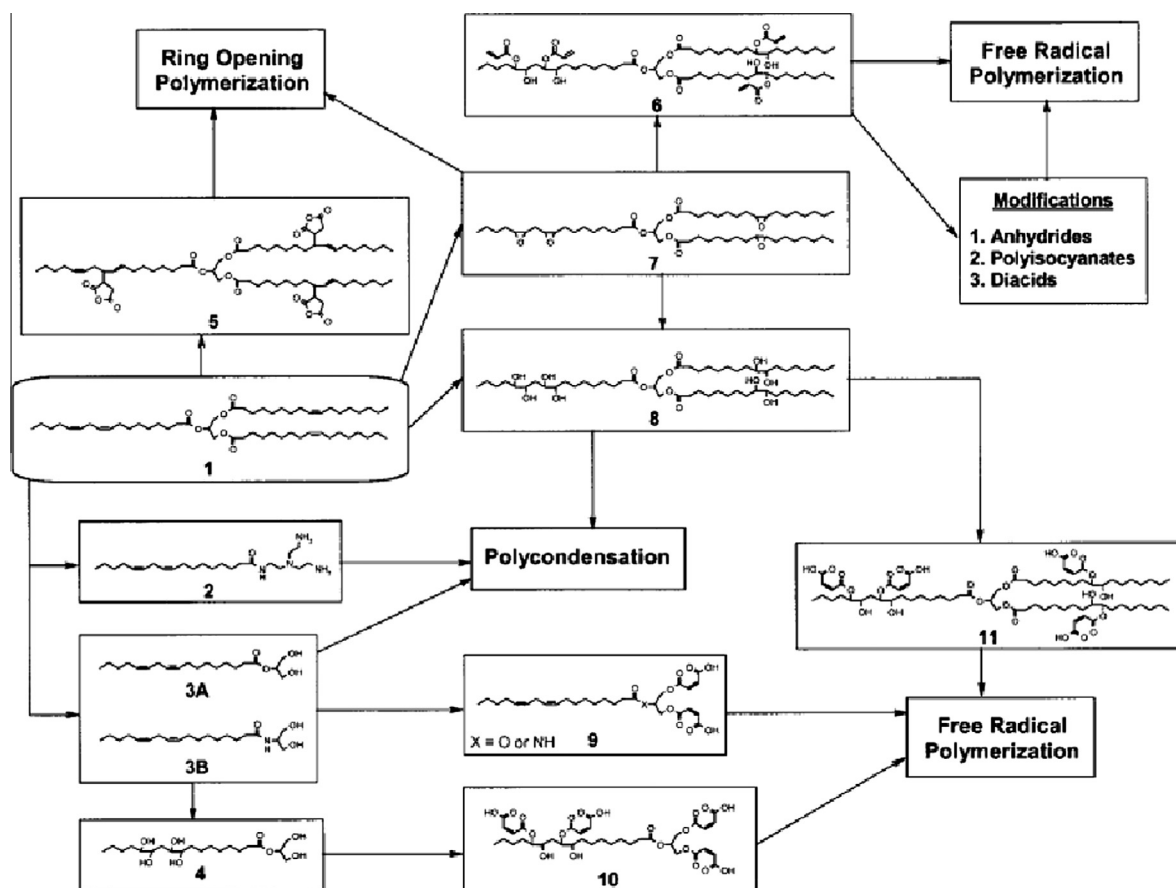


Fig. 1. Chemical pathways leading to polymers from triglyceride molecules. Reprinted with permission of Wiley [5].

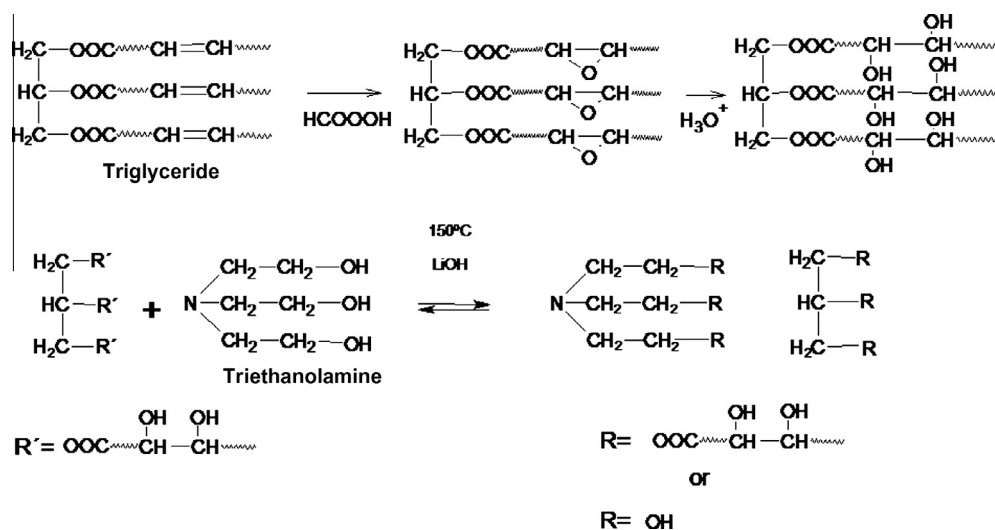


Fig. 2. Simplified scheme of hydroxylation and alcoholysis reactions of vegetable oil [20].

authors [17–19] have worked with soybean and linseed oil, in order to obtain monoglyceride maleate half esters. They modified the alcoholized vegetable oil with maleic anhydride, and the resulting products were polymerized by free

radical reactions with reactive comonomers like styrene, in some cases to be used as composite matrices.

Another possibility is to functionalize the unsaturation sites and also to obtain the monoglycerides (Fig. 1(4)). For

example, by alcoholysis of an unsaturated triglyceride, followed by hydroxylation (epoxidation followed by oxirane ring-opening) [20]. The simplified scheme of two steps is shown in Fig. 2. In a first step, the triglyceride reacts with peroxy formic acid to give an epoxidized triglyceride as an intermediate product and subsequently the hydroxylated oil. In the second step, the product of the first step reacts with triethanolamine to give an alcoholized product [20]. If the vegetable oil is naturally hydroxylated (for example: castor oil), the alcoholysis can be carried out to increase the concentration of reactive hydroxyl groups. Several works have reported on the use of alcoholized castor oil or alcoholized hydroxylated oils for the production of polyurethanes obtained by polycondensation reactions with different isocyanate components [12,20,21]. The hydroxyl groups in the resulting monomers can be further reacted with molecules containing anhydride, diacid or epoxy groups to form monomers useful for free-radical polymerization.

Desroches' review on vegetable oil derived bio-polyurethanes [6] presents a detailed review of different possible synthetic routes and includes a useful list of commercial bio-based polyols that can be applied in the production of polyurethanes.

Other alternative routes have been considered although not all of them have yet found use as composite matrices. One of these routes, and a versatile one is that of the thiol-ene chemistry [22]. It has been proved to be useful for the production of polyols for polyurethane formulations or to synthesize polyamine oils that become the curing agent of epoxidized vegetable oils or alternatively, it can also lead to the production of thermoplastics by thiol-ene polyaddition [23–25]. Montero de Espinosa et al. [26] also focused on olefin metathesis and thiol-ene chemistry as synthetic methods and polymerization techniques. A catalytic route from fatty acids has led to the synthesis of intermediates for nylon 11 and 12 [27].

It is generally perceived that with time these new alternatives will find a place in the production of composites.

### 3. Vegetable oil-based composites

#### 3.1. Glass fiber composites

Among the typical reinforcements for polymer composites are the ubiquitous glass fibers (GFs). Thus, it is understandable that they have also been considered as reinforcement of plant oil-based thermoset resins. Examples of these are unsaturated polyester and epoxy resins, or elastomer precursors such as polyols that are further crosslinked with synthetic or plant oil-based comonomers, using different curing and compounding processing methods. Although there is a large variety of plant oils available, soybean oil appears frequently in the literature due to the large production volume associated to it. Table 1 includes examples of these composite materials to give a fast glimpse of the broad range of properties that are possible to obtain from the use of vegetable oil-based polymers by using different modifications, crosslinking or polymerization routes, processes, fillers and fibers from macro to

micro and nanosizes. In particular examples of thermoset-glass fiber composites are included.

Khot et al. utilized an acrylated epoxidized soybean oil to produce glass fiber composites by resin transfer molding [5]. Depending on the fiber content, Young's moduli of 5.2 to 24.8 GPa were measured for the composites bearing 35 and 50 wt.% of GF, respectively, and tensile strengths of 129–463 MPa, for the same samples.

Other authors studied GF composites prepared from a mixture of synthetic and bio-based epoxy resins. Chandrashekhara et al. used an epoxidized soy oil based resin mixed with a commercial epoxy-amine system formulated for use in pultrusion [28]. The soybean oil was transesterified to obtain the methyl or allyl esters of the fatty acids that were further epoxidized. Mixtures with the synthetic epoxy resin were formulated from 0 to 30 wt.% of the bio-resin and they were cured by addition of an amine hardener under a heating protocol that considered cure and postcuring. Since the epoxy groups in the fatty acid chains are not terminal, the resulting molecular structures contain a large concentration of dangling chains that have a plasticizing effect, leading to more flexible materials than the synthetic counterparts. Pultruded GF composites (63 wt.%) were prepared with this resin and it was observed that although the tensile and flexural properties were not strongly affected by the replacement of the synthetic epoxy by the bio-based resin, there was a clear improvement of the resistance of the composite to impact damage. This was the result of the already discussed flexibility of the fatty acid chains and also the comparatively lower reactivity of the bio-based resin with respect to the commercial epoxy. An additional and much welcomed output of this study was the observed reduction of the force needed to pultrude the composite bars (almost 30% reduction for the formulation made with a 30% replacement of the epoxy resin by the bio-based one). This benefit was explained by the lubricity properties contributed by the oil-based epoxy resin.

The plasticizing effect of the dangling chains was also observed in other type of resins, and thus, it was reported by Husić et al. who prepared a soy-based polyol crosslinked with crude polymeric diphenyl methane diisocyanate (pMDI) and reinforced with up to 70 wt.% of glass fiber fabric [29]. In this particular case, a short molecule polyol was added to increase the rigidity of the composite. Tensile and flexural properties were comparable to the results measured for an analogous glass fiber composite prepared with a synthetic commercial polyurethane.

Cationic polymerization is another means of crosslinking modified oils and Lu and Larock utilized this type of reaction to prepare soybean oil and low saturation-soybean oil-based composites reinforced with 0–50 wt.% GF mats [30]. The resins were reacted with styrene and divinyl benzene (DVB), but previously the oils had to be isomerized in the presence of rhodium catalyst to obtain species with more reactive conjugated unsaturations. The mixture contained 50 wt.% of vegetable oil and variable proportions of styrene and divinyl benzene (10–20 wt.% of the last one). The reaction consisted of a slow curing program from 60 to 110 °C, requiring 15 h at this last temperature. Generally speaking, the interfacial adhesion of these resins to

**Table 1**  
Examples of polymer composites prepared from plant oil derived polymers.

Polymeric matrix	Fiber/particle	%	Process	Modulus (Pa)	Strength	Other improved properties	Ref.
ESO (10% replacement of epoxy) + epoxy-amine	Glass fiber	63	Pultrusion	$5.64 \times 10^{10}$ (T)		Lubricity, 21% reduction of the pulling force with 10% epoxy-ESO replacement	[28]
AESO	Glass fiber	35	RTM	$5.20 \times 10^9$ (T)	$.29 \times 10^8$ (T)		[5]
Low saturated soy oil/St/DVB (50:20:20). Cationic crosslinking	Glass fiber	50	Compression molding (GF-mats)	$2.48 \times 10^{10}$ (T)	$4.63 \times 10^8$ (T)		[30]
		52		$1.50 \times 10^8$ (T)	$7.90 \times 10^6$ (T)		
Soy oil-polyurethane	Glass fiber	70	Hand lay-up	$1.71 \times 10^{10}$ (T)	$2.59 \times 10^8$ (T)	Plastification by bio-resin incorporation	[29]
Linseed oil (DCDP-ROM crosslinked)	Glass fiber	0		$0.91 \times 10^6$ (T)			[31]
Conjugated soy oil (St-DVB crosslinked)	Wheat straw	40	Compression molding	$6.80 \times 10^8$ (T)			[36]
		0		$4.59 \times 10^8$ (T)	$1.47 \times 10^7$ (T)		
Conjugated soy oil (DVB crosslinked)	Corn stover	75		$2.16 \times 10^9$ (T)	$8.30 \times 10^6$ (T)		[37]
		80		$1.40 \times 10^9$ (T)	$7.4 \times 10^6$ (T)		
Methacrylic anhydride modified soybean oil	Regenerated cellulose		Compression molding	$1.80 \times 10^{10}$ (T)	$1.44 \times 10^8$ (T)	High impact resistance	[40]
AESO	Hemp	20	RTM	$4.40 \times 10^9$ (T)	$3.50 \times 10^6$ (T)		[5]
AESO (St crosslinked)	Keratin fibers (from chicken feathers)	0	RTM	$8.96 \times 10^8$ (F)	$3.48 \times 10^7$ (F)	Low dielectric constant and expansion coefficient	[47]
		30		$1.59 \times 10^9$ (F)	$4.52 \times 10^7$ (F)		
Linseed oil (St radical polym.)	Pine woodflour	40		$1.50 \times 10^9$ (T)	$1.99 \times 10^7$ (T)		[41,42]
				Aged (654 days)	Aged (654 days)	$2.10 \times 10^9$ (T)	
Castor oil (PU)	Banana fiber	0	Hand-lay up	$5.89 \times 10^6$ (T)	$1.96 \times 10^6$ (T)		[38]
Castor oil (PU)	MDI-modified cellulose	15(vol.) untreated NaOH treat	43	$5.10 \times 10^7$ (T)	$4.80 \times 10^6$ (T)		[39]
				$5.40 \times 10^7$ (T)	$1.01 \times 10^7$ (T)	$4.87 \times 10^6$ (T)	
Tung oil (PU)	Pine woodflour	0		$9.10 \times 10^8$ (T)	$2.60 \times 10^7$ (T)	Improved impact resistance	[44]
				$3.03 \times 10^9$ (T)	$4.49 \times 10^7$ (T)		
ESO (amine cured)	Nanoclay	0		$1.20 \times 10^6$ (T)	$1.27 \times 10^6$ (T)		[48]
				$3.54 \times 10^6$ (T)	$4.34 \times 10^6$ (T)		
Conjugated low saturated soy oil (St-DVB crosslinked)	Nanoclay (reactive clay by using a vinyl-modifier)	0		$2.56 \times 10^8$ (C)	$2.50 \times 10^7$ (C)	Improved barrier properties and thermal degradation behavior	[53]
				2	$5.84 \times 10^8$ (C)		
Castor oil (waterborne PU)	Nanocellulose	0	Casting	$1.16 \times 10^6$ (T)	$5.42 \times 10^6$ (T)	Elongation remains $\geq$ 300%. Nanocellulose favors phase separation	[57]
				4	$4.83 \times 10^6$ (T)		
Castor oil (PU from alcoholized oil)	Nanocellulose	0	Casting	$4.80 \times 10^8$ (T)	$2.76 \times 10^7$ (T)		[12]
		0.5		$6.36 \times 10^8$ (T)	$1.92 \times 10^7$ (T)		
		1		$6.80 \times 10^8$ (T)	$3.12 \times 10^7$ (T)		

(T) Tensile results.

(C) Compression results.

% All the concentrations are given as weight percent, except where specifically indicated.

the glass fibers was not high and the fibers showed clean surfaces protruding from the fracture surface. However, the authors could observe that adhesion increased with crosslinking density as higher concentration of DVB was utilized in the formulation. The addition of 50 wt.% of glass fibers to the low saturated soybean oil-styrene-DVB material (50:20:20 weight ratio, the rest being the initiator and modifier) produced an increase in Young's modulus from 150 to 2730 MPa and in tensile strength from 7.9 to 76 MPa. The

authors indicated that the soybean oil-based composites have good structural damping properties, which can be advantageous for applications where the reduction of noise and vibration is required.

Henna et al. [31] used dicyclopentadiene (DCPD)-modified linseed oil crosslinked with DCDP as matrix for glass fiber composites. Increasing DCDP concentration lead to higher rubbery modulus (dynamic-mechanical measurements), since the network had fewer free dangling side



chains together with a lower molecular weight between crosslinking points, thus, producing a more rigid material. Similar arguments were used to explain the increase of  $T_g$  under those conditions.

The incorporation of glass fibers did not change the position of the  $\alpha$  transition as observed by the maximum of  $\tan \delta$ , but it reduced the height of the peak, since the material gained rigidity. Regarding the tensile properties, a 74.6 times higher Young's modulus was reported for the 60:40 (modified oil-DCDP) composite containing 40 wt.% of glass fibers.

From the above examples, most of them summarized in Table 1, it is clear that high GF loads can be reached with good wetting of the fibers, what allows reaching tensile modulus as high as 56.4 GPa [28] and hundreds of MPa in strength. In all cases, the replacement of synthetic chemicals by bio-based monomers leads to reduced fragility of the components, due to the plasticizing effect of the fatty acid dangling chains, which also showed to have a lubricant affect in pultrusion of the glass fibers.

### 3.2. Other macro and micro-synthetic fillers/reinforcements

Aiming to reduce the environmental impact of different waste materials, some of them have been considered as polymer fillers; this solution being particularly interesting when the matrices utilized are also environmentally friendly. Following this line of thought, Ray et al. investigated the behavior of a blend of an epoxy resin and maleated castor oil co-reacted with an amine and filled with 10 wt.% of fly ash [32]. Except for the reduced costs, there were little extra benefits in composite performance due to the addition of the ashes. On the other hand, the partial replacement of the resin with a bio-epoxy one, resulted in improved impact strength for the bio-modified formulation, reduced glass transition temperature ( $T_g$ ), and higher intensity of the  $\tan \delta$  peak (dynamic-mechanical temperature-scans), which suggests that these materials could be used in applications for damping of mechanical vibrations.

Analogously, Bassyoumi et al. prepared a polyurethane (PU) composite from castor oil (the polyol component), polymeric diphenyl methane di-isocyanate (pMDI), and milled waste-light bulbs (particle size  $\leq 300 \mu\text{m}$ ) as filler. Treatment of the glass with  $\gamma$ -aminopropyltriethoxysilane was considered in order to improve adhesion to the matrix by co-reaction with the isocyanate component [33]. The benefits of the glass addition were mainly observed in the retarded thermal degradation, reduced swelling and increased hardness, with all these improvements being more important in the treated-particle composites.

Improved water resistance or damping properties have been reported for PU-polyester nonwoven fabric and interpenetrated epoxy-polyurethane network filled with titanate whiskers, both systems derived also from castor oil [34,35].

### 3.3. Natural fiber/filler composites

The advances in the production of polymers from bio-resources have been accompanied by the growing interest

to develop composites that incorporate bio-based particles and fibers.

Pfister and Larock presented an interesting comparison of the behavior of different cationically cured plant oils used as matrices of agricultural fibers [36]. They considered composites prepared from corn, soybean, fish, and linseed oils using up to 75 wt.% of different natural fibers, corn stover, wheat straw, and switch-grass fibers. The composites showed a largely increased rigidity with respect to the unfilled thermosets, but they were also much more brittle. The Young's moduli reported were in the range of 1.6–2.3 GPa and the tensile strengths were between 5.5 and 11.3 MPa. One interesting observation was that higher degree of unsaturation of the natural oil lead to better thermal and mechanical properties of the composites, which can be linked to the higher crosslinking density that can be achieved in these materials. On the other hand, wheat straw fibers offered the best performance composites.

The same authors have also investigated composites from corn stover and conjugated soybean oil or conjugated linseed oil cured with DVB by radical copolymerization [37]. Corn stover is a large volume residue left after harvest and, as already mentioned in the case of other residues, environmental reasons were involved in finding a use for this waste material. The composites considered had a large proportion of bio-based components, up to 90% in those prepared with a matrix containing 50% natural oil, and overall concentration of 80 wt.% of corn stover in the composite. The Young's moduli and tensile strength of these composites reached 1.4 GPa and 7.4 MPa, respectively, and although traditional wood plastic composites can reach better performance, these "green" composites could still find application in automotive and wall panels, ceiling tiles, furniture, windows and doors.

Castor oil-based polyurethanes were chosen as matrices for banana fibers processed by hand lay-up of short random fiber-mats, followed by compression molding at room temperature [38]. The banana fibers were chemically modified by NaOH extraction, a typical treatment of vegetable fibers that eliminates plant fiber components (extractable chemicals, lignin and hemicelluloses) increasing the fiber roughness and cellulose concentration. The authors investigated the effects of varying the fiber volume fraction and length on the tensile modulus and strength, and reported that the optimum response for both types of composites occurs when working with 30 mm fibers at 15 vol.%. The properties were higher if working with treated fibers because of the improved chemical and mechanical interactions at the interface (a reaction of the isocyanate with fiber-OH groups was proposed).

Similar type of interactions are to be expected in the castor oil-based polyurethane composites prepared by Miao et al. [39], who reported a 5-times increase of the tensile strength by addition of 43 wt.% of MDI-modified cellulose to the formulation of the composite.

Resin transfer molding was the method chosen to prepare an acrylated epoxidized soybean oil (AESO)-hemp fiber composite [5]. The sample with 20 wt.% of hemp showed a Young's modulus of 4.4 GPa. The authors further proposed the preparation of hybrid composites that incor-

porate also GF, to combine the high performance of the synthetic fibers with the low cost of the plant fibers.

Hybrid thermoset composites made from methacrylic anhydride modified soybean oil and different natural fibers were reported by Adekunle et al. [40]. They used 2D woven fabrics made from jute and from regenerated cellulose, and combination of both mats (hybrids). However, the best overall properties were found for the regenerated cellulose composites with tensile strength and modulus of 144 MPa and 18 GPa, respectively.

Mosiewicki et al. investigated the behavior of thermoset composite materials made from a linseed oil unsaturated resin cured with styrene by peroxide initiated radical polymerization [41]. The pine wood flour (WF) used as reinforcement had a tremendous impact on the glass transition temperature of the polymer (upwards shift of 40 °C in the sample that contained 30 wt.% WF), accompanied by increased glassy and rubbery storage modulus. All these characteristics pointed out to strong interfacial interactions, which was supported by scanning electron microscopy (SEM) images of fracture surfaces showing perfectly polymer-coated WF, negligible pull out of the low aspect ratio flour and completely filled lumens in the wood cells. Additionally, Pukanszky's model was applied to analyze the flexural strength of the composites [42]. The fitting parameter of the model, related to the interfacial strength, also showed good correlation with a strong interfacial adhesion. At concentrations above 30 wt.% of WF the composites showed increasing degrees of porosity, because of flour aggregation.

Although not frequently treated in the literature, oil-based polymers and composites may suffer chemical aging if some unsaturations remain unreacted after the modification and/or the crosslinking steps. The chemical changes involved correspond to the same complex mechanisms of oxidation-crosslinking that takes place during oil drying. Mosiewicki et al. showed that important variations of the properties accompany the chemical changes [43]. Using the pine WF- linseed oil -based composite discussed above, the authors studied the variations in flexural properties of the materials and reported increases of the modulus and strength (1.5 GPa and 19.9 MPa, respectively, for the recently prepared composite with 40 wt.% WF, and 2.1 GPa and 32.2 MPa for the same sample after 654 days).

The same research group has also studied polyurethane-pine wood flour composites prepared from a modified tung oil. Tung oil is a drying oil with a long history in the industry of varnishes and paints because of its good drying properties and the quality of the coatings obtained. The oil was modified by hydroxylation of the unsaturations followed by alcoholysis with triethanolamine. The high hydroxyl value of the obtained polyol was well fitted to prepare rigid polyurethanes. WF and microcrystalline cellulose were used as reinforcements [20], with the best performance corresponding to the WF composites, what was explained by the better dispersion of this reinforcement. Specific interactions were expected in these systems because of the co-reaction between the OH groups of the matrix and reinforcement through the isocyanate component. The pine-WF composites were further studied to determine the effect of the WF concentration on the final properties of the materials [44]. The excellent compatibility between WF and the bio-polyurethane al-

lowed reaching composites with higher modulus and higher strength, as compared with the neat polymer, but simultaneously with similar extensibility and much higher fracture resistance; a behavior that had been highlighted in nanocomposites [45], but that was quite unusual for microcomposites. These materials (below 30 wt.% WF) showed ultimate elongation comparable to that of the neat polymer, and even higher values for WF concentrations of 10 and 15 wt.%. The 30 wt.% composite had a tensile modulus more than threefold the value of the unfilled polyurethane and the same was true for the total energy measured during the falling dart impact test (123 and 389 J/m for the 0 and 30 wt.% composite, respectively). In this case, the fitting parameter of the Pukanszky model for tensile strength also indicated strong interfacial interactions; the reported value being between 5 and 7, while a value higher than three is indicative of good interface in the composite.

The authors also followed the degradation of the composites buried in vermiculite inoculated with a mixed bacterial culture and soil with natural flora [46] for more than a year, and found that the more important degradation step occurred during the first 60 days, and was probably related to the hydrolysis and scission of dangling chains that correspond to the fatty acids segments of the oil.

Although not much treated in the literature, interesting composites have been developed from soybean resins and hollow keratin fibers from chicken feathers [47]. These fibers are low density, hollow, hydrophobic and as shown by the authors well wetted by an acrylated epoxidized soybean oil (AESO) and soybean oil pentaerythritol glyceride maleate resins. In both cases the comonomer chosen to attain crosslinking was styrene, and the composites were light, with low dielectric constant and thermal expansion coefficient, which made them potential candidates for electronic applications. Carbonized chicken feathers were also investigated as possible sources for low cost carbon fibers.

The above examples (see also Table 1) showed that the bio-derived thermoset composites have tensile modulus mostly in the range of 1–3 GPa. Many of the authors point out to their improved impact resistance and their potential use as damping materials, due to the mechanical energy dissipated by the relaxation of the dangling chains. Large modulus increase is also seen in elastomers, where the addition of the natural fibers/particles gives leather-like characteristics to these materials. Synergy has also been reported, consisting in obtaining composites with higher rigidity than the bio-polymer without appreciable loss of its extensibility. Finally, although scarcely reported, oxygen-driven crosslinking via unreacted oil unsaturations (when these are present) causes important changes in the material properties (sometimes beneficial changes), what cannot be neglected in mass production.

## 4. Vegetable oil based nanocomposites

### 4.1. Nanoclay composites

Since the global surge of interest in nanostructured and nanocomposite materials, nanoclays have occupied a large proportion of the efforts of researchers around the world,

because of the natural source for the particles and the promise of improving barrier as well as mechanical properties of the nanocomposites. Thus, it is only understandable that they appear frequently in the literature as proposed reinforcements for plant oil-based nanocomposites.

For example, Liu et al. prepared networks from an epoxidized soybean oil (ESO) with nanoclay as reinforcement [48]. While the tensile properties were improved up to 8 wt.% of clay addition, higher concentrations lead to properties reduction. These results were explained by the immobilization (or partial immobilization) of the polymer chains due to the presence of the silicate layers below 8 wt.% and the inevitable aggregation that took place at a concentration of clay of 10 wt.%. The dynamic mechanical analysis showed that these materials had glass transition temperatures in the range of 11.8–20.7 °C (from 0 and 5 wt.% clay, respectively).

Uyama et al. used an epoxidized soybean oil (ESO) cationically crosslinked at high temperature in the presence of organically modified montmorillonite (0–20 wt.%) [49]. In this case, dynamic mechanical analysis (DMA) showed that the rubbery storage modulus increased with the clay concentration, but also the  $T_g$  shifted from –2 to 4 °C for samples bearing 0–15 wt.% of clay, respectively. This change was explained as the result of the co-reaction of ESO with the modified clay, which together with the rigidity of the clay afforded freestanding flexible films instead of a soft one without structural value.

Partial replacement (up to 20 wt.%) of a commercial unsaturated polyester resin (UPE) with an epoxidized methyl soyate (EMS) cured with (35 wt.% of styrene) was used to prepare clay nanocomposites [50]. As it is frequent when handling nanoparticles, the dispersion of the nanoclay required the use of solvent and sonication. In general, the replacement of the commercial resin by the bio-derived one resulted in lower moduli and  $T_g$ , for which reason nanoclays were added to the formulation. As it was already discussed for glass fiber composites, the toughness of the materials was increased by the use of the bio-resin; the energy absorption during deformation and failure was more than double when replacing 10 wt.% of the UPE by the bio-resin in the 1 wt.% clay nanocomposites.

Kaushik et al. prepared a polyurethane-nanoclay composite, with castor oil as the polyol component, 1,4-butane diol as chain extender and a stoichiometric quantity of MDI as crosslinker [51]. A quaternary ammonium modified montmorillonite was used to reinforce the polyurethane, varying the concentration from 0 to 5 wt.%.

X-ray diffraction is a technique commonly used to detect the degree of dispersion of the clays. If the structure corresponds to intercalated silicate layers, the (001) peak shifts to lower angle due to the increase of the interlayer spacing. On the other hand, if the structure corresponds to exfoliated clay nanocomposites, no peaks can be observed in the X-ray diffraction (XRD) pattern. In the considered study, there were delaminated stacks of silicate layers, but also individual platelets, and also agglomerates, situation that was corroborated by transmission electron microscopy (TEM) observation (both in Fig. 3). Tensile results shown in Fig. 4 are in agreement with the good dispersion observed; Young's modulus, tensile strength, as

well as elongation at break increase with the clay concentration, a very interesting result, since in traditional composites higher rigidity is usually obtained at the cost of lower elongation. Besides the expected improvement of the thermal degradation behavior, the incorporation of nanoclays also resulted in the improvement of the barrier properties to the diffusion of vapor and liquid water. The water vapor permeability at 98% relative humidity (RH) and 25 °C dropped from  $513 \times 10^{-8} \text{ mm}^2 \text{ s}^{-1}$  for the neat polymer to  $0.67 \times 10^{-8} \text{ mm}^2 \text{ s}^{-1}$ , for the composite containing 5 wt.% of modified montmorillonite. This remarkable improvement is due to the tortuosity of the diffusion path, but also to the strong H-bonding interactions formed between the PU matrix and the platelets, which stabilizes the composite structure and reduces the availability of polar groups to attract water molecules.

Chen et al. worked with a mixed system of polyurethane prepared from castor oil and TDI partially reacted and interpenetrated with epoxy-amine [52]. They also reinforced the grafted-IPN with montmorillonite (MMT) in clay/polymer ratios from 1/100 to 7/100. The addition of MMT increased the  $T_g$  of the materials (about 7 °C) but also the height of the  $\tan \delta$  peak (well above the value of 0.3, as measured by DMA) and its width. Both features are indicative of a material that could be used for mechanical damping. While a small MMT addition, one part per hundred, improved the tensile and impact properties, higher concentrations of clay do not have further beneficial effect.

Cationically copolymerized conjugated soybean oil and low saturated soybean oil with styrene and divinyl benzene was also used as matrix of an organo-modified montmorillonite clay nanocomposite [53]. The sodium-clay was modified by the usual ionic exchange with (4-vinylbenzyl) triethylammonium chloride in aqueous solution and the obtained dispersion consisted in a mixture of intercalated and partially exfoliated montmorillonite for concentrations below 2 wt.% and intercalated above that value, as determined by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). The polymeric

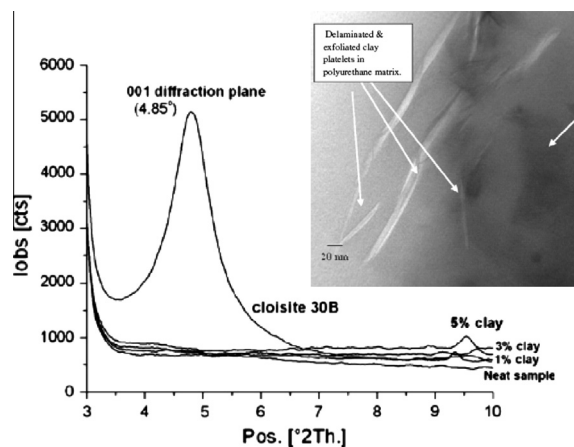


Fig. 3. WAXRD of castor oil based clay nanocomposites with varying percentages of clay. Reprinted with permission of Elsevier [51].



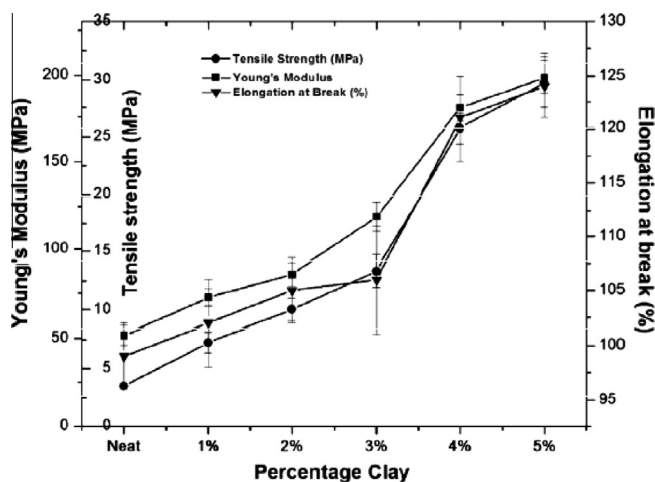


Fig. 4. Tensile strength (MPa), Young's modulus (MPa) and elongation at break (%) for various polyurethane clay nanocomposites. Reprinted with permission of Elsevier [51].

matrix consisted on 50 wt.% of the oil-based resin, 20 wt.% of styrene and 10 wt.% of DVB, the rest being the modified initiator. The glass transition temperature of these materials (from the maximum in the peak of  $\tan \delta$ , DMA temperature scans) decreased with MMT addition from 12 to 6 °C for the conjugated soybean oil, and from 23 to 18 °C for the conjugated low saturated oil (0–5 wt.% MMT, respectively). The effect was explained as resulting from the increased viscosity of the medium that lead to incomplete mixing of the initiator and reduced propagation of the chains. On the other hand, the presence of up to 2 wt.% of the nanoclay clearly improved the barrier properties to water vapor and the thermal stability of the composites, as already observed for other clay composites. The compressive modulus was also improved (from 256 to 584 MPa at 0 and 2 wt.% of montmorillonite, respectively, for the composite based on the conjugated low saturated soybean oil).

In some cases, hybrid reinforced composites have been fabricated; Liu et al. extruded soybean oil/epoxy-based composites reinforced with glass fibers and modified with organo-modified clays [54]. Miyagawa et al. also prepared hybrid composites, incorporating organically modified nanoclay and alumina nanowhiskers with diameter of 2–4 nm and aspect ratio of 20–100 and treated with an amino-terminated ethoxy-silane [55]. The composites had an epoxy-anhydride matrix where 30–50 wt.% of the epoxy resin was replaced by two different epoxidized vegetable oils, linseed oil and soybean oil. The nanoparticles were dispersed in the epoxy using sonication and the resin was cured with anhydrides. No changes in dispersion level were observed in the composites as a function of the bio-resin concentration. The addition of 5 wt.% of exfoliated nanoclay to the bio-based epoxy material lead to a 30% increase of the storage modulus at 30 °C, while the use of an equal concentration of the alumina whiskers produced a 50% increase in identical conditions, which was most probably related to the different aspect ratio of the nanoparticles. The use of epoxidized linseed oil (ELO), which had a higher epoxy functionality and lower molecular weight than the epoxidized soybean oil (ESO), resulted in a transparent polymer differ-

ently from the phase separated opaque material produced from ESO. Actually, the separation of a rubbery phase in ESO based-composites lead to increased fracture toughness: 0.525, 0.520 and 1.54 MPa m<sup>1/2</sup>, for the neat epoxy system, the 50% ELO and the 30% ESO, respectively.

As it has been frequently reported for synthetic-based polymer composites, the addition of nanoparticles/nanofibers largely improves mechanical properties at comparatively low loadings (Table 1). When adequate dispersion of the nanofillers is obtained strength is preserved or even much improved. In particular, the use of nanoclays improves thermal degradation behavior as well as vapor barrier properties.

#### 4.2. Other nanoparticles and nanofibers

Lligadas et al. reported studies on epoxidized linseed oil (ELO)-based composites containing polyhedral oligomeric silsesquioxanes (POSS) [56]. To prepare the samples, 3-glycidylpropylheptaisobutyl-T8-polyhedral oligomeric silsesquioxane was dissolved in a minimum of acetone and mixed with ELO to obtain 2, 5 and 10 wt.% POSS concentrations. Energy-dispersive X-ray spectroscopy (SEM-EDX) allowed Si-mapping showing a good dispersion of the POSS is obtained, although the DMA results showed that the incorporation of the silsesquioxane increased the  $T_g$  of the materials up to 5 wt.% concentration (44 °C and 52 °C for the 0 and 5 wt.% samples), but higher concentrations resulted in reduced  $T_g$  (42 °C for the 10 wt.% samples).

A waterborne polyurethane synthesized from castor oil and polyethyleneglycol crosslinked with isophorone diisocyanate was used as the matrix in a cellulose nanocrystals composite with concentrations from 0.2 to 5 wt.% [57]. The crystals obtained by acid hydrolysis of cellulose from *Eucalyptus globulus* had average length and diameter of  $518.0 \pm 183.4$  nm and  $21.7 \pm 13.0$  nm, respectively. A good dispersion of the bio-nanoreinforcement was observed; the Young's modulus of the elastomeric material increased with the nanofiber concentration from 1.16 MPa for the neat PU to 4.83 MPa at 4 wt.% cellulose. At higher concentrations

the modulus dropped because of the agglomeration of the nanocrystals. On the other hand, the tensile strength showed a maximum at 1 wt.% of nanocellulose (12.22 MPa compared to 5.42 MPa for the unreinforced PU), while the elongation at break was maintained above 300% for all the materials. An interesting observation was that the addition of nanocellulose enhanced phase separation between soft and hard segments, with the largest hydrogen bonding interactions occurring between the cellulose crystals and the hard segments, which resulted in the shift of the glass transition temperature of the hard segments towards higher temperature.

Similarly, Maafi et al. prepared a polyurethane from castor oil and hexamethylene diisocyanate (HDI) reinforced with cellulose fibers from alfa stems [58]. As in the previous case strong interactions between matrix and fibers were reported due to H-bonds, but also to co-reaction between polymer and fibers. An important shift from 3336 to 3319  $\text{cm}^{-1}$  in the infrared NH absorption was reported for the composite containing 25 wt.% of cellulose. The glass transition temperature and mechanical properties of the composites increased steadily up to 20 wt.% of fibers, which was also an indication of the good dispersion obtained.

Wik et al. synthesized an alcoholized castor oil for the production of solid polyurethanes reinforced with nanocellulose (NC) obtained by acid hydrolysis of microcrystalline cellulose [12]. The chemical bonding of the NC to the matrix was used to explain the significant increase in tensile modulus with the addition of just 0.5 wt.% of NC (479.5 MPa and 636.4 MPa for the unfilled PU and the nanocomposite, respectively). From the reported results, it appears that dispersion is better at 0.5 wt.% of NC and some aggregation is already present at concentrations as low as 1 wt.%. Tensile properties of the unfilled and filled castor oil based-polyurethane are summarized in Table 1.

## 5. Special applications

### 5.1. Composite coatings and adhesives

Among the various possible applications of the oil-derived polymer composites, adhesives and coatings have received much attention. Konwar et al. prepared a polyester resin from seed oil of *Mesua ferrea* L. (also known as Ceylon ironwood, a hard wood tree from South Eastern Asia) reinforced with nanoclays in order to obtain a coating with improved performance of hardness, mechanical properties, impact and also chemical resistance, as well as gloss [59]. Glycerolysis of the oil followed by reaction with anhydride and then, with a hydroxy-acid produced highly branched molecules. The carbonyl containing polyester resin was then reacted with a poly(amido-amine)-epoxy mixture in the presence of the nanoclay. Hydrogen bonding between the nanoplatelets and the resin occurred through the amine as well as carbonyl moieties present in the matrix. The addition of only 2.5 wt.% nanoclays improved the tensile strength from 2.7 to 7.1 MPa, and also the elongation at break from 24% to 145%, while the impact hardness improved about 19%. Chemical resistance to water and acids

was improved with nanoclay addition up to a concentration of 2.5 wt.%, as well as thermal stability, gloss and hardness. The biodegradability of the films was also investigated using the broth culture technique with bacterial strains, resulting in larger bacterial growth in the nanocomposite than in the unfilled films.

Similar results, regarding hardness, tensile properties, thermal stability and biodegradation were reported by the same group, for a clay-nanocomposite prepared from reactive mixtures of epoxy-amine and bio-based polyurethane derived from *Mesua ferrea* L. seed oil or the corresponding diethanolamide derived fatty acids [60].

An interesting study focused on an alkyd soy oil resin reinforced with polyaniline (PAni), 0.5–2 wt.% [61]. The authors reported that for concentrations of PAni higher than 1.5 wt.% phase separation occurred in 24 h. FTIR and UV-Vis techniques indicated the presence of strong H-bonds between the alkyd resin and PAni. The scratch hardness and impact resistance increased with PAni, although for the last property there was improvement only up to 1 wt.%. This improvement and the shorter drying time of the films containing PAni suggested that they could be used as corrosion protective coatings.

Other materials have been proposed as specialty coatings, such as one prepared from castor oil (urethane macromers containing carboxylic groups) with isophorone diisocyanate, propionic or tartaric acid and hydroxymethyl methacrylate [62]. Silver or gold nanoparticles were incorporated into the formulation and the polymer was cross-linked by irradiation in the presence of a photoinitiator. Good dispersion of the nanoparticles was reported, with a rather wide distribution of particle sizes, which were around 10 nm and 4 nm for the silver and gold particles, respectively. The composite films had reduced hydrophobicity with increased nanoparticles concentration and improved mechanical properties.

Silica nanoparticles have been considered to improve the performance of a coating prepared from castor oil and an isocyanate alkyl triethoxy silane, further hydrolyzed to form an organic-inorganic hybrid coating [63]. Similarly, Sharmin et al. prepared a mixture of DGEBA epoxy and castor oil in a ratio of 70/30 by weight, and 10 wt.% of prehydrolyzed TEOS [64]. After the reaction an organic-inorganic hybrid material was obtained, that was used to prepare films by reaction with TDI. The biohybrid coating was transparent, flexible, glossy and hard, showing to be scratch and impact resistant.

### 5.2. Composite foams

Polyols obtained from vegetable oils can be used to prepare composite polyurethane foams. The most widely reported methods to synthesize the oil-based polyols are the hydroxylation of the carbon-carbon double bonds (present in the fatty acid segments of the oils) and alcoholysis to obtain mono and diglycerides. Through these modifications, the hydroxyl group concentration in the modified oils increases, as compared to the initial oils, reaching values high enough to prepare rigid polyurethanes. In addition to polyol, an isocyanate source and a

catalyst, foaming of polyurethanes requires a surfactant agent and a foaming agent. Flexible to rigid foams with wide diversity of properties can be achieved depending on the polyol and the isocyanate components, the stoichiometric ratios, additives and the preparation procedure.

Rigid cellular polyurethane composites made with natural fibers have been recently reported by Kuranska and Prociak [65]. They replaced up to 80% of a synthetic polyol by a rapeseed oil based polyol, and used flax and hemp fibers of 0.5 mm length, to obtain composite foams with densities of about 40 kg/m<sup>3</sup>. The concentration of fibers added is limited by the cell growth and the thermal insulation requirements. In general, the properties were comparable to those obtained with a synthetic polyol, and allowed using a large percentage of biobased materials. High fiber concentrations (above 5 wt.%) affected the cell anisotropy index, since elongation of the cells in the foam rise direction was observed.

Although castor oil is a vegetal triglyceride naturally containing hydroxyl groups from the ricinoleic acid, it cannot be used without chemical modification in the production of highly rigid foams [66], because its hydroxyl value is not high enough for this purpose. Mosiewicki et al. reported the synthesis and characterization of castor oil based polyol by the alcoholysis of the oil with triethanolamine [11]. The synthesized polyol was then used in the formulation of polyurethane foams with and without reinforcement. The selected reinforcement/reactive filler was pine wood-flour and acceptable foams were prepared using up to 15% by weight of filler, although the compression properties decreased and the thermal conductivity slightly increased

with the addition of wood flour (from 39.4 mW/m<sup>2</sup>C to 45.3 mW/m<sup>2</sup>C for the bio-based foams with 0 and 15 wt.% WF, respectively). The characteristic rising times of the bio-foams were longer as compared with a commercial foam system, for both, unfilled and filled samples, which allowed achieving more uniform composite liquid mixtures before reaction. The thermal stability of the foams improved by addition of WF and by the total replacement of the commercial polyol by the castor oil derived polyol. On the other hand, the micro-sized filler introduced cell disruption.

Fig. 5 shows the scanning electron micrographs of the rigid foams formulated with the natural polyol as a function of the wood flour content. There is no preferential orientation in the cells, being the cellular structure of the unfilled foams, predominantly spherical and evenly distributed, with few broken cells. In general, the cells appear closed for the unfilled foam, with diameters ranging from 0.12 to 0.5 mm. The addition of WF to the formulation is responsible for an increase in the viscosity of the initial mixture, which turns to be less expandable, giving rise to a more distorted structure of cells, with a larger cell size distribution (less uniform sizes).

Zhu et al. reported on the properties of soy polyol based rigid polyurethane foams reinforced with cellulose microfibrils and with nanoclays [67]. As discussed in the previous work the incorporation of the microfibrils and nanoclays affected the cellular structure of the foam, so that the cell size decreased and the fraction of small cells increased, which affected the mechanical properties. Thus, more rigid

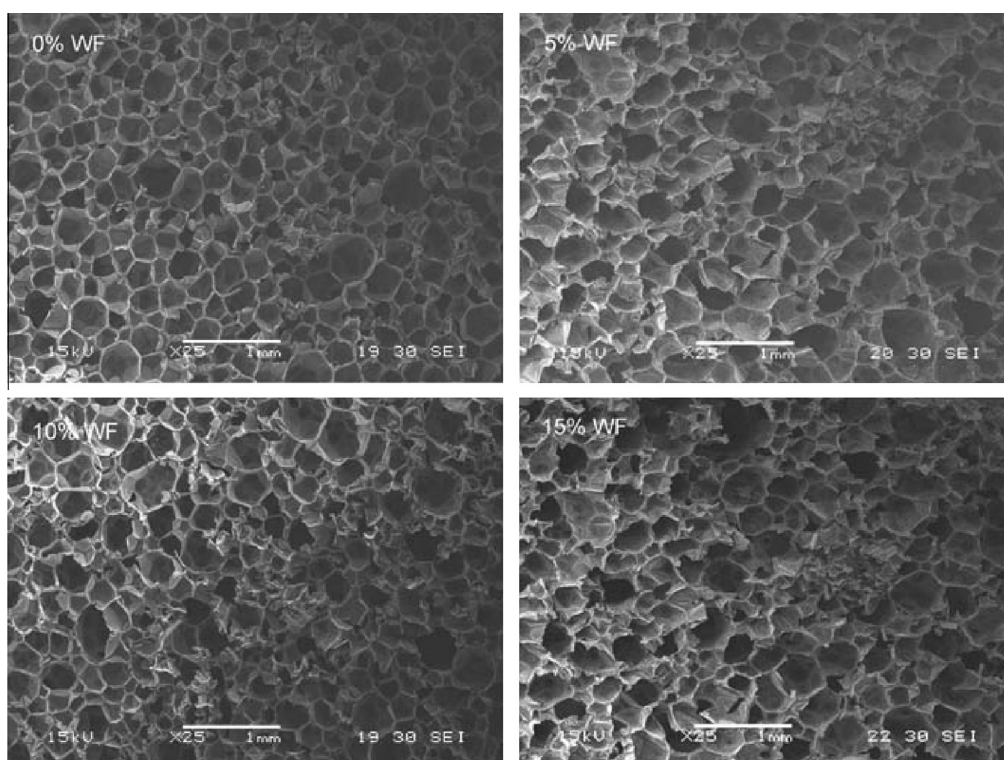


Fig. 5. Scanning electron micrographs of the natural foams obtained with a castor oil based polyol as a function of the wood flour content [11].

composite foams were obtained (the basis of comparison was the compressive strength of the foams).

Taking advantage of the wide versatility of polyurethanes, Aranguren et al. used castor oil to obtain polyurethane microfoams with different foaming levels that were reinforced with pine wood-fibers or hemp [68]. Semi-structural applications could benefit from the low density and good mechanical properties of this type of polyurethanes, for example for the manufacture of car interior panels or acoustic insulation panels for the construction industry, among others. In this work, a surfactant agent was used, but no catalyst in order to have a relatively low reaction rate that allowed for the fibers incorporation. Microfoamed composites with preferential orientation were prepared from long hemp fibers. Also, samples with random arrangement of short hemp or wood fibers were obtained. As in other studies, aging was observed due to oxidative crosslinking reactions that involve remnant unmodified unsaturations in the vegetable oil-based polyol. As a result, the modulus and strength of the material increased with time, and very interestingly, there was no decrease of the deformation to rupture, and for this reason the aged materials showed higher toughness than the original composites.

### 5.3. Shape memory materials

Shape-memory polymers are a group of smart materials with the capability to modify their shape, by fixing a temporary shape and self-recovering their original dimensions on requirement as response to an external stimulus [69,70].

When the external stimulus is temperature, the value that switches the response of the material is chosen to be above the glass transition temperature ( $T_g$ ) for crosslinked amorphous polymers, or a melting temperature ( $T_m$ ) for semicrystalline polymers. Usually, above the switch temperature ( $T_{\text{switch}}$ ) the material is rubbery and thus, it can be easily deformed into a temporary shape by an external force. This shape can be fixed by cooling the material below the corresponding transition temperature and the original shape can be further recovered by heating above the chosen  $T_{\text{switch}}$ . The permanent shape of the material is fixed by chemical or physical crosslinks that are stable in the range of temperatures used.

Some authors have considered the use of bio-derived precursors to prepare shape memory materials. In particular, it is remarkable the extensive work that the Larock's group has realized on thermoset polymers obtained by cationic polymerization of several unsaturated oils and styrene and/or divinyl benzene, which could be considered for the preparation of smart composites [10,71,72].

Rana et al. studied the behavior of a hyperbranched polyurethane prepared from castor oil, polycaprolactone diol, butanediol and MDI [73]. The triglyceride contributed to the formation of a hyperbranched structure and helped to improve the dispersion of the carbon nanotubes (CNTs). The segmented polyurethanes obtained were semicrystalline with shape memory properties. The overall crystallinity increased with addition of 2 wt.% CNT or reducing the hard segments concentration, while the recovery of the

original form was improved with increasing concentrations of CNT and hard segments.

Given the efforts dedicated to research on this type of polymers, it is very probable that more publications will appear soon on smart bio-composites in the next future.

## 6. Summary and future trends

Plant oils have already shown their versatility as sources for polymers and precursors. Almost from the beginning of the revival that started at the end of last century, they were also proposed as composite matrices, and it is clear from the work summarized in this review that the trend is continuously growing and with promising results. Some of the biopolymers and precursors mentioned are nowadays commercial and there are companies that offer derived bio-based polymers (epoxy, alkydic and polyurethane precursors being the most frequently found) for specific applications.

The research in the chemistry arena, that will allow offering new or improved derived chemicals in the future, has now permeated to the engineering and materials fields. Interdisciplinary efforts are recognized as necessary to improve formulations as well as processing conditions and materials performance in final applications. Clearly, this is the case observed in the publications that cover from the synthesis and characterization of the polymers to the selection of the reinforcement/filler and the various characterization techniques of materials structure and performance (mechanical and fracture), including specific ones (fire resistance, hardness, thermal and electrical conductivity, etc.).

Different particles and fibers have already been tried, from typical glass fibers to natural ones (wood flour and vegetable fibers), including nanosized inclusions such as nanoclays, carbon nanotubes, nanocellulose and also conductive polymer aggregates or organic-inorganic nanostructured copolymers. In all cases, compatibility was intrinsic to the matrix-filler system or it could be developed by using compatibilizing agents or filler modifications. Different processes have also been utilized, clearly the most common being casting and molding, but resin transfer molding and pultrusion have also been reported. Efforts in this area are needed to facilitate the transfer of technology to profitable industrial production.

It is also interesting to remark that although the initial use of plant oil based polymers was presented as a partial (minimum) replacement of synthetic polymers to introduce "green" materials in the formulation and little more than that, the trend is to increase the percentage of bio-based materials maintaining good overall performance and/or with tailored special properties, a goal for which the production of composites and nanocomposites is perfectly well fitted.

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## References

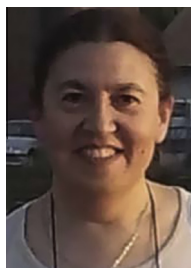
- [1] Wool R. In: Wool RP, Sun XS, editors. *Polymers and composite resins from plant oils in bio-based polymers and composites*. Burlington (USA): Elsevier Academic Press; 2005. p. 56–113.
- [2] Belgacem MN, Gandini A. In: Belgacem MN, Gandini A, editors. *Materials from vegetable oils: major sources, properties and applications in monomers, polymers and composites from renewable resources*. Oxford (UK): Elsevier; 2008. p. 39–66.
- [3] Lu Y, Larock RC. Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications. *ChemSusChem* 2009;2(2):136–47.
- [4] Xia Y, Larock RC. Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chem* 2010;12(11):1893–909.
- [5] Khot SN, Lascala JJ, Can E, Morye SS, Williams GI, Palmese GR, et al. Development and application of triglyceride-based polymers and composites. *J Appl Polym Sci* 2001;82:703–23.
- [6] Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B. From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. *Polym Rev* 2012;52:38–79.
- [7] Larock RC, Dong XY, Chung S, Reddy CK, Ehlers LE. Preparation of conjugated soybean oil and other natural oils and fatty acids by homogeneous transition metal catalysis. *J Am Oil Chem Soc* 2001;78:447–53.
- [8] Meiorin C, Aranguren MI, Mosiewicki MA. Vegetable oil based thermoset copolymers with shape memory behavior and damping capacity. *Polym Int* 2012;64(5):735–42.
- [9] Meiorin C, Aranguren MI, Mosiewicki MA. Smart and structural thermosets from cationic copolymerization of a vegetable oil. *J Appl Polym Sci* 2012;124(6):5071–8.
- [10] Li FK, Larock RC. Synthesis, structure and properties of new tung oil-styrene-divinylbenzene copolymers prepared by thermal polymerization. *Biomacromolecules* 2003;4:1018–25.
- [11] Mosiewicki MA, Dell'Arciprete GA, Aranguren MI, Marcovich NE. Polyurethane foams obtained from castor oil based polyol and filled with wood flour. *J Compos Mater* 2009;43(25):3057–72.
- [12] Wik VM, Aranguren MI, Mosiewicki MA. Castor oil-based polyurethanes containing cellulose nanocrystals. *Polym Eng Sci* 2011;51:1389–96.
- [13] La Scala J, Wool RP. Effect of FA composition on epoxidation kinetics of TAG. *J Am Oil Chem Soc* 2002;79(4):373–8.
- [14] Petrovic ZS, Zlatanic A, Lava CC, Sinadinovic-Fiser S. Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids – kinetics and side reactions. *Eur J Lipid Sci Technol* 2002;104:293–9.
- [15] Lu J, Khot S, Wool RP. New sheet molding compounds resins from soybean oil. I. Synthesis and characterization. *Polymer* 2005;46:71–80.
- [16] La Scala J, Wool RP. Property analysis of triglyceride-based thermosets. *Polymer* 2005;46:61–9.
- [17] Wool RP, Kusefoglu S, Palmese G, Khot S, Zhao R. US Pat., 6 121 398; 2000.
- [18] Can E, Kusefoglu S, Wool RP. Rigid, thermosetting liquid molding resins from renewable resources. I. Synthesis and polymerization of soy oil monoglyceride maleates. *J Appl Polym Sci* 2001;81:69–77.
- [19] Mosiewicki MA, Aranguren MI, Borrajo J. Mechanical properties of linseed oil monoglyceride maleate/styrene copolymers. *J Appl Polym Sci* 2005;97:825–36.
- [20] Mosiewicki MA, Casado U, Marcovich NE, Aranguren MI. Polyurethanes from tung oil: polymer characterization and composites. *Polym Eng Sci* 2009;49:685–92.
- [21] Hu YH, Gao Y, Wang DN, Hu CP, Zhu S, Vanoverloop L, et al. Rigid polyurethane foam prepared from a rape seed oil based polyol. *J Appl Polym Sci* 2002;84:591–7.
- [22] Desroches M, Caillol S, Lapinte V, Auvergne R, Boutevin B. Synthesis of bio-based polyols by thiol-ene coupling from vegetable oils. *Macromolecules* 2011;44:2489–500.
- [23] Tüürinc O, Meier MAR. Fatty acid derived monomers and related polymers via thiol-ene (click) additions. *Macromol Rapid Commun* 2010;31:1822–6.
- [24] Stemmelen M, Pessel F, Lapinte V, Caillol S, Habas J-P, Robin J-JA. Fully bio-based epoxy resin from vegetable oils: from the synthesis of the precursors by thiol-ene reaction to the study of the final material. *J Polym Sci Part A: Polym Chem* 2011;49:2434–44.
- [25] Firdaus M, Meier MAR. Renewable co-polymers derived from vanillin and fatty acid derivatives. *Eur Polym J*, in press. doi:10.1016/j.eurpolymj.2012.10.017.
- [26] Montero de Espinosa L, Meier MAR. Plant oils: the perfect renewable resource for polymer science? *Eur Polym J* 2011;47:837–52.
- [27] Jacobs T, Rybak A, Meier MAR. Cross-metathesis reactions of allyl chloride with fatty acid methyl esters: efficient synthesis of  $\alpha,\omega$ -difunctional chemical intermediates from renewable raw materials. *Appl Catal A: General* 2009;353:32–5.
- [28] Chandrashekhara K, Sundararaman S, Flanigan V, Kapila S. Affordable composites using renewable materials. *Mater Sci Eng A* 2005;412:2–6.
- [29] Husic S, Javni I, Petrovic ZS. Thermal and mechanical properties of glass reinforced soy-based polyurethane composites. *Compos Sci Technol* 2005;65:19–25.
- [30] Lu Y, Larock RC. Fabrication, morphology and properties of soybean oil-based composites reinforced with continuous glass fibers. *Macromol Mater Eng* 2007;292:1085–94.
- [31] Henna PH, Kessler MR, Larock RC. Fabrication and properties of vegetable-oil-based glass fiber composites by ring-opening metathesis polymerization. *Macromol Mater Eng* 2008;293:979–90.
- [32] Ray D, Ghorui S, Bandyopadhyay NR, Sengupta S, Kar T. New materials from maleated castor oil/epoxy resin blend reinforced with fly ash. *Ind Eng Chem Res* 2012;51:2603–8.
- [33] Bassyouni M, Sherif SA, Sadek MA, Ashour FH. Synthesis and characterization of polyurethane – treated waste milled light bulbs composites. *Compos Part B* 2012;43:1439–44.
- [34] Satheesh Kumar MN, Manjula KS, Siddaramaiah. Castor oil-based polyurethane– polyester nonwoven fabric composites: mechanical properties, chemical resistance, and water sorption behavior at different temperatures. *J Appl Polym Sci* 2007;105:3153–61.
- [35] Chen S, Wang Q, Wang T, Pei X. Preparation, damping and thermal properties of potassium titanate whiskers filled castor oil-based polyurethane/epoxy interpenetrating polymer network composites. *Mater Des* 2011;32:803–7.
- [36] Pfister DP, Larock RC. Cationically-cured natural oil-based green composites: effect of the natural oil and the agricultural fiber. *J Appl Polym Sci* 2012;123(3):1392–400.
- [37] Pfister DP, Larock RC. Thermophysical properties of conjugated soybean oil/corn stover biocomposites. *Biores Technol* 2010;101:6200–6.
- [38] Merlini C, Soldi V, Barra GMO. Influence of fiber surface treatment and length on physico-chemical properties of short random banana fiber-reinforced castor oil polyurethane composites. *Polym Test* 2011;30:833–40.
- [39] Miao S, Liu Y, Wang P, Zhang S. Castor oil and microcrystalline cellulose based polymer composites with high tensile strength. *Adv Mater Res* 2012;399–401:1531–5.
- [40] Adekunle K, Patzelt C, Kalantar A, Skrifvars M. Mechanical and viscoelastic properties of soybean oil thermoset reinforced with jute fabrics and carded lyocell fiber. *J Appl Polym Sci* 2011;122(5):2855–63.
- [41] Mosiewicki MA, Borrajo J, Aranguren MI. Mechanical properties of woodflour/linseed oil resins composites. *Polym Int* 2005;54(5):829–36.
- [42] Pukanszky B, Tudos F, Jancar J, Kolarik J. The possible mechanisms of polymer–filler interaction in polypropylene–CaCO<sub>3</sub> composites. *J Mater Sci Lett* 1989;8:1040–2.
- [43] Mosiewicki MA, Rojas O, Sibaja MR, Borrajo J, Aranguren MI. Aging study of linseed oil resin/styrene thermosets and their composites with wood flour. *Polym Int* 2007;57(7):875–81.
- [44] Casado U, Marcovich NE, Aranguren MI, Mosiewicki MA. High strength composites based on tung oil polyurethane and wood flour: effect of the filler concentration on the mechanical properties. *Polym Eng Sci* 2009;49(4):713–21.
- [45] Wu Q, Henriksson M, Liu X, Berglund LA. A high strength nanocomposite based on microcrystalline cellulose and polyurethane. *Biomacromolecules* 2007;8:3687–92.
- [46] Aranguren MI, González JF, Mosiewicki MA. Biodegradation of a vegetable oil based polyurethane and wood flour composites. *Polym Test* 2012;31(1):7–15.
- [47] Wool RP. In: Wool RP, Sun XS, editors. *Bio-based composites from soybean oil and chicken feathers, in bio-based polymers and composites*. Burlington (USA): Elsevier Academic Press; 2005.
- [48] Liu Z, Erhan SZ, Xu J. Preparation, characterization and mechanical properties of epoxidized soybean oil/clay nanocomposites. *Polymer* 2005;46:10119–27.
- [49] Uyama H, Kuwabara M, Tsujimoto T, Nakano M, Usuki A, Kobayashi S. Green nanocomposites from renewable resources: plant oil-clay hybrid materials. *Chem Mater* 2003;15:2492–4.
- [50] Haq M, Burgueño R, Mohanty AK, Misra M. Bio-based unsaturated polyester/layered silicate nanocomposites: characterization and thermo-physical properties. *Compos Part A* 2009;40:540–7.
- [51] Kaushik A, Ahuja D, Salwani V. Synthesis and characterization of organically modified clay/castor oil based chain extended polyurethane nanocomposites. *Compos Part A* 2011;42:1534–41.



- [52] Chen S, Wang Q, Wang T. Damping, thermal, and mechanical properties of montmorillonite modified castor oil-based polyurethane/epoxy graft IPN composites. *Mater Chem Phys* 2011;130:680–4.
- [53] Lu Y, Larock RC. Novel biobased nanocomposites from soybean oil and functionalized organoclay. *Biomacromolecules* 2006;7:2692–700.
- [54] Liu Z, Erhan SZ, Calvert PD. Solid freeform fabrication of soybean oil-based composites reinforced with clay and fibers. *J Am Oil Chem Soc* 2004;81(6):605–10.
- [55] Miyagawa H, Mohanty A, Drzal LT, Misra M. Effect of clay and alumina-nanowhisker reinforcements on the mechanical properties of nanocomposites from biobased epoxy: a comparative study. *Ind Eng Chem Res* 2004;43:7001–9.
- [56] Lligadas G, Ronda JC, Galia M, Cádiz V. Bionanocomposites from renewable resources: epoxidized linseed oil-polyhedral oligomeric silsesquioxanes hybrid materials. *Biomacromolecules* 2006;7:3521–6.
- [57] Gao Z, Peng J, Zhong T, Sun J, Wang X, Yue C. Biocompatible elastomer of waterborne polyurethane based on castor oil and polyethylene glycol with cellulose nanocrystals. *Carbohydr Polym* 2012;87:2068–75.
- [58] Maafi EM, Tighzert L, Malek F. Elaboration and characterization of composites of castor oil-based polyurethane and fibers from alfa stems. *J Appl Polym Sci* 2010;118:902–9.
- [59] Konwar U, Karak N, Mandal M, Mesua ferrea L. Seed oil based highly thermostable and biodegradable polyester/clay nanocomposites. *Polym Degrad Stab* 2009;94:2221–30.
- [60] Dutta S, Karak N, Saikia JP, Konwar BK. Biocompatible epoxy modified bio-based polyurethane nanocomposites: mechanical property, cytotoxicity and biodegradation. *Biores Technol* 2009;100:6391–7.
- [61] Alam J, Riaz U, Ahmad S. Nanostructured polyaniline reinforced sustainable resource (soy oil alkyd) based composites. *Polym Compos* 2010;2010(31):32–7.
- [62] Melinte V, Buruiana T, Balan L, Buruiana EC. Photocrosslinkable acid urethane dimethacrylates from renewable natural oil and their use in the design of silver/gold polymeric nanocomposites. *React Funct Polym* 2012;72:252–9.
- [63] Mülazim Y, Cakmak E, Kahraman MV. Preparation of photo curable highly hydrophobic coatings using a modified castor oil derivative as a sol-gel component. *Progress Org Coat* 2011;72:394–401.
- [64] Sharmin E, Akram D, Ghosal A, Rahman O, Zafar F, Ahmad S. Preparation and characterization of nanostructured biohybrid. *Progress Org Coat* 2011;72:469–72.
- [65] Kuranska M, Prociak A. Porous polyurethane composites with natural fibres. *Compos Sci Technol* 2012;72:299–304.
- [66] Baser SA, Khakhar DV. Castor oil-glycerol blends as polyols for rigid polyurethane foams. *Cell Polym* 1993;12(5):340.
- [67] Zhu M, Bandyopadhyay-Ghosh S, Khazabi M, Cai H, Correa C, Sain M. Reinforcement of soy polyol-based rigid polyurethane foams by cellulose microfibrils and nanoclays. *J Appl Polym Sci* 2012;124(6):4702–10.
- [68] Aranguren MI, Rácz I, Marcovich NE. Microfoams based on castor oil polyurethanes and vegetable fibers. *J Appl Polym Sci* 2007;105(5):2791–800.
- [69] Wei ZG, Sandström R, Miyazaki S. Review. Shape-memory materials and hybrid composites for smart systems. Part I. Shape-memory materials. *J Mater Sci* 1998;33:3743–62.
- [70] Behl M, Lendlein A. Shape-memory polymers. *Mater Today* 2007;10(4):20–8.
- [71] Li F, Larock RC. New soybean oil-styrene-divinylbenzene thermosetting copolymers. VI. Time-temperature-transformation cure diagram and the effect of curing conditions on the thermoset properties. *Polym Int* 2003;52:126–32.
- [72] Li F, Larock RC. New soybean oil-styrene-divinylbenzene thermosetting copolymers. V. Shape memory effect. *J Appl Polym Sci* 2002;84(8):1533–43.
- [73] Rana S, Karak N, Cho JW, Kim YH. Enhanced dispersion of carbon nanotubes in hyperbranched polyurethane and properties of nanocomposites. *Nanotechnology* 2008;19(49):495707.



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