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Mini Review

Microwave Synthesis of Vegetable Oil-Based Polymers for Coating Applications - A Mini Review

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ISSN: 2770-6613

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Submission: August 23, 2023
Published: September 05, 2023

Volume 5 - Issue 2

How to cite this article: Antonella Hadzich, Daniel Obregón and Santiago Flores*. Microwave Synthesis of Vegetable Oil-Based Polymers for Coating Applications - A Mini Review. Polymer Sci peer Rev J. 5(2). PSPRJ. 000607. 2023.
DOI: 10.31031/PSPRJ.2023.05.000607

Abstract

Microwave processing technology has spread its use rapidly in various areas due to its higher efficient reactions, rapid and controlled heating, and safe use with precise temperature and pressure control. Nowadays, this green alternative has triggered enormous interest in organic synthesis, specifically in developing vegetable oil-based polymers for coating applications such as alkyds, epoxies, esteramides and urethanes. The present summary aims to highlight recent investigations that have used microwave heating to obtain polymers from vegetable oil sources for diverse coating applications.

Keywords: Microwave-assisted synthesis; Resins; Vegetable oil; Coating

Microwave-Assisted Synthesis of Oil-Based Resins

Alkyd resins

Alkyd resins are polyester resins modified with unsaturated fatty acids obtained from semi-drying or drying vegetable oils [1-3]. Specific properties, characteristics, and applications depend on the degree of unsaturation of the fatty acid source, oil proportion, and selected polyalcohol's or polyacids [4]. Alkyd resins continue to be one of the largest types of coatings used worldwide and have expanded its domestic and industrial use to innovative applications like artistic mediums [5], textile printing, and self-healing coatings. Extensive research has been made on alkyd resins synthesized with oils of different kinds, being a recent trend the use of non-traditional or non-edible plants to take advantage of native resources, look for better properties, or replace high-consumption sources. Recently, conventional synthesis processes are being replaced by Microwave (MW) heating for the manufacturing of oil-based resins. Long-chain alkyd resins were prepared by microwave irradiation and characterized as oil-based artistic mediums using a non-traditional source, Sacha inchi oil [6]. Reaction times were reduced by around 12-13 hours when using microwave heating instead of the conventional system. Also, more homogeneous heating allowed control of chain cross-linking avoiding polymer gelation. Furthermore, sunflower oil-based alkyd resins were also synthesized by microwave irradiation with the incorporation of recycled Polyethylene Terephthalate (PET) for textile printing [7]. Authors emphasized that microwave exposure did not affect the elongation of polymers and its application properties. The energy efficiency of the microwave treatment process, and reduction of reaction time for sample preparation from hours to minutes was also highlighted. Otherwise, PET glycolyzates are used as a partial substitute for phthalic anhydride, the only component of an alkyd resin that is non-renewable. There are more studies that take advantage of microwave power to recycle PET by chemical depolymerisation [8-10]. Chemical-recycled PET obtained through microwave-assisted extraction could produce sustainable coatings such as epoxy, polyesters, alkyd, acrylic, and polyurethanes [11].

Epoxy resins

Epoxy resins are thermoset polymers that are derived commonly from diglycidyl ethers of bisphenol-A (or F) and epichlorohydrin [12], components that provide high-performance film properties [13]. Just before application, epoxy resins must be mixed with cross-linking agents such as amines or polyamides, and the surface must be properly prepared to ensure its durability [12,14]. Epoxy resins have found widespread usage in relatively mature markets like marine and industrial maintenance, due to its superior adhesion and chemical resistance to metals [14]. However, its main components and cross-linkers have been related to health and environmental problems [15]. High processing costs and toxicity issues of epoxy resins have increased the need to find renewable alternatives. In this context, vegetable oils have been transformed into high-value-added bio-based epoxy resins by epoxidation, a chemical process that converts double bonds into oxiranes (epoxides) with an oxidizing agent and oxygen carriers [16,17].

Epoxidized oils are green materials that can be used as intermediates or monomers in the surface coating field [18]. Several oils have been chemically transformed to prepare bio-based epoxy resins under conventional heating [19,20], but few studies have used microwave technology for this purpose. Epoxidation is an exothermic reaction that can have heat/mass transfer limitations in conventional reactors, which can be overcome by the power and temperature control of microwave devices [21]. Also, higher temperatures can be achieved to ensure the reduction of the reaction time and increase the rate of oxirane group content [22]. Soybean oil was epoxidized by microwave heating, producing higher yields and uniform oil-aqueous suspensions, and diminishing by half the reaction time in comparison with traditional processes [23]. Nevertheless, authors pointed out that the stirring speed is limited in microwave devices. Moreover, epoxidized derivatives were obtained from tall oil fatty acids, by-products from Kraft pulping process, with microwave irradiation [24].

Authors found that microwave heating power apparently accelerates ring opening reactions during epoxidation of fatty acid chains that have more than one unsaturation. Microalgal oils were also epoxidized with formic acid and hydrogen peroxide under microwave-assisted conditions and controlled pressure for the production of epoxy thermosetting resins [22]. Some deficiencies of epoxidized oils are strongly related to the length or degree of unsaturation of the aliphatic chains; for example, providing flexibility but reducing the mechanical strength of bio-based epoxy [25]. However, cross-linking of epoxidized oils can be enhanced by the addition of maleinized oils, unsaturated oils reacted with maleic anhydride [26]. Maleinization of grape, hemp, and linseed oils was successfully achieved by microwave heating in shorter times and with higher viscosity products in comparison with conventional synthesis [27]. Similar results were obtained with soybean [28], and grape seed [29] oils.

Polyesteramide resins

Polyesteramides are high performance polymers that combine good properties of polyamides and polyesters [30]. These resins have attracted great attention because of the effective antibacterial and anticorrosive protection they provide [31] and their stability at high temperatures [32]. But their application as coatings is limited due to their high curing temperatures, high melting point and low chemical resistance [32]. Polyesteramides have been synthesized from seed oils to ensure faster drying, better thermal stability, resistance against chemicals and water, hardness, corrosion protective efficiency [32,33]. First, vegetable oils undergo a base-catalyzed aminolysis to obtain N, N-bis (2-hydroxy ethyl) fatty amides, which are subsequently reacted with different dibasic acids through polycondensation [32,34]. These bio-based polyesteramides are attractive protective resins, but their conventional heating method is very time consuming due to its multiple steps [35]. Only a few studies were carried out using microwave heating to transform vegetable oils into polyesteramides, despite being a greener route.

Cottonseed oil was converted to polyesteramide precursors through microwave technique [36]. Researchers observed that microwave energy saves time and generates better product yields. Microwaved bio-based polyesteramides were synthesized with Jatropha oil, a non-edible source, and reacted again under MW irradiation conditions to produce urethane-modified polyesteramide resins [37], and polyetheramide and urethane-modified polyetheramide coatings [38]. The resins had a good protective behavior under various corrosive media and good immersion performance in water, xylene and HCl, respectively. A waterborne linseed oil-based polyesteramide was prepared with a domestic microwave oven as a promising biodegradable coating [35]. The reaction was reduced to less steps and did not require the addition of any solvent.

Polyurethane resins

Polyurethanes (PU) are polymers obtained by combining hydroxyl bases (polyols) with diisocyanato's [39], usually Toluene Diisocyanate (TDI) or Methylene Diphenyl Diisocyanate (MDI). Their versatility due to many raw materials available on the market with extreme properties (from soft to rigid structures), has made them suitable materials for many applications [40]. Polyurethanes are applied as a high-performance coating in automotive appliances and wood industries [41]. Environmental concerns and depletion and high costs of petroleum-based resources have forced researchers to use bio-based materials for the manufacturing of polyurethanes [39]. Vegetable oils have been extensively used for PU applications by introducing hydroxyl groups into unsaturated bonds of fatty acid chains, components known as polyols. Polyols derived from oils have been synthesized with different pathways such as amidation-esterification, hydroformylation, epoxidation-ring opening, ozonolysis, and metathesis, among others [42]. Properties of these bio-based polyurethanes are related to the type and amount of oil, polyol (the number and distribution of hydroxyl groups), and isocyanate [43]. Vegetable oil-based polyurethane coatings have shown to have excellent toughness, abrasion resistance, low-temperature flexibility, corrosion and chemical resistance, [42].

Also, the use of oils has reduced or eliminated the use of solvents in the synthesis of this type of resin [42]. It has been reported that urethane linkages provide a faster drying, better toughness and resistance to abrasion, chemicals, and UV irradiation than alkyd resins [41]. Recently, a few studies have applied microwave technology to convert vegetable oils into multifunctional polyols. Rapeseed oil-based polyols were synthesized in a mixed conventional and microwave two step heating process to obtain flexible foams [44]. First, epoxidized oils were obtained with conventional equipment, and then, the ring opening of the epoxy groups to hydroxyls was carried out under microwave irradiation. Microwave heating reduced reaction time by 75% compared to a traditional synthesis process. Other oil-based PU polyols were also prepared with an adapted domestic microwave oven with rapeseed oil but recycled Polyethylene Terephthalate (PET) components [45]. MW polyols had properties similar to traditionally synthesized polyols. However, the MW process required shorter times and consumed much lower energy than conventional electrical heating.

Conclusion

A wide variety of polymers based on vegetable oils have been obtained with microwave heating for coating applications. Vegetable oils and renewable monomer sources appear as a more promising alternative due to their wide availability, low cost, and versatile properties in comparison with traditional petroleum-based products. Microwave irradiation, a technique that aligns with the principles of green chemistry, has been shown to provide many advantages such as fast reactions, high yields, homogenous products, and reduced side reactions over conventional heating. Overcoming new challenges such as the synthesis of high-viscosity polymers is one of the next steps for the industrial scale-up of the microwave synthesis process. Efficient reactions with biodegradable sources are the key to a sustainable future.

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