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Synthesis of Biocomposites from Natural Oils- a Review

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Abstract. The dependence on petrochemicals for production of polymers has been declining not only because of the depletion in fossil fuels but also due to environmental concerns. Extensive research has been undertaken worldwide to explore renewable resource for the production of polymers and biocomposites. Vegetable or plant oil is one such main and valuable renewable resource. The functional groups in natural oils can be activated by condensation polymerization and presently various types of condensation polymers, such as polyurethanes, polyesters and polyether's, are being produced by this route. These natural oils can be used to produce a variety of biocomposites with modified properties to serve varied purposes. No doubt, these natural oils have been at the researchers focus to replace or augment the traditional petro based polymers and resins. Soybean, safflower, sunflower and canola oil which have been traditionally used in organic coating, paints and varnishes are now being experimented and researched, to produce biocomposites for modern day applications. This paper reviews the extensive work undertaken for the synthesis of biocomposites from natural oils.

Keywords: Biocomposites, Triglycerides, Resin, Polyurethane, Thermoset, Vegetable oil, Polyols, Copolymerization, SOMG, SMC, Tg.

1. Introduction

The polymers obtained from natural oils are biopolymers in the sense that they are generated from renewable natural sources; they are often biodegradable as well as non-toxic. Some biopolymers obtained from natural oils are flexible and rubbery. Generally, they are prepared as cross-linked copolymers. Bacterial polyesters are obtained from a large number of bacteria when subjected to metabolic stress.

Most of the common oil contains fatty acids that vary from 14 to 22 carbons in length, with 1–3 double bonds. There are some oils comprise fatty acids with other types of functionalities (e.g., epoxies, hydroxyls, cyclic groups and furanoid groups) and on a molecular level, these oils are composed of many different types of triglyceride, with numerous levels of unsaturation. The triglycerides constituting any plant oil can be chemically modified so as to become monomers or comonomers for several polymerization reactions. The fatty acid esters derived from the triglyceride vegetable oils are an attractive source of raw materials for polymer synthesis. Triglyceride oils are used in food industry as well as for the production of coatings, inks, plasticizers, lubricants and agrochemicals. Vegetable oils are excellent renewable source of raw materials for the manufacture of polyurethane components such as polyols. To use soybean oil as a monomer for the preparation of polyurethanes, it should be suitably functionalized. The transformations of the double bonds of triglycerides of oils to hydroxyls and their application in polyurethanes are the subject of many studies. These polyurethanes from vegetable oils have high strength as well as stiffness, environmental resistance and long life and it is the main technological advantages of these oils.

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2. Literature Review

Can et. al., 2000 prepared rigid thermoset polymers from soybean oil monoglyceride maleates with styrene by radical copolymerization. First part of the reaction involves formation of soybean oil monoglycerides (SOMGs) then SOMG were reacted with maleic anhydride at 100°C temperature to produce the SOMG maleate half esters. Liu et. al., 2001 prepared soybean oil-based composites by the solid free forming fabrication (SFF) method. Epoxidized soybean oil is solidified with a gelling agent, and composites are formed by fibre reinforcement with glass, carbon, and mineral oil. Mehta et. al., 2004 synthesized biobased resin using plant bio-fibres and a blend of unsaturated polyester resin from derivatized vegetable oil. These biocomposites replace existing glass fibre-polyester composites which are use in housing applications. Shabeer et. al., 2005 synthesized a soy based epoxy resin, epoxidized allyl soyate (EAS) from regular food grade soybean oil by the process of transesterfication and epoxidation. Two types of crosslinking agents were employed in this study.

Bonnaillie et. al., 2006 prepared thermosetting foam with a high bio-based content from Acrylated epoxidized soybean oil and carbon dioxide. They applied a pressurized carbon dioxide foaming process that produces polymeric foams from acrylated epoxidized soybean oil (AESO). Badri et.al., 2006 synthesized biocomposites from oil palm resources to study the effect of oil palm empty fruit bunch (EFB) on the mechanical properties of high density rigid polyurethane (PU).They prepared resin by mixing the palm kernel oil-based polyester (functionality of 3) with tetramethylhexanediamine as curing agent, silicone-type of surfactant and EFB fibre as a filler. Then this resin reacted with 4, 4'-diphenylmethane diisocyanate (MDI) to produce high density rigid PU. Sharma et. al., 2006 discussed the synthesis and characterization of new polymers from different natural oil such as soybean, corn, tung, linseed, castor, and fish oil investigated the conversion of natural oil to polymers to augment the use of petroleum products as the source of polymeric raw materials. Natural oil, such as vegetable oil, now mainly used in the food industry, offer alternatives, and recent research has studied new routes of synthesis of polymers from natural oil. The effects of different levels of unsaturation in the natural oil and various types of catalysts and comonomers on the properties of copolymers are considered.

Shabeer et. al., 2007 prepared a soy-based resin by the process of transesterfication and epoxidation of regular food grade soybean oil. Lu. et. al., 2007 prepared thermoset resins for sheet molding compound (SMC) and bulk molding compound applications from soybean oil. The SMC resins were prepared from maleated hydroxylated soybean oil (MHSO) and maleated acrylated epoxidized soybean oil (MAESO) with styrene. Zhang et. al., 2007 synthesized polyurethane (PU) flexible foams by substituting a portion of base polyether polyol with soybean oil-derived polyol (SBOP) and crosslinker polyol and styrene acrylonitrile (SAN) copolymer-filled polyol.

Sharma et. al., 2008 synthesized various types of useful condensation polymers, such as polyurethanes, polyesters and polyether's. As vegetable oil are one of the most readily available alternative renewable resources and the functional groups present in natural oil can be activated for condensation polymerization, they have converted natural oil into the polymer chain. They found various useful properties of polyurethane products for their widespread applications. Jalilian et. al., 2008 synthesized and characterized a polyurethane networks from new soybean oil-based polyol and a bulky blocked polyisocyanate. For this they prepared a new soybean oil-based polyol with high functionality of hydroxyl groups and built-in (preformed) urethane bonds.

Yaakob et. al., 2010 prepared a series of biocomposites using prepared polyurethane (PU) sheet and different amounts of oil palm trunk (OPT) fiber dust and characterized. For this first they obtained a monoglyceride from oleic acid through a direct esterification process and then utilized it to prepare PU sheet.

3. Synthesis of biocomposites

3.1. Soybean based Biocomposites

Soybean oils are biodegradable vegetable oil and available in bulk quantity. Natural soybean oil possesses a triglyceride structure with highly unsaturated fatty acid side chains. This unsaturation in these oils provides ideal monomers for the preparation of various polymers. Polymers derived from soybean oils have been investigated [17-21]. Polymers from different soybean oils show different properties, and the cross-linking density of the bulk polymers affects their thermophysical properties.

By cationic copolymerization of regular soybean oil, low saturated soybean oil or conjugated low saturated soybean oil with styrene and divinylbenzene we can prepared various copolymers. It is initiated by boron trifluoride diethyl etherate which results in polymers ranging from soft rubbers to hard thermosets, depending on the oil and the stoichiometry used. The miscibility of the initiator improved with a Norway fish oil ethyl ester. The copolymerization of soybean oil with styrene and norbornadiene or dicyclopentadiene initiated by boron trifluoride diethyl etherate synthesized heterogeneous polymeric materials with good mechanical properties and thermal stability.

3.2. Modified Soybean Oil Polymers

Triglycerides have various active sites in their structures like the double bond, the ester group, the allylic carbons, and the carbons α to the ester group. Hence there are various chemical pathways for functionalization of these triglycerides [14].The soybean fatty acid and poly (hydroxy alkanoate) (PHA) reacted under UV irradiation to form a cross-linked biopolyester. The esterification reaction takes place along with cross-linking via a free radical mechanism. A bacterial polyester containing olefinic groups in the side chains was prepared by feeding pseudomonas oleovorans with soybean fatty acids. The cross-linked biopolyester, obtained thermally at 600C with benzoyl peroxide initiation having highest crosslinking density [12].

3.3. Fish Oil Polymers

Fish oil is available as a byproduct in the production of fishmeal. It is biodegradable. It has a triglyceride structure with a high percentage of polyunsaturated omega 3 fatty acid side chains and contain as many as 5–6 nonconjugated carbon–carbon double bonds per ester side chain. It has many applications in the production of protective coatings, lubricants, sealants, inks, animal feed and surfactants.

3.4. Corn Oil Polymers

Corn oil is one of the cheapest commercially available vegetable oils. It is used in food and livestock feed as well as in the production of ethanol. It has a triglyceride structure, with carbon–carbon double bonds per molecule in fatty acid side chains. Due to high degree of unsaturation in corn oil, it is possible to copolymerize it with other monomers. Corn and soybean oils have similar chemical structures with three fatty acid chains composed of oleic acid, linoleic acid and linolenic acid.

3.5. Tung Oil Polymers

Tung oil is one of the oldest known drying oils extracted from the seeds of the tung tree. It has numerous applications in the paint industry. Its main constituent is glyceride of elaeostearic acid with a conjugated triene structure. Due to its highly unsaturated, conjugated system it rapidly undergoes polymerization. It has been polymerized by both free radical and cationic polymerizations. Tung oil is cationically copolymerized [17-19] with divinylbenzene in the presence of boron trifluoride diethyl etherate to produce hard plastics. Tung oil can also be copolymerized with styrene and divinylbenzene by thermal polymerization.

3.6. Natural Linseed Oil Polymers

Linseed oil is produced from the linseed seed. It is a fatty acid ester triglyceride, composed of about 53%linolenic acid, 18%oleic acid, 15%linoleic acid, 6% palmitic acid and 6% stearic acid. It is traditionally used as a drying oil for surface-coating applications and for making it superior drying oil in terms of film properties, different olefinic monomers, such as styrene have been copolymerized with linseed oil. Linseed oil is polymerized by cationic, thermal, free radical polymerization and by oxidative polymerization [15].

3.7. Castor Oil Polymers

Castor oil is a vegetable oil obtained from the castor bean of castor plant. It is a triglyceride in which approximately 90 percent of fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. Epoxidized castor oil has been used for the preparation of interpenetrating polymer networks (IPN). It is observed that the cross-linked IPNs from the epoxidized oil and adducts of tung oil with maleic anhydride had very good compatibility [3]. The hydroxyl groups of epoxidized castor oil form hydrogen bonds with the carbonyl groups in tung oil. These hydroxyls are more reactive towards tung oil adducts than epoxidized cottonseed oil. Styrenated castor oil and linseed oil can be prepared by the macromer technique [10]. The copolymerization of dehydrated castor oil with styrene [6,5] has been reported. A blend of dehydrated castor oil and epoxy resin and the miscibility of the blends of epoxidized dehydrated castor oil and poly (methyl methacrylate) has been reported [2].

3.8. Polymers from Other Oils

Drying and semidrying oils such as sesame, sunflower, safflower, walnut oil are also used for the preparation of polymer by different methods. A substantial research has been done on the polymerization of high oleic sunflower oil with different comonomers. The copolymers of sunflower oil and styrene were formed via free radical mechanism. The Ritter reaction is used to study acrylamide functionality on the triglyceride of sunflower oil.Biobased resins are prepared [1] by the addition of a derivatized vegetable oil (Methyl ester of soybean oil (MESO), epoxidized methyl linseedate (EML)) to the unsaturated polyester resin (UPE) matrix. The initiator used was methyl ethyl ketone peroxide (MEKP) and promoter used was cobalt (II) naphtenate (CoNap). This bioresins are then used for the fabrication of a biocomposites using an optimum amount of natural fibre (30% volume). The natural fibre used is a non-woven hemp mat, which contains 10% poly (ethylene terephthalate) (PET) as filler. It produced plastic and composite plaques which were cut into required shapes for various tests.

Hydro chlorofluorocarbon (HCFC) and pentane blown rigid polyurethane (PU) foams are synthesized from polyols derived from soybean oil [16]. The foams prepared from these polyols were found to have comparable mechanical and insulating properties to those of commercially available polypropylene oxide (PPO)-based foams. It was observed that the soybean polyol derived PU foams were more stable. Researchers also studied the thermal stabilities of PU-based on various vegetable oils, the structure and properties of PUs prepared from halogenated as well as non-halogenated soybean polyols. They modified epoxidized soybean oil (ESBO) with hydrochloric acid, hydrobromic acid, methanol and hydrogen. From these polyols, four types of polyol polyurethanes were prepared [11]. A series of urethane acrylates can be derived from soybean fatty acid modified hyper branched aliphatic polyesters [7]. Nahar (Mesua ferrea L.) seed oil contains mainly triglycerides of linoleic, oleic, palmitic and stearic acids. Polyester, polyesteramide, polyurethane and polyurethane amide resins are synthesized from nahar seed oil [24]. Synthesized aliphatic amine, and phthalic anhydride can be employed as crosslinking agents for the transesterfication and epoxidation of regular food grade soybean oil [9] to produce Epoxidized allyl soyate (EAS), novel soy based epoxy resin. Soy-based resin can be produced by transesterfication and epoxidation of regular food grade soybean oil [17]. Radical copolymerization of the soybean oil monoglyceride maleates with styrene yield thermosetting liquid molding resins [4,24] whereas sheet moulding compound resins can be derived from soybean oil [25] by using maleated hydroxylated soybean oil (MHSO) and maleated acrylated epoxidized soybean oil (MAESO) with styrene, MgO as thickening agent, Formic acid for the epoxidation reaction. Polyurethane (PU) flexible foams can be synthesized by substituting a portion of base polyether polyol with soybean oil-derived polyol (SBOP) [26] and substituent, crosslinker polyol and styrene acrylonitrile (SAN) copolymer-filled polyol. Biopolymer from the palm oil resources [13] can be synthesized.

4. Conclusion

In recent years, natural oils have become the best alternative for petroleum-based polymers. The fossil-based monomers are harmful to environment. These are non-renewable as they are derived mainly from petroleum-based materials and day by day fossil-based feedstocks are depleting very rapidly. Hence, it has become the main goal for the researchers in coming years to produce viable polymers from the natural resources. Different research groups in the world are studying the properties of natural oils and their composites for utilization as polymers, resins, varnishes and paints.

The vegetable oils provide a large variety of options for the preparation of different polymers. All the vegetable oils are triglycerides of fatty acids and most contain unsaturated groups. Only a few contain other groups such as hydroxyl in castor oil, safflower oil and lesquerella oil, and oxirane group in vernonia oil.

The unsaturation present in these oils makes them ideal for the preparation of bio-based polymers. The polymerization of these oils is carried out via free radical and cationic polymerization reactions.

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6. References

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