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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.

Contents

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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 authors [17–19] have worked with soybean and linseed oil, in order to obtain monoglyceride maleate half esters.

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