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REVIEW

Vegetable oil based eco-friendly coating materials: A review article

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Abstract Vegetable oils (VO) constitute the single, largest, easily available, low cost, non-toxic, non-depletable, biodegradable family yielding materials that are capable of competing with fossil fuel derived petro-based products. The outstanding feature of VO is their unique chemical structure with to unsaturation sites, epoxies, hydroxyls, esters and other functional groups along with inherent fluidity characteristics. These enable them to undergo various chemical transformations producing low molecular weight polymeric materials with versatile applications, particularly as chief ingredients in paints and coatings. In this manuscript, we have briefly described important VO derived materials such as alkyds, polyesteramides, polyetheramides, polyurethanes, epoxies, polyols, along with their preparation and applications as protective coatings. A small portion of the review is also dedicated to the future perspectives in the field. Inspite of their extensive utilization

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Abbreviations : ASO, *Annona squamosa*; BPA, bisphenol A; BMF, butylated melamine formaldehyde; CO, castor oil; CCO, coconut oil; DI, drying index; DSC, differential scanning calorimetry; FTIR, Fourier transform infrared; Tg, glass transition temperature; HYP, hyperbranched; IPN, interpenetrating polymer networks; IV, iodine value; LO, linseed oil; MFO, *Mesua ferrea* L. seed oil; MW, microwave; NMR, nuclear magnetic resonance; PAO, palm oil; PEA, polyesteramides; PEtA, polyetheramides; PU, polyurethanes; PGO, *Pongamia glabra*; RSO, rubber seed oil; SO, soybean oil; St, styrene; TDI, toluylene 2,4-diisocyanate; TGA, thermogravimetric analysis; VO, vegetable oils; VRO, vernonia; VOC, volatile organic contents; WB, waterborne.

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in the world of coatings, literature survey revealed that in the past (from 1990s to date) no review has come up describing the chemistry and applications of VO polymer based coating materials.

Contents

1. Introduction

The consumer and industrial interests in the development of eco-friendly materials have catapulted the environmentally benign agricultural resources as feedstocks of the polymer industry. Today, due to interdisciplinary approaches through research and technological innovations in oleo-chemistry, biosciences, biotechnology and engineering, it is possible to design eco-friendly specialty chemicals from nature's abundant renewable resources. Polymers are obtained from renewable resources such as starch, lignin, protein, cellulose, chitosan, shellac, rosin, polyhydroxyalkanoates, furanone, alginate, wool fibres and vegetable oils [VO]. They find innumerable industrial applications such as plasticizers, biodiesel, lubricants, adhesives, biodegradable packaging materials, printing inks, paints and coatings. VO are non-toxic, non-depletable, domestically abundant, non-volatile and biodegradable resource. They yield polymers capable of competing with fossil fuel derived petro-based products. Such polymers find applications in the development of paints and coatings, besides their other industrial applications (Dutton and Scholfield, 1963; Wisniak, 1977; Baumann et al., 1988; Schuchardt et al., 1998; Lu and Larock, 2009; Xia and Larock, 2010; Salimon et al., 2012).

VO were used as the primary constituent in paints and coatings even during the days of cave paintings. Today, due to several environmental and health hazards cropping up from fossil fuel derived products, and fear of depletion of petroleum resources by the end of 21st century, the polymer chemists and technologists have reverted to the extensive utilization of VO derived materials in paints and coatings. Several VO based materials have been developed and are tailor made for various end use applications. The area holds immense potential and significance globally. Literature survey reveals that VO have enormous potential, significance and applications in the world of coatings. However, inspite of this, in the recent past no review has come up describing the chemistry and applications of VO and polymers based thereupon as coating materials. In the preceeding sections, we have described some important VO polymeric materials (alkyds, polyesteramides, polyetheramides, polyurethanes, epoxies and polyols) with special emphasis on their use as protective coatings.

2. VO in coatings

VO and their derivatives find applications in coatings owing to their unique structural attributes. The preceeding sections describe briefly the role of VO as corrosion inhibitors and polymeric binders in coatings.

2.1. VO as corrosion inhibitors

Besides their use in coatings and paints as binders, VO and plant extracts have also been used as *natural corrosion inhibitors*. An excellent review in this regard has been compiled by Raja and Sethuraman (2008). Srivastava and Sathiyanathan et al. have also reported the use of *Ricinus communis* or castor oil [CO] for corrosion inhibition of steel in acid media (Srivastava and Srivastava, 1981; Sathiyanathan et al., 2005). *Pongamia glabra* [PGO] and *Annona squamosa* [ASO] have shown corrosion inhibition for steel in acid media (Raja and Sethuraman, 2008). A recent review has also appeared on the use of VO and other extracts for corrosion inhibition (Dar, 2011). Extracts from leaves and VO from seeds of several edible and medicinal plants have also been employed for anticorrosion behavior against alkaline and acid media as well as chloride ions (Dar, 2011; Lahhit et al., 2011). Here, the anticorrosion activity is attributed to the presence of heterocyclic constituents such as alkaloids, flavonoids, tannins, cellulose, and others.

2.2. VO as polymeric coatings

Natural VO are triacylglycerols of fatty acids. They contain suitable functionalities in their backbone such as double bonds, epoxies, hydroxyls, esters and other functional groups that can undergo several chemical reactions. One such example is drying of VO, which in general, occurs as a natural phenomenon in VO that are termed as “drying oils”. VO have the tendency to dry or form films in their virgin forms; this behavior is directly related to their fatty acid composition. Drying is an inherent characteristic of VO, and depends upon their unsaturated portion, i.e., the number of carbon–carbon double bonds (iodine value or drying index), their conjugation or nonconjugation and the geometrical arrangement of the substituents about the double bonds, i.e., cis or trans (Lu and Larock, 2009; Meir et al., 2007). Usually, drying or semi-drying VO are used in surface coatings. Non-drying VO may also be utilized for this purpose by the incorporation of suitable entities (e.g., hydroxyls) or modifiers (vinyls, acrylics, acrylic co-polymers) in VO backbone, through chemical reactions to transform them as film formers (contrary to drying or semi-drying VO, where drying occurs as a natural phenomenon). In fully saturated fatty triesters, methylene group α- or β- to the ester link can form hydroperoxide by oxidation. However, it is a very slow and insignificant reaction for film formation, though it may serve as a potential point of reaction for film degradation or breakdown. Drying VO can react with atmospheric oxygen to form polymeric materials with crosslinked structures (Meir et al., 2007; Lu and Larock, 2009). The oxidation of drying VO by air involves hydrogen abstraction from a bisallylic group between two double bonds in a polyunsaturated fatty acid chain. The reaction leads to peroxidation, perepoxidation, hydroperoxidation, epoxidation and crosslinking through radical recombination. Another major advantage is the inherent flexibility retention and fluidity characteristics of VO and some of the derivatives therefrom. As a consequence, VO may also be used as reactive diluents, or in some cases, VO may form free flowing coating materials, without the use of any solvent. This facilitates the formation of solventless coatings, thus cutting off the use of volatile organic contents [VOC].

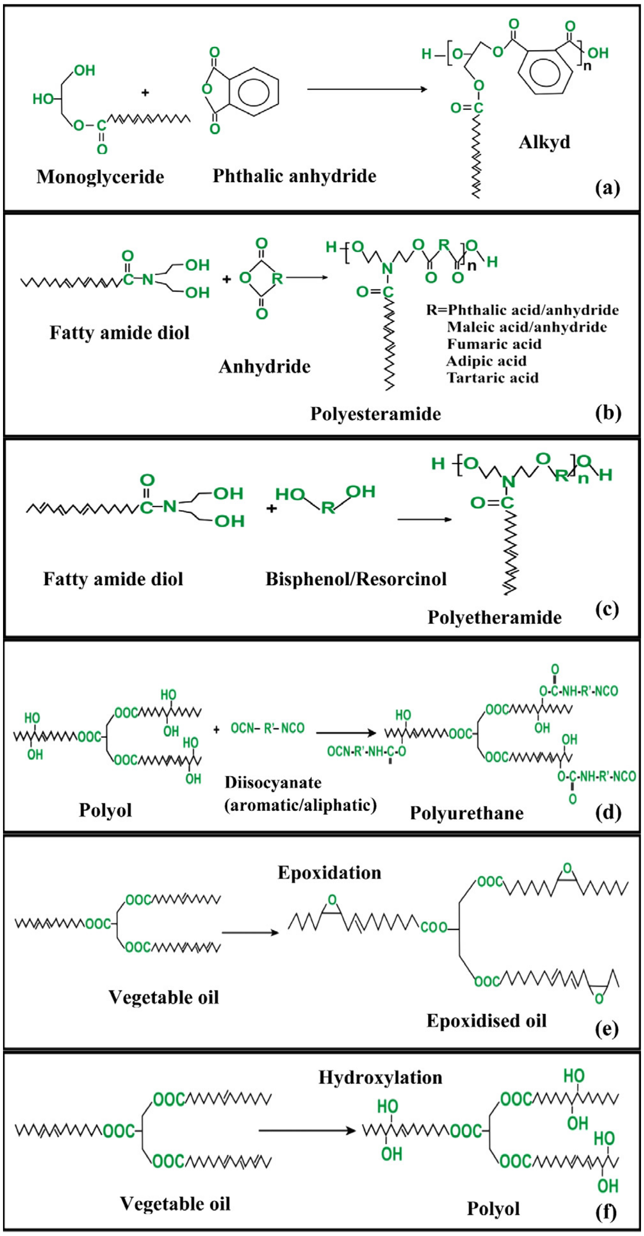

Figure 1 Chemical transformation of VO to polymeric coating materials (a) alkyd, (b) polyesteramide, (c) polyetheramide, (d) polyurethane, (e) epoxy, and (f) polyol.

VO in their virgin forms require longer drying times. The films formed from virgin VO do not meet the desirable physico-mechanical and corrosion resistance performance. Consequently, several chemical reactions are carried out at the functional groups present in VO. The common chemical reactions that are carried out in VO are hydrogenation, tranesterification, auto-oxidation, epoxidation, hydroxylation, acrylation, isocyanation, and others. Such reactions finally result in the formation of monomers/polymers actively being used as binders for coating materials. VO based monomers/polymers generally contain double bonds, active methylene, ester, epoxide, hydroxyl and carboxyl groups present in their backbone. The double bonds and active methylene act as functional sites for the introduction of acrylic polymers and co-polymers. The epoxides undergo curing reactions with acids, anhydrides, amines, carboxylic acids and others producing tough and chemically resistant coatings. The hydroxyls can be treated with acids or anhydrides to form polyesters and with isocyanates to produce polyurethane coatings. Such reactions increase the cross linking improving scratch hardness and impact resistance performance of coatings. The polar groups (epoxides, hydroxyls, carboxyls, urethanes) present in polymeric backbones are adhesion promoters as can be predicted by contact angle studies and the aliphatic fatty acid chains confer flexibility to the polymeric coatings.

Some of the polymers derived from VO have been exemplified in the following sections.

2.2.1. Alkyds

Alkyds are oil-modified polyesters, consisting of a polyol (usually glycerol, trimethalolpropane or pentaerythritol), a multi-functional acid (phthalic acid or trimellitic acid) and an unsaturated fatty acid formed by polycondensation reaction. They find important application as binders in surface coatings. They are classified as short (30–42%), medium (43–54%), long

(55–68%) and very long ($\geq$68%), based on the percent weight fraction of VO in the resin (Hofland, 2012). The two most important methods for the synthesis of alkyds are:

(i) fatty acid process
(ii) monoglyceride process

The structure of a typical alkyd resin is given in Fig. 1a. About 60–70% of an alkyd resin comprises of biologically derived or degradable raw materials (fatty acids, glycerol, pentaerythritol and the rest as non-biodegradable (phthalic acid) (Hofland, 2012). Alkyds are available in two forms, i.e., "drying" or "non-drying" alkyds; the former refers to alkyds with drying VO, containing polyunsaturated fatty acids while the latter refers to alkyds obtained from non-drying VO fatty acids. They show good gloss retention, durability, and weathering resistance while poor chemical resistance, particularly in alkaline media due to the presence of a higher number of ester groups. Numerous publications have been cited on the use of alkyds in coatings (Dutta et al., 2006; Haseebuddin et al., 2009; Hofland, 2012). Furthermore, the lower cost of the components of alkyds, i.e., fatty acids (since derived from sustainable resources), facilitates the lower cost of alkyds. An additional advantage is their biodegradable nature as well as their compatibility with other polymers, which provides them an altitude above the other VO derivatives (Hofland, 2012). Traditional drying of alkyds involved air drying or oven drying (at higher temperatures). Drying of alkyd coatings is attributed to the auto-oxidation at active groups. Often, driers are added to accelerate the drying process; these include the traditionally used carboxylates of lead that have now been replaced with cobalt, zirconium, zinc, calcium and iron. Efforts are being directed towards the utilization of environment friendly diluents, catalysts, driers, pigments and additives for alkyd based coatings (Muizebelt et al., 2000).

Chlorinated rubber seed oil [RSO] alkyd resins showed flame retardancy and superior drying characteristics relative to their unchlorinated counterparts (Ikhouria et al., 2007). Acrylated *Albizia benth* [ABO] medium oil alkyds showed improved characteristics in terms of drying time, flexibility, adhesion, scratch resistance, impact resistance and chemical resistance (Akintayo and Adebowale, 2004). Alkyd-acrylic hybrid binders have been prepared with different alkyd–acrylic ratios. The reaction was carried out via free radical polymerization of acrylic monomers in the presence of an unsaturated alkyd resin using the emulsion polymerization technique (Heiskanen et al., 2010). In another report by Araujo et al., LO and SO modified alkyd paints were subjected to marine and industrial atmospheres. Their corrosion aspects were studied by polarization curves and electrochemical impedance spectroscopy (Araujo et al., 2010). The blends of *Mesua ferrea* oil [MFO] based alkyd and bisphenol epoxy resins were prepared by solution technique in benzene/petroleum ether solvent mixture (50:50 w/w). Coatings prepared with amine hardener showed good scratch hardness attributed to better compatibility between the amine-cured epoxy and alkyd residue and also due to greater crosslinking of the epoxy resin. The studies showed good performance of the blends with respect to drying time, hardness, flexibility, gloss, thermal stability, and chemical resistance, in particular against alkalis (Dutta et al., 2006). Alkyd paints with low solvent content are formulated with reactive diluents. Crosslinking mechanisms of high solid alkyd paints in the presence of reactive diluents were studied by NMR and Mass spectrometry. Their cure schedule and performance characteristics have also been studied (Muizebelt et al., 2000).

The last decade triggered extensive research efforts on new coating systems based on alkyds. These include waterborne coatings, organic–inorganic hybrid and nanocomposite coatings from alkyds, with improved performance relative to their traditional counterparts. Aigbodion et al. have synthesized waterborne [WB] alkyds based on RSO for coating applications (Aigbodion et al., 2003). In the recent past, Saravari et al. have synthesized water reducible acrylated alkyds obtained from monoglycerides. The monoglycerides were derived by glycerolysis of interesterification products of tung and palm oil (Saravari et al., 2005). High solids air drying alkyd coatings have been prepared by Haseebuddin and coworkers (Haseebuddin et al., 2009). Emulsifiable air drying alkyd resins with acrylamido tertiary butane sulfonic acid as monomer showed better thermal, chemical and coating properties than those prepared with dimethylol propionic acid as monomer (Athawale and Nimbalkar, 2010). Alam et al. have developed nanoferrite/alkyd composites, which showed improved coating properties over plain alkyds (Alam et al., 2009a,b). Dhoke and Khanna have also carried out similar work on nano Fe_2O_3/alkyd WB coatings. The coatings have shown good corrosion resistance, abrasion resistance and scratch hardness (Dhoke and Khanna, 2009a). Nano-ZnO/WB alkyd coatings have shown good corrosion resistance, UV resistance and mechanical properties. The inclusion of ZnO nanoparticles in silicone-modified alkyd WB coatings improved heat-resistance and mechanical properties of the coatings, as a function of ZnO content (Dhoke and Khanna, 2009b,c). Sailer and their research group carried out the synthesis of alkyd ceramers as protective coatings through the sol–gel technique (Sailer et al., 1998). In order to obtain improved coatings, alkyd resin was obtained as an interesterification product of CO and jatropha oil [JO], which showed excellent water and acid resistance at par with commercial alkyd (Saravari and Praditvatanakit, 2013). In a recent manuscript, Pathan and Ahmad prepared WB alkyd from SO and CO for use as anticorrosive protective coatings modified by the inclusion of s-triazine ring (Pathan and Ahmad, 2013a,b). These alkyd coatings showed good performance in alkaline media as compared to the solvent borne alkyd coatings which are susceptible to alkaline hydrolysis.

2.2.2. *Polyesteramides [PEA]*

PEA are amide modified alkyds obtained by esterification reaction between VO amide diol and an acid/anhydride. They contain repeating ester and amide units in their backbone and possess improved properties over alkyds such as hardness, ease of drying, water vapor resistance and resistance to chemicals, in particular, alkalis (Mahapatra and Karak, 2004; Zafar et al., 2004, 2008b; Alam et al., 2009a,b; Chaudhari et al. 2013a; Meshram et al. 2013). The preparation of PEA occurs in two steps as discussed below:

(i) amidation of VO such as linseed oil [LO], soybean oil [SO], PAO, coconut oil [CCO], argemone oil [AGO], PGO, JO, laurel oil, neem oil, cottonseed oil with diethanolamine in presence of sodium methoxide produces amide diols. These are monomers with two hydroxyl groups and pendant VO (fatty) chains. They serve as excellent starting material for the development of PEA, polyetheramide and poly-urethaneamide resins that have found extensive applications in the surface coating industry.

(ii) *esterification reaction between hydroxyl groups of amide diols with an anhydride*, which finally results in PEA (Ahmad et al., 2003, 2007; Aqeel et al., 2010; Zafar et al., 2010a,b,c,d; Alam and Alandis, 2011a,b).

The presence of ester, amide moieties and pendant (fatty) chains confer synergistic properties of either component to PEA, such as improved chemical resistance, in particular, resistance to alkaline media, thermal stability and imparts flexibility. In addition, fatty chains also serve as functional sites for further modifications. The double bonds and amide groups, as well as extensive hydrogen bonding, influence the mechanical and thermal stability of PEA (Pramanik et al., 2012; Chaudhari et al., 2013b).

About 50% of PEA is bioderived and biodegradable and the rest is non-biodegradable. The structure of PEA, as presented in Fig. 1b, was confirmed by FTIR and NMR techniques; their thermal analyses and antibacterial studies were carried out by standard methods.

PEA from different VO have been modified by acrylic/vinyl monomers (styrene [St], vinyl acetate) (Ahmad et al., 2006a,c), copolymers such as poly (ST-co-maleic anhydride) (Zafar et al., 2004, 2008a,b; Alam et al., 2009a,b; Alam and Alandis, 2012a), poly (ST-co-butylmethacrylate) (Mistry and Agarwal, 2009), melamine (Ahmad et al., 2006a,b), pyromellitimide ring (Abd El-Wahab et al., 2011), metal/metalloid as hydroxides (aluminium, boron) (Ahmad et al., 2004, 2005), acetates (Mn, Cu, Zn, Cd, Co) (Zafar et al., 2007a,b, 2008a,b, 2011) and isocyanates (Ahmad et al., 2004, 2005). These modified PEA showed improved performance in terms of drying/curing (which occurs at elevated temperatures in plain PEA), physico-mechanical, chemical/corrosion behavior and thermal stability relative to the pristine PEA coatings. The synthesis of VO PEA, generally involves high reaction temperatures (above 120 °C) and times (above 5–6 h) and occurs in the presence of solvents (Ahmad et al., 2003, 2007; Zafar et al., 2004, 2008a,b, 2010a,b,c; Alam and Alandis, 2011b). Ahmad and coworkers have carried out the synthesis of LO and PGO PEA in the absence of VOC, at relatively lower temperature (Ahmad et al., 2007; Zafar et al., 2007c, 2010c). To reduce the preparation times and temperatures of PEA, recent studies cover the microwave [MW] assisted synthesis of VO PEA. The synthesis overall required four minutes of time in comparison to the conventional methods which required two to six hours (Zafar et al., 2010b,c; Alam and Alandis, 2011a,b). Their latest accomplishments include the synthesis and characterization of VO based waterborne PEA (Zafar et al., 2010b,c). Water borne microwave processed CO PEA/(preformed) ZnO nanoparticle composite has potential for use as a nanodrug vehicle (Khan et al., 2011). Bioactive metal (Sn, Cd, Zn) containing CO, SO, CCO PEA using adipic, sebacic, citric, tartaric, succinic acids by Bharathi et al. have shown promising antibacterial and antifungal activities to be used as effective nano drug vehicle and biocidal coatings in future (Bharathi et al., 2009a,b, 2010a,b; Khan et al., 2011). CO based biodegradable greener PEA were prepared, where PEA served as a catabolite for *Bacillus subtilus* and *Pseudomonas aeruginosa* and showed biodegradation with time (Pramanik et al., 2012).

2.2.3. Polyetheramides [PEtA]

PEtA consists of alternating amide and ether moieties. It has been introduced in the world of VO based polymers by Alam et al. (2013). The synthesis of PEtA is a two step process: (i) preparation of VO amide diols, and (ii) condensation reaction between amide diols, bisphenol A [BPA] and resorcinol (Alam et al., 2004, 2010; Ahmad et al., 2005a,b; Akintayo et al., 2011; Meshram et al., 2013). About 50% of PEtA is bioderived and degradable in nature. PEtA have been obtained from LO, SO, JO, olive and cottonseed oil (Alam et al., 2004; Ahmad et al., 2005a,b, 2010; Akintayo and Akintayo, 2010; Akintayo et al., 2011; Alam and Alandis, 2012a, 2012b, 2012c). The structural elucidation of PEtA was carried out by spectroscopic techniques (FTIR, ^{1}H NMR, ^{13}C NMR); their thermal and curing behavior were studied by TGA and DSC. The structure of PEtA is provided in Fig. 1c. PEtA contain ether and amide groups in their backbone, which are responsible for good adhesion and chemical resistance of their coatings. In PEtA coatings, drying occurs by solvent evaporation followed by baking (thermal polymerization through migration of double bonds) at elevated temperatures. PEtA has also been used in combination with an isocyanate, to synthesize poly (ether amide urethane), and BMF, where curing of coatings occurs at ambient and elevated temperatures, respectively. The curing occurs in three steps: (i) solvent evaporation, (ii) curing with atmospheric moisture and by chemical reaction with BMF, respectively, as well as (iii) auto-oxidation within pendant fatty amide backbone (Alam et al., 2004, 2010; Ahmad et al., 2005a,b; Akintayo et al., 2011). Acrylated PEtA coatings show improved drying characteristics, impact resistance, flexibility and hardness (Akintayo and Akintayo (2010)). As a combination of ether and amide functional groups in a single backbone, PEtA are expected to outperform PEA in coating performance.

PEtA is still in its cradle stage in the world of coatings and holds immense scope for exploration and applications.

2.2.4. Polyurethanes [PU]

PU are formed by polyaddition reaction between (di-or poly-) isocyanates (toluene 2,4-diisocyanate [TDI], diphenylmethane diisocyanate, naphthylene 1,5-diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate) and (di- or polyhydric) alcohols or other compounds containing active hydrogen atoms, which serve as raw materials for one and two pack PU. VO amide diols and polyols have been used as starting materials for PU synthesis along with aliphatic and aromatic isocyanates (Yadav et al., 2009; Kashif et al., 2010; Zafar et al., 2010a). VO diols are obtained by base catalyzed amidation of virgin VO as discussed in the previous section. VO polyols are either naturally available or obtained by chemical reactions involving ester groups or unsaturation of VO backbone as mentioned in the preceeding section. These react with different isocyanates producing PU (Javni et al., 2000; Sharmin et al., 2007a,b; Akram et al., 2008; Alam et al., 2008; Petrovic, 2008; Xu et al., 2008; Akram et al., 2010; Jalilian et al., 2010). Several other VO based monomers/polymers which have hydroxyl end groups, e.g., amide diols (Yadav et al., 2009; Kashif et al., 2010; Zafar et al., 2010a,b,c), alkyds (Athawale and Nimbalkar 2010; Patel et al., 2011), PEA (Ahmad et al., 2004), PEtA (Alam et al., 2004; Akintayo et al., 2011) and their modified counterparts such as acrylated (Sharmin et al., 2007a,b), metal/metalloid incorporated polymers

(Ahmad et al., 2004; Zafar et al., 2007a,b,c), have also been used for the synthesis of PU coatings. VO PU primarily contain urethane moieties; along with these, they may also contain functional groups such as ester, amide, acrylics, vinyls, double bonds and others (Ahmad et al., 2004; Sharmin et al., 2007a,b; Akram et al., 2010). The presence of these functional groups improves the adhesion, impact resistance, scratch hardness, and flexibility and also imparts good chemical resistance to coatings. The typical structure of PU derived from VO polyols is provided in Fig. 1d. A number of publications have also appeared on VO PU interpenetrating polymer network [IPN] coatings. IPN are polymeric networks where one polymer is being polymerized in the immediate presence of the other. Generally, acrylic monomers, isocyanates and VO polyols are selected as starting materials for their preparation (Ashraf et al., 2005; Dutta et al., 2009; Shan et al., 2011; Kong et al., 2013; Das et al., 2013). The percentage of bioderived and degradable content in VO based PU depends upon the type of isocyanate and diol or polyol.

The advantage of PU coatings over the previously mentioned materials is that they generally show curing or drying at ambient temperatures. In case where a coating material shows high temperature curing or drying (> 100 °C), it is treated with an isocyanate to lower down its curing temperature from elevated to ambient temperature (Ahmad et al., 2005a,b). In TDI based PU, advantage is taken of disparity in activity of the two isocyanate groups. For urethanation reactions taking place < 120 °C, one isocyanate is utilized during urethanation reaction and the other is consumed through moisture curing, at ambient temperature. Generally, curing of PU coatings involves three steps: solvent evaporation, chemical reaction of free isocyanates of PU with moisture and auto-oxidative crosslinking within the backbone of VO derivatives (Sharmin et al., 2007a,b). The presence of carbamate linkages, hydroxyls, free isocyanates in single VO PU backbone results in extensive hydrogen bonding. PU coatings are characterized by excellent durability, resistance to corrosion, abrasion, water and chemicals, mineral oils and many solvents. However, their significant characteristic which enables their maximum applications in the field of coatings is their ability to cure at ambient temperature through a simple curing route. However, VO PU are generally obtained as low glass transition temperature Tg (30 °C) materials which often show lower thermal stability (Javni et al., 2000). PU prepared from polyols obtained by the coupling of epoxidized SO and lactic acid exhibited higher Tg (31–96 °C). Similarly, the incorporation of inorganic segments has also shown improved Tg in VO PU coatings (De Luca et al., 2006; Akram et al., 2010). The chemical, water and corrosion resistance tests of the dried films were found to be significantly affected by the content and type of fatty acid oligomer as well as ionic content in the PU (Patel et al., 2010a,b). The properties of the final PU coatings are governed by the structure, chemical composition, segment length and concentration, the ratio of soft to hard segments, and other parameters. The advantages of these PU coatings are their low cost, availability from a renewable resource, potential biodegradability and good storage stability (6 months). Hyperbranched [HYP] PU synthesized from the monoglyceride of MFO, poly(ε-caprolactone)diol, TDI and glycerol yielded mechanically strong and thermally stable coatings (Deka and Karak, 2009). Recently, SO PU have been used as electrical insulating coatings offering excellent thermal and electrical insulating properties (Jalilian et al., 2010). Two-pack PU coatings based on acid functional acrylic copolymer modified alkyds for industrial maintenance coatings have also been prepared (Patel et al., 1998). LO based urethane styrenated macromers formed yellow colored flexible and transparent films, which showed good acid but poor alkali resistance. The presence of St caused increased thermal resistance and decreased hydrophilicity (Koprululu et al., 2008). Recently, MW assisted preparation of zinc incorporated polyurethaneamide coatings was carried out. The coatings produced were cured at ambient temperature through moisture and auto-oxidative curing process. These showed good physico-mechanical and corrosion resistance performance (Zafar et al., 2011a). Green PU insulator coatings are prepared from CO and poly (ethyleneterphthalate) [PET] (Moeini, 2007). Both virgin as well as metal/metalloid containing PU coatings from LO, CO, PGO have shown corrosion protection and antimicrobial activity due to the presence of metal, urethane and isocyanate (Ahmad et al., 2002, 2004; Sharmin et al., 2007b, 2012; Akram et al., 2010; Deka et al., 2010). Recent research work on VO PU is focused on the synthesis and characterization of WB PU (Lu and Larock, 2008; Gao et al., 2009; Ni et al., 2010), organic–inorganic hybrid PU (De Luca et al., 2006; Patel et al., 2010a,b), PU is derived from renewable resource based isocyanate (Hojabri et al., 2009), high solids PU (Somani et al., 2004), HYP PU (Deka and Karak, 2009; Deka et al., 2010; Karak et al., 2009) and others.

2.2.5. *Epoxies*

VO such as VRO, Euphorbia and Cephalocroton species are rich in vernolic acid, fatty acid with naturally occurring oxirane ring as one of the constituents of their triglyceride backbone. Oxirane ring can also be incorporated at unsaturation sites of VO by chemical reaction, which is better known as epoxidation. Epoxidation can be carried out by various procedures such as epoxidation by peracids, chemo-enzymatic epoxidation, by hydrogen peroxide, using dioxirane, phase transfer catalyst and others (Köckritz and Martin, 2008; Hazmi et al., 2013). Fig. 1e shows the structure of an epoxy resin. Epoxies can be cured with suitable curing agents, (amines, amides, acids, anhydrides) to yield cured polymer with desirable characteristics (Boquillon and Fringant, 2000; Ahmad et al., 2001, 2006b; Sharmin et al., 2004). Literature survey reveals that LO, SO, ASO, RSO, crambe, rapeseed, maize oils, *Santalum album*, anchovy, and other VO have been successively epoxidized in the recent past.

The pure VO epoxies have 100% "greener" content. They show high flexibility and good corrosion resistance particularly against moisture and chemicals owing to their long hydrophobic chains (Ahmad et al., 2001; Chen et al., 2002; Das and Karak, 2009, 2010; Shah and Ahmad, 2012). VO epoxies are often associated with hydroxyls as evident by their spectral studies. It is expected that utilization of VO epoxies in coatings may reduce our dependence on petro-based chemicals and may also cut off the cost of coatings and paints without any compromise on their performance and service life. Epoxidized fatty acids have been used in paint and coating applications (Trumbo and Otto, 2004). Cationically thermally cured coatings have been developed from epoxidized SO (Raghavachar et al., 2000). Ahmad et al. have studied coating properties of epoxidized ASO (cured with a series of amine curing agents) and epoxidized LO-BMF based systems (Ahmad et al., 2006d).

Natural oxirane containing VRO, epoxidized SO, LO and MFO have been used as reactive diluents in coating applications (Das and Karak, 2009). Films obtained from blends of VO epoxies with poly vinyl chloride and poly vinyl alcohol have shown biodegradability behavior and may find application in biobags and food packaging (Riaz et al., 2010, 2011). VO epoxy blends with polymethylmethacrylate and polystyrene have been used as corrosion protective coatings (Ahmad et al., 2001). MFO monoglyceride and epichlorohydrin based epoxy coatings have been prepared by Das and Karak, both in the absence and presence of dihydroxy compounds like tetrabromobisphenol-A and BPA, which showed efficient overall performance (Das and Karak, 2010). Amine cured coatings obtained from terminally epoxidized triglyceride based on epoxidized 10-undecenoic acid triglyceride, have shown excellent UV stability. The coatings obtained have shown good adhesion, hardness, and solvent resistance (Earls et al., 2004). Crivello, Narayan and Soucek et al. have prepared epoxidized VO based UV curable coatings and organic–inorganic hybrid coatings (Chen et al., 2002; Zou and Soucek, 2004; Zong et al., 2005). Green composites and nanocomposites based on epoxidized VO have also been reported for use as reinforced composites, high performance materials and coatings (Uyama et al., 2003; Boquillon and Fringant, 2000; Tsujimoto et al., 2010).

2.2.6. *Polyols*

Polyols constitute one of the important derivatives of VO. Better known as oleochemical polyols, they generally consist of long aliphatic chains with various functional groups principally hydroxyls, double bonds, active methylene groups and often $-OCH_3$, –Cl, –Br, –OCOH and oxirane ring (Sharmin et al., 2007a,b; Akram et al., 2008, 2009, 2010; Vashist et al., 2013; Ghosal et al., 2013; Hazmi et al., 2013). Polyols available in nature mainly comprise of Ricinoleic and Lesquerollic acids, the most abundant constituent (–OH containing) fatty acids of VO obtained from the seeds of *Ricinus communis* or CO and LSO, respectively. Other examples are *Strophantus, Coriaria, Cardamine impatiens, Sebastiana commersoniana* and *Capparis zeylanica,* which also contain a hydroxyl group bearing fatty acids. In the laboratory, polyols are usually obtained by hydroformylation followed by the hydrogenation of VO (using rhodium or cobalt catalysts), epoxidation at unsaturation of VO and subsequent catalytic hydrogenation or by the reaction of oxirane moieties by water, HCl/HBr, low molecular weight mono/polyfunctional alcohols, amino-alcohols or acids (Generation I polyol) and ozonolysis followed by hydrogenation (Generation II polyol). Such methods have been employed on various VO e.g., LO, PGO, SO, canola, rapeseed, lumbang, and RSO to obtain their respective polyols. The structure of a typical VO polyol is provided in Fig. 1f.

Research on polyols is several decades old. Polyols (both generation I and II) are rich in hydroxyls, active methylenes and double bonds. These functional groups can undergo various chemical modifications; nonetheless, over the years, research has been focused mainly on the synthesis (involving –OH) and characterization of PU with applications as foams, lubricants, cosmetics, adhesives, plasticizers and coatings. It is presumed that the complicated structures of VO polyols and PU limit their other modifications. Scant literature is available on derivatization reactions (acrylation and metallation) of chemically derived and natural polyols (Sharmin et al., 2007a,b). These resins combine the advantages of flexibility conferred by long aliphatic triester chains of VO as well as polarity of hydroxyl moieties. These are one of the important building blocks of the polymer industry, mainly as the focal point for PU synthesis.

The pure VO polyols have 100% "greener" content like VO epoxies. The properties of VO polyol derived PU depend on the number, distribution, site of hydroxyls (in the middle or closer to the end of the triglyceride chain), level of unsaturation in the fatty triester chains of the parent polyol, type, position and structure of isocyanates and urethane content of the final PU. The number of hydroxyls on each chain in VO polyols and their stereochemistry is also variable depending upon the hydroxylating agents and other reaction conditions. It is worth mentioning that in epoxy polyol polyesters from VO, the distribution of hydroxyl groups is not homogenous, which is responsible for different properties and characteristics of VO based polyols compared to petrochemical ones. In such a case, often the reproducibility of results cannot be guaranteed. Generally, hydroxyl groups are present in the middle of fatty triester chains in VO. On crosslinking, significant steric hindrance is produced by long aliphatic dangling chains. These cause imperfections, do not support stress and render flexibility to the polyol, acting as plasticisers (Javni et al., 2000; Brasil et al., 2007; Ferrer et al., 2008; Petrovic, 2008; Xu et al., 2008; Akram et al., 2009, 2010; Dai et al., 2009). The presence of hydroxyl groups is associated with extensive hydrogen bonding in VO polyols as evident by spectral studies. Hydroxyl groups impart good adhesion between the coating material and the substrate.

LO and PGO polyol PU coatings have shown anticorrosion as well as antibacterial behavior (Sharmin et al., 2007b; Akram et al., 2010). Acrylonitrile and methylmethacrylate modified LO polyol PU have produced good scratch resistant, impact resistant and flexible coatings (Sharmin et al., 2007a). Boron incorporated CO and LO polyol PU coatings have yielded glossy and transparent coatings obtained at ambient temperature (Akram et al., 2008, 2009). In a report by Zhong and coworkers, novel coatings with excellent properties have been formulated from novel SO phosphate ester polyols which were successfully incorporated into solventborne and waterborne baked coatings (Zhong et al., 2001). Coatings were produced with improved adhesion, low VOC, excellent impact resistance, good hardness, milder curing conditions, and lower cost (Zhong et al., 2001). Biodegradable photo-crosslinked polymer networks could be produced from CO and 7,10-dihydroxy-8(E)-octadecenoic acid (Kim et al., 2010). VO polyester polyol as environmentally friendly (green) coating formulations with low VOC have been reported by Argyropoulos et al. The coatings showed good hydrolytic resistance and flexibility (Argyropoulos et al., 2009). Polyols have been prepared from CO and epoxy resin for PU coatings (Somani et al., 2003). SO polyol based tack free coatings were obtained though at elevated temperatures in lower time periods (Fornof et al., 2006). Coatings from CO, glycolyzed PET, AA and blocked isocyanate showed excellent chemical resistance in acidic and basic media as well as electrical insulation (Moeini, 2007). Recently, metal containing PU from LO have shown antibacterial efficacy along with good physico-mechanical and chemical resistance behavior (Sharmin et al., 2012). In order to obtain advance surface coating materials, CO as a natural polyol has been used as a raw material in HYP PU coatings (Thakur and Karak, 2013).

3. Future perspectives

The use of VO in paints and coatings is decades old and well studied. Today emphasis is being laid on research pertaining to the modifications of these materials to introduce novel properties, improved performance coupled with environment friendliness at affordable costs. VO coatings are being tailor-made for specific uses as antimicrobial, biocompatible, biodegradable, corrosion protective, low or no VOC, architectural, decorative, electrical insulating, paper packaging and self-healing coatings. After the extensive utilization of VO in several fields, particularly in the field of coatings, there are still several issues to be resolved such as:

- VO based alkyds, epoxies, polyols, PEA, and PEtA are obtained by chemical reactions involving cumbersome processes in the presence of VOC, at elevated temperatures, which often cause localized overheating (due to higher temperatures) at the walls of the reaction vessel. This inhomogenous heating leads to the formation of various side products and results in reduced yield. Besides these drawbacks, VO coatings generally show prolonged curing times, multi-step cure schedules, at very high temperatures. For use as environment friendly coatings, these features should be taken care of. MW assisted synthesis process is a clean and green process rendering the synthesis of polymers in a short period of time. This technique if utilized in the preparation of VO polymers may serve as an ultimate answer to the drawbacks such as their high preparation times facilitating good yield of reaction product in a very short span of time. Another alternate may be the enzymatic synthesis approach, which has been provided exhaustively in the literature. With rigorous efforts and active research, biocatalysis may become a well-identified tool for the preparation and biodegradation of VO polymers. MW assisted enzymatic reactions may serve to be a challenging but path breaking approach, in this context.
- Advantage should be taken of inherent fluidity of VO that may result in the development of low or no VOC coatings, i.e., cutting off the use of solvents during processing, formulation and application of coatings.
- Greener isocyanates may proposedly be used as green curing agents for VO coatings. The use of low/no solvent or water as solvent in coatings is another environment friendly approach.
- Another fruitful approach is the preparation of self cured "smart" VO coatings such as by the use of copolymers. The approach provides a wider platform for potential use of semi-drying or non-drying VO in coatings as paints.
- Genetic transformation of oilseeds may be carried out to improve VO productivity to yield VO with desirable fatty acid composition and to improve the performance of VO derived polymers for use in coatings.

These parameters, to some extent, are being taken care of today and require further considerations in future, too.

4. Summary

VO are abundantly available, easy to procure and cost effective sources of nature. These bear unique natural functional attributes and potential biodegradability as renewable feedstocks for environment friendly materials. VO have found practical applications as biodiesel, lubricants, cutting fluids (metal cutting and forming), coatings and paints along with other applications. Although the use of VO in paints and coatings is decades old and well studied, today emphasis is being laid on research pertaining to the modifications of these materials to introduce novel properties, improved performance coupled with environment friendliness at affordable costs. With persistent and extensive research efforts, VO coatings may compete well with their petro based counterparts in performance and applications and may establish themselves as "greener" precursors to environment friendly coatings, in future.

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