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Recent advances in vegetable oils based environment friendly coatings: A review

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ABSTRACT

The overarching goal worldwide for the scientific community is “sustainable development” today, for an everlasting sustainable and green tomorrow. The strategy includes (i) harvesting renewable resources instead of fossil fuels, (ii) using environment friendly routes, and (iii) engineering material degradation pathways operating under reasonable time frames. The concept revolves around the focal point of “Green” or “Sustainable” Chemistry. In the world of coatings, the idea has already made its debut in the form of environment friendly technologies-low or no solvent, high solids, hyperbranched, water borne and UV curable coatings, utilising monomers/polymers derived from renewable resources. Vegetable oils [VEGO] constitute Mother Nature’s most abundant, cost-effective, non toxic, and biodegradable resource. They have been traditionally used for several non-food applications mainly coatings since primitive times. Today, the implementation of the modern technologies coupled with the full fledged use of VEGO based monomers or polymers in the field as raw materials, is an excellent effort toward sustainable future in the world of coatings globally. The review highlights some state-of-the art-modifications of VEGO as environment friendly-low or no solvent, high solids, hyperbranched, water borne and UV curable coatings. The article provides a handy overall vision of VEGO based environment friendly coatings on a single platform. These approaches can be well employed on those oils that are non-edible, non-medicinal and are left unexplored, unutilised or underutilised to date, thus adding value to an unutilised or underutilised sustainable resource.

Contents

Abbreviations: BMF, butylated melamine formaldehyde; CasO, castor oil; DGEBA, diglycidyl epoxy of bisphenol A; DMPA, dimethylol propionic acid; DPE, dipentaerythritol; FAD, fatty amide diol; HS, high solids; HYP, hyperbranched; HBPA, HYP polyamine; HPU, HYP polyurethane; LinO, linseed oil; MFO, *Mesua ferrea* oil; MG, monoglycerides; MMT, montmorillonite; MWCNT, multiwalled carbon nanotubes; NC, nanocomposites; HEFA, N,N'-bis(2-hydroxyethyl)fatty amide; PAA, poly(amido amine); PANI, polyaniline; PCD, poly(ϵ-caprolactone) diol; PEsterA, polyesteramide; PU, polyurethanes; RSO, rubberseed oil; SoyO, soybean oil; SunFO, sunflower oil; TDI, toluene-2,4-diisocyanate; TO, tung oil; UV, ultra violet; VEGO, vegetable oils; VOC, volatile organic compounds; VOMM, VO macro-monomer; WB, waterborne; WPU, waterborne polyurethane.

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1. Introduction

In the past two decades, research and development efforts have undergone vast changes globally, due to the ever growing consumer expectations of good quality and performance coupled with lower cost, escalating prices of petro-based chemicals due to the fear of depleting stocks by the end of twenty first century, concerns related to energy consumption and environmental contamination (improper waste management, greenhouse effect, health problems), regulations such as Clean Air Act Ammendment, 1990 and rapid innovations. These challenges related to predictions, regulations and innovations have forced the coatings industry to change its gears worldwide and resulted in the exploration and utilization of sustainable alternatives to chemicals derived from petro-based products (Lochab et al., 2014). The researchers in industry and academia are actively engaged to explore and formulate new strategies to meet the mandatory limits through the "tapping of our green gold-the naturally available resources" primarily:-

(i) to cut off the increasing raw material costs of the petro-based products
(ii) to develop environmentally benign formulations
(iii) to expedite their post-service degradation
(iv) to add value to an otherwise waste material

As a consequence, some "environmentally friendly" or "green" technologies have evolved, with special emphasis being laid on the excessive utilization of renewable resources such as vegetable oils [VEGO] and also reducing or eliminating the use of volatile organic compounds [VOC]. Considering the vast amount spent on corrosion and its mitigation programs worldwide, we understand that the proper utilization of our domestically abundant sustainable resources such as VEGO thriving on our acres of agricultural lands may prove as silver lining, in this regard (Balachandran et al., 2013; Miller, 2014). This review article describes the recent advances in the modifications and applications of VEGO as environment friendly protective coatings, role of VEGO based components in governing the properties of these coatings, and further encourages the application of these approaches on non-edible and non-medicinal VEGO, adding value to a waste or unutilized sustainable resource.

2. VEGO and their chemical transformations

VEGO constitute a broad class of sustainable resources rendering a plethora of value added functional materials. They comprise one of the most important components of biomass. They are tri-esters of glycerol and fatty acids (saturated and unsaturated). VEGO mainly consist of triglycerides as major (93–98 wt%) and diglycerides, monoglycerides and phosphoglycerides as minor components. VEGO and their derivatives find applications in coatings owing to their unique structural attributes and tendency to form films (depending upon their unsaturated portion). Considering their degree of unsaturation, described by their iodine value, VEGO are classified as "drying" (iodine value > 130), "semi-drying" (100 < iodine value < 130) and "non-drying" (iodine value < 100)as in linseed oil [LinO], soybean oil [SoyO] and palm kernel oil, respectively (Alam et al., 2014; Xia and Larock, 2010). Usually, drying or semi-drying oils are used in surface coatings. Non-drying oils may also be utilized for the purpose by the incorporation of suitable entities (e.g., hydroxyls) or modifiers (vinyls, acrylics, acrylic co-polymers) in oil backbone, through chemical reactions to transform them as film formers. In virgin oils, longer drying times are required while the films formed do not meet the desirable physico-mechanical and corrosion resistance performance. Consequently, several chemical transformations are carried out through the important functionalities and active sites of VEGO such as hydroxyls, oxiranes, double bonds, allylic carbons, esters, alpha carbon to the ester group and others. About 90% reactions occur at carboxyl functionality while the rest involve unsaturation sites (Gunstone, 2001). Some of them have been exemplified in Fig. 1. VEGO undergo glycerolysis reaction resulting in the formation of monoglycerides or diglycerides that are used as raw materials in the production of alkyds. Amidation (base catalysed) is carried out at carboxyl functionality, producing fatty amide diols/polyols that serve as starting material for the development of polyesteramides [PEsterA] and polyetheramides. Another much explored important reaction is transesterification reaction also occurring at carboxyl functionality. Epoxidation and hydroxylation reactions occurring at double bonds of VEGO produce epoxies and poyols, respectively. The former render strong thermosets when cured by suitable curing agents such as amines, acids, amides, while the latter yield polyester and polyurethane [PU] coatings on treatment with acid/anhydride or isocyanates. Maleinization, acrylation, vinylation, hydrohalogenation are few other examples involving reactions at double bonds of VEGO (Ahmad et al., 2004; Lligadas et al., 2013; Maisonneuve et al., 2013; Miao et al., 2014; Montero de Espinosa and Meier, 2011; Mosiewicki and Aranguren, 2013).

The coatings obtained from fossil fuel derived petro-based chemicals such as vinyls, acrylics, epoxies, PU, polyesters and others, are often (i) costly, (ii) toxic, (iii) hazardous after use (non-biodegradable), and (iv) may require ample of hazardous solvents during processing and coating applications, thus causing environmental contamination and health hazards on exposure. VEGO derivatives are generally devoid of these drawbacks bearing advantages of cost effectiveness, non-toxicity, biodegradability, requiring no or low solvents due to their inherent fluidity characteristic. VEGO coatings are available for specific uses as antimicrobial, biocompatible, biodegradable, corrosion protective, architectural, decorative, electrical insulating, paper packaging, and self-healing coatings. However, due to long aliphatic hydrophoebic chains, they are often low on mechanical strength, lack toughness and are water insoluble (Bordes et al., 2009; Lligadas et al., 2010). Thus to further augment the performance of VEGO coatings, and to compete with their petro-based counterparts, several innovative and state-of-the-art modifications have been accomplished in the field.

3. Low solvent or "zero solvent" coatings

VEGO chains are flexible due to the the presence of long aliphatic fatty acid chains. VEGO derivatives generally serve as solvents or reactive diluents in coatings, often in combination with commercial resins, and themselves participate in chemical reactions occurring