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A Review of Vegetable Oil-Based Polymers: Synthesis and Applications

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Abstract

The reviewed work addressed the shift in focus from conventional polymers to bio-based and renewable polymers. The environmental attributes of the renewable polymers make them preferred choice of matrix. The properties of the matrices from renewable origin could compete in high end applications. The composition of the fatty acids in plant seed oil was discussed and the determination of the level of unsaturation used the iodine value. This review also extensively discussed the values of various fatty acid components present in the oils. Areas of application of the thermosetting polymers obtained from plant seed oils were also discussed.

Keywords

Polymer, Fatty Acid, Renewable, Bio-Based, Iodine Value

1. Introduction

Health-related issues, stringent environmental protection policies, search for cost-effective and alternative materials, and the quest for renewability, sustainability, and high-performance materials for technical applications have led to intense research in the production of renewable thermosetting polymers from plant seed oils and shift in focus from the petrochemical based polymers. Bio-based polymers are gaining overwhelming interest and recognition worldwide due to the health, safety, and environmental concerns associated with the conventional synthetic polymers. These bio-based polymers are renewable, biodegradable, and environmentally-friendly. The examples of the bio-based polymers are thermosetting polymers from plant seeds such as soybean oil, sun flower oil, cashew nut oil and linseed oil rapeseed oil. There are also the thermoplastic counterparts such as poly-lactic acid PLA from maize/corn, poly-hydroxy buterate poly-capro lactone and so on.

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Cost is a significant barrier to the development of renewable materials; however, their production has become a viable proposition as technologies have evolved. Inflation in the price of petroleum and an increasing awareness of the end-of-life disposal of the fossil-based plastics has also helped to establish the renewable materials. Bio-based polymers can now be used as natural, sustainable alternatives to traditional petrochemical-derived materials such as phenol-formaldehyde, epoxy resin, unsaturated polyester resin, polyurethane, phenolic resin, and iso-cyanate resin in the manufacture of composite and in coating applications.

The polymer used in composite manufacturing is referred to as a matrix. The work of a matrix is to act as a binder and stress distributor. The stress should be transferred to the fiber that carries the load. Thermoset resins from plant seed oils are capable of replacing thermosetting resins from petrochemicals, particularly because of their positive environmental attributes. Unsaturated polyester resin, phenolic resin, formaldehyde, vinyl ester, polyurethane, and epoxy resin have been used extensively in composite manufacturing and some of them are in the coating industry. The plant oils cannot be used on their own in composite application unless they are suitably functionalized in order to add cross-linkable functionalities to the fatty acids.

Plant Oil Triglycerides

Triglycerides from plants, such as soy bean, palm, rapeseed or sun flower, can be utilised [1]-[9]. The triglyceride compound must be isolated and purified, and also functionalised to obtain the requested reactivity. Various chemical modification reactions are possible; the most common goes via an epoxidation reaction. Therefore, not only would the use of plant oil based resins in liquid moulding resins reduce volatile organic compounds emissions, thereby reducing health and environmental risks, but it would also promote global sustainability [10] [11].

Thermosetting polymers have several advantages over thermoplastics because they have higher service temperature, better stiffness, fatigue resistance, low creep, no stress relaxation, and relative ease of processing due to lower viscosity. Upon curing, thermosetting matrix forms a permanent 3-dimensional network that cannot be reprocessed. The cross-links tie all the polymer molecules together; even when heated, these molecules cannot flow past each other, or around each other. This is the reason they do not melt, and it is very difficult to break the molecules apart; thus, they cannot be remolded or reshaped once they are cross-linked. A major disadvantage of thermoset polymers is that they are difficult to recycle.

Plant oils are vegetable oils extracted from plant sources, as opposed to animal fats; they are quite abundant in nature [12]. Soybean, linseed, castor, sunflower, rape seed, and palm oils are some examples of plant oils [12]. Soybean oil, for example, has been used extensively in the food processing industry in salad dressings, sandwich spreads, margarine, and mayonnaise—and also in non-food applications such as inks, plasticizers, crayons, paints, and soy candles [12]. Soybean oil (SBO) is the most readily available and one of the lowest-cost vegetable oils in the world [13]. Linseed oil has been used mainly in non-food applications as an impregnator and varnish in wood finishing, as a pigment binder in oil paints, and as a plasticizer and hardener in putty. Inedible vegetable oils include processed linseed oil, tung oil, and castor oil, and they are widely used in lubricants, paints, coatings cosmetics, and pharmaceuticals. In general it would be right to say that plant oils are renewable raw materials for a wide variety of industrial products, including coatings, inks, plasticizers, lubricants and paints [8] [9] [14]. Soybean oil is the most abundant of all plant oils, and it is mainly grown in the USA. Plant oils are triglycerides and contain various fatty acids [15] such as linoleic, linolenic, oleic, palmitic, and stearic acid [16]. These fatty acids differ in chain length, composition, distribution, and location [15]. Some are saturated and some are unsaturated, which results in differences in the physical and chemical properties of the oil [15]. Plant oils are also relatively cheap [17].

2. Fatty Acids of Vegetable Oil-Based Polymers

Recently, polymers developed from renewable resources have attracted much attention due to their environmental and economic advantages [18]-[20]. The growing environmental awareness and new rules and regulations are compelling the industries to seek more ecologically friendly materials for their products [21]. Commercial markets for biodegradable and biobased polymers are expected to increase substantially in the coming years [21]. However, the physical and chemical properties of conventional soybean oil limit its use for many industrial applications. Soybean resins are based on triglycerides, which are the major component of plant and animal oils [6]. Triglycerides are composed of three fatty acid chains joined by a glycerol center [6] [7] [11] [22]-[24].

Figure 1 shows the triglyceride molecule of typical plant seed oil. The fatty acids have various levels of saturation and unsaturation [12], and it is the unsaturated part that is functionalized to give the desired matrix which is used in composite manufacture. The liquid resin obtained after functionalization of the triglycerides with various chemical groups can also go through free radical polymerization reactions for complete curing. Many active sites from the triglycerides, such as double bonds, allylic carbons, and ester groups, can be used to introduce polymerizable groups [15]. The chain lengths of the fatty acids in naturally occurring triglycerides can be of varying lengths; 16, 18, and 20 carbon atoms are the most common (**Table 1**) [25].

Triglycerides in plant oils typically contain 10 or more different fatty acids. Fatty acids can be saturated, unsaturated [26], isolated, or conjugated. Some of the unsaturated fatty acids can either be mono-unsaturated (containing 1 carbon-carbon double bond) or polyunsaturated (containing more than two carbon-carbon double bonds). **Table 2** shows the fatty acid composition of various oils [27].

The iodine values of unsaturated fatty acids and their triglycerides are given in **Table 3** [28].

The iodine value is directly related to the level of unsaturation of the fatty acids, which means that the higher the iodine value the higher the level of unsaturation. In soybean oil and linseed oil, linoleic acid and linolenic acid (respectively) predominate in their triglycerides, and the more unsaturated a fatty acid is, the more susceptible it is to functionalization. This means that linseed oil will be easier to modify than soybean oil since the linolenic acid predominating in linseed oil has three carbon-carbon double bonds in its chain, and thus more reactive sites, whereas linoleic acid (which predominates in soybean oil) has two carbon-carbon double bonds in its chain. Triglycerides are divided further into three main groups according to their iodine values [25]. When the iodine value is more than 130, it is said to be drying oil; with iodine values of between 90 and 130, it is termed

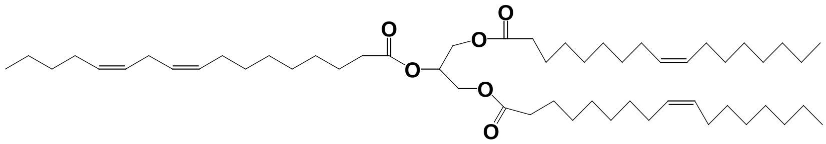

Figure 1. A triglyceride molecule, the major component of natural oils [12].

Table 1. Some fatty acids in natural oils [25].

Name	Fomular	Structure
Myristic acid	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$
Palmitoleic acid	$C_{16}H_{30}O_2$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic acid	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$
Oleic acid	$C_{18}H_{34}O_2$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic acid	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4CH=CH\text{-}CH_2\text{-}CH=CH(CH_2)_7COOH$
Linolenic acid	$C_{18}H_{30}O_2$	$CH_3\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}CH=CH(CH_2)_7COOH$
α-Eleostearic acid	$C_{18}H_{30}O_2$	$CH_3\text{-}(CH_2)_3\text{-}CH=CH\text{-}CH=CH\text{-}CH=CH(CH_2)_7COOH$
Ricinoleic acid	$C_{18}H_{33}O_3$	$CH_3(CH_2)_4CH\text{-}CH\text{-}CH_2\text{-}CH=CH(CH_2)_7COOH$ (OH on CH)
Vernolic acid	$C_{18}H_{32}O_3$	$CH_3(CH_2)_4CH\text{-}CH\text{-}CH_2\text{-}CH=CH(CH_2)_7COOH$ (epoxide O)
Licanic acid	$C_{18}H_{28}O_3$	$CH_3(CH_2)_3CH=CH\text{-}CH=CH\text{-}CH=CH(CH_2)_4C\text{-}(CH_2)_2COOH$ (=O on C)

Table 2. Fatty acid composition of various oils [27].

Fatty acid	Castor oil (%)	Linseed oil (%)	Oiticica oil (%)	Palm oil (%)	Rape seed oil (%)	Refined tall oil (%)	Soybean oil (%)	Sunflower oil (%)
Palmitic acid	1.5	5	6	39	4	4	12	6
Stearic acid	0.5	4	4	5	2	3	4	4
Oleic acid	5	22	8	45	56	46	24	42
Linoleic acid	4	17	8	9	26	35	53	47
Linolenic Acid	0.5	52	-	-	10	12	7	-
Ricinoleic Acid	87.5	-	-	-	-	-	-	-
Licanic acid	-	-	74	-	-	-	-	-
Others	-	-	-	2	2	-	-	-

Table 3. Iodine values of unsaturated fatty acids and their triglycerides [28].

Fatty acid	Number of carbon atoms	Number of double bonds	Iodine value of acid	Iodine value of triglyceride
Palmitoleic acid	16	1	99.8	95.0
Oleic acid	18	1	89.9	86.0
Linoleic acid	18	2	181.0	173.2
Linolenic acid and α-Eleostearic acid	18	3	273.5	261.6
Ricinoleic acid	18	1	85.1	81.6
Licanic acid	18	3	261.0	258.1

semi-drying oil; and with a value of less than 90, it is non-drying oil [25]. The average degree of unsaturation is measured by the iodine value [25].

3. The Modifications of Vegetable Oils Based on Triglyceride Ester

3.1. Monomers Based on Carbon-Carbon Double Bond Modifications in the Vegetable Oils

The carbon–carbon double bonds in the fatty acid chains of the vegetable oils can undergo various reactions to attach different polymerizable functionalities, such as acrylates, to increase the reactivity of the vegetable oils. Acrylated epoxidized soybean oil (AESO), synthesized from the reaction of acrylic acid with epoxidized soybean oil (**Figure 2**) [29] has been extensively studied in polymers and composites [30].

3.2. Monomers Based on Triglyceride Ester Modifications in the Vegetable Oils

The modifications of the fatty acid carbon-carbon double bonds, the incorporation of more reactive carbon–carbon double bonds through chemical modifications of the triglyceride ester groups is another promising approach to more reactive monomers. Wool and co-workers have developed a series of vegetable oil monoglyceride maleates copolymerized with ST to give rigid thermoset polymers [32] [33]. **Figure 3** shows the preparation and polymerization of soybean oil monoglyceride (SOMG) maleate half esters.

4. The Application Areas

The utilization of renewable resources in energy and material applications is receiving increasing attentions in

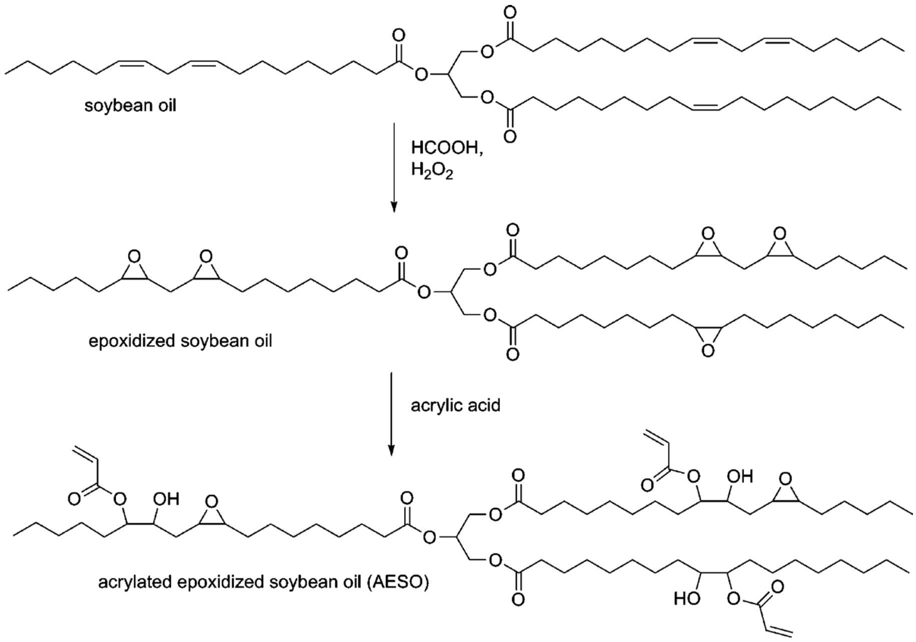

Figure 2. Synthesis of acrylated epoxidised soybean oil [31].

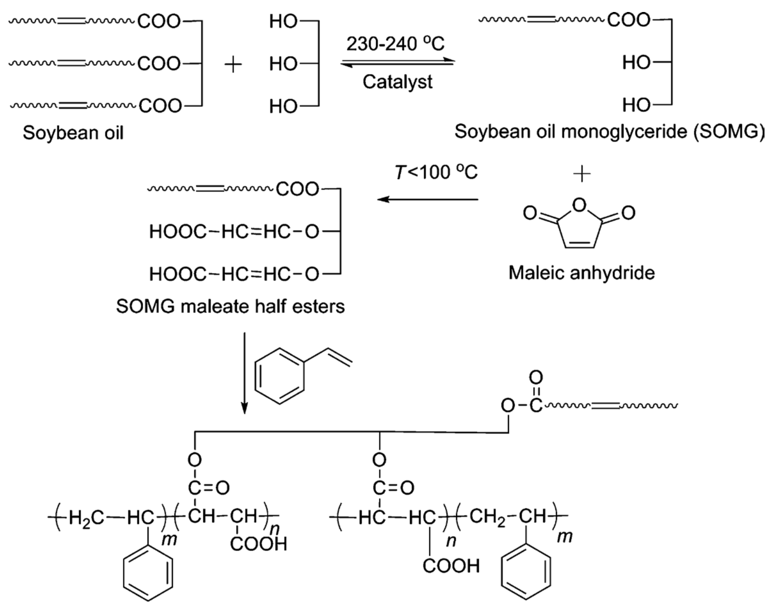

Figure 3. Synthesis and polymerization of soybean oil monoglyceride maleates [32].

both industrial and academic settings, due to concerns regarding environmental sustainability [34] [35].

The use of vegetable oils as renewable raw materials for the synthesis of various monomers and polymeric materials is reviewed [36]. Vegetable oils are generally considered to be the most important class of renewable resources, because of their ready availability and numerous applications [36]. Recently, a variety of vegetable oil-based polymers have been prepared by free radical, cationic, olefin metathesis, and condensation polymerization [36]. The polymers obtained display a wide range of thermo physical and mechanical properties from soft and flexible rubbers to hard and rigid plastics, which show promise as alternatives to petroleum-based plastics [36].

Triglyceride based oil from renewable resources are now being used in paints, adhesives and composite industry. Their application as matrix in composite industry has opened new markets in construction, automobile, marine, military, sports and leisure. The tight environmental regulations have forced many companies to embrace the use of the renewable materials. The application areas of the vegetable oil-based polymers can be further explored.

5. Conclusion

Plant seed oils are renewable alternatives to petrochemicals, but they cannot be used in their raw form except they are suitably modified. The unsaturated carbon-carbon double bonds in the fatty acid must be made to react with other monomers because the aim of the modification is to attach cross linkable functionalities to the fatty acid in order to have cross-linked thermoset material after curing. After modification and subsequent curing of the polymer, the final product should be a rigid thermoset material which cannot be reprocessed or melted. The level of unsaturation of the various fatty acids determines the type of polymerization that should be carried out. The in-depth study and the understanding of the fatty acids of the plant seed oils are paramount for their modification and further application in high technical area.

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