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BIODEGRADABLE PLANT OIL POLYMERS AND ITS EXTENDING APPLICATIONS - A REVIEW

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ABSTRACT

The review covers the recent developments and applications of biodegradable polymers. Over population, depleting resources, increasing dependence on non bio degradable plastics, global warming and environmental awareness leads to an in depth study about vegetable oil-based polymers as an alternative sustainable feedstock. Fats and oils are primarily water-insoluble hydrophobic substances. In the plant and animal kingdom oils are made up of one mole of glycerol and three moles of fatty acids commonly referred as triglycerides. Highly reactive sites like double bond in allylic positions and esters in the oil make it a highly interested raw material for polymer synthesis. Many polymers have excellent biocompatibilities and unique properties including shape memory, elasticity, tensile and mechanical strength. Novel polymers can be fabricated with reinforcing the polymer with fibre or nano materials. Some essential applications of plastics like packaging, textiles, coatings, automobile components, biomedical devices and household items makes it a daily object.

KEYWORDS: Polymers, Bio Degradable Materials, Fats, Renewable Resources And Triglycerides.

INTRODUCTION

Continuously increasing price of petroleum and depleting fossil feedstock and an increase in environmental awareness researchers are actively trying to produce polymeric materials from biorenewable resources to replace the traditional petroleum-based plastics (Liu et al., 2014).Vegetable oils are one of the most important classes of bio-resources for producing polymeric materials. The fundamental parts of vegetable oils are triglycerides-esters of glycerol with three unsaturated fats. A few exceptionally responsive sites incorporating double bonds in allylic positions and the ester groups are available in triglycerides from which an extraordinary assortment of polymers with various structures and functionalities can be prepared. Vegetable oil-based polyurethane, polyester, polyether, and polyolefin are the four most important classes of polymers, many of which have excellent biocompatibilities and unique properties including shape memory (Miao et al., 2013). The most important aspect of synthesizing biodegradable polymers is related to their ability to undergo degradation within the biosphere on coming into contact with micro-organisms, enzymes, or under natural environmental conditions (Narine et al., 2005). Biodegradable (hydrolytically and enzymatically degradable)

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EXISTING POLYMERS

Polymers are widely used in almost all the fields because of its excellent mechanical properties, high corrosion resistance, thermal stability and low cost (Shakina et al., 2015). Existing polymers are mostly choking the earth's atmosphere as well as the biosphere. Currently conventional polymers made from fossil fuels are in use. The depleting petro chemical resources and non bio degradability of existing polymers urge people to reduce the usage of petro chemical polymers. In most of the time polymer usage can't be avoided completely. So researchers find an alternative source to produce nature friendly bio degradable polymers from vegetable oil.

Source: www.shutterstock.com

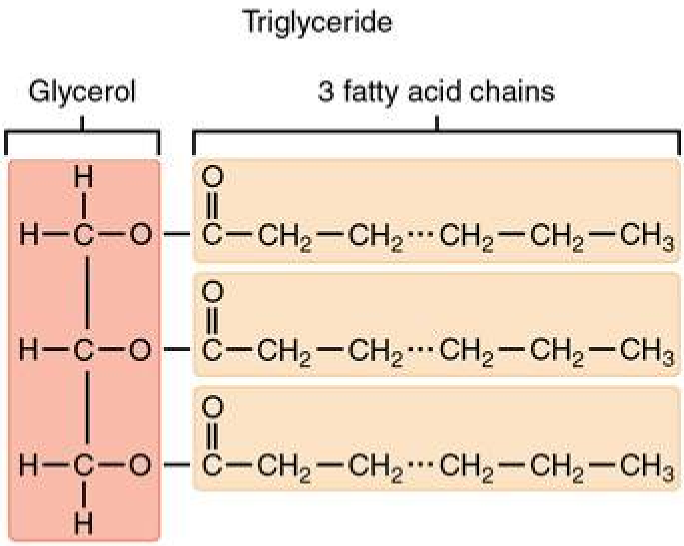
Scheme 1.Valley dumped with polymers

NATURAL POLYMERS

In nature polymer chains arecommon in cellulose, lignin, and starch. Cellulose is abundant in all plants, although some plants produce more than others. Lignin is typically found in wood, and starch is common in plants such as corn, potatoes, and wheat. Plants, wood, corn, potatoes, and wheat are all raw materials that are renewable and readily available. Natural polymers are bio degradable, bio compatible and non toxic (Bendale, 2018).

SYNTHETIC POLYMERS

The chemical transformation of the non edible oil triglyceride affords a wide variety of monomers for the synthesis of cross linked structural polymers. The modification of triglycerides can be performed using the reactivity of the functional groups in their structure (Espinosa et. al., 2011).Unsaturation of long hydrocarbon side chain to make the cross linking easy on polymerization and improves flexibility, good drying after baking, high electric insulation and thermal stability (Nair 2004). The side chain gives hydrophobic nature to the polymer. Its covering is water repellent and climate-safe. These resins gangs extraordinary protection from acids and alkalis, antimicrobial property, terminate and insect resistance.



Source: www.study.com

Scheme 2.General structure of a triglyceride molecule

DIFFERENCE BETWEEN NATURAL AND SYNTHETIC POLYMERS

The major difference between synthetic polymers and polymers found in nature is that the natural polymers contain oxygen and nitrogen. The oxygen and nitrogen in the polymer structure permit the polymer to biodegrade (Bendale, 2018).

TYPES OF VEGETABLE OILS

There are plenty of vegetable oils such as canola oil, corn oil, olive oil, cotton seed oil, linseed oil, palm oil, rape seed oil and soybean oil are available worldwide at the present time (Tan, 2010).

Scheme 3.Common Fatty Acids, Structures, and Formulas

Name	Scientific Name	Structure	Formula	CN/DB	Type
Caprylic	Octanoic acid	$CH_3(CH_2)_6COOH$	$C_8H_{16}O_2$	8:0	Saturated
Caprylic	Octanoic acid	$CH_3(CH_2)_6COOH$	$C_8H_{16}O_2$	8:0	Saturated
Capric	Decanoic acid	$CH_3(CH_2)_8COOH$	$C_{10}H_{20}O_2$	10:0	Saturated
Lauric	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	$C_{12}H_{24}O_2$	12:0	Saturated
Myristic	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	$C_{14}H_{28}O_2$	14:0	Saturated
Palmitic	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	$C_{16}H_{32}O_2$	16:0	Saturated
Stearic	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	$C_{18}H_{36}O_2$	18:0	Saturated
Arachidic	Eicosanoic acid	$CH_3(CH_2)_{18}COOH$	$C_{20}H_{40}O_2$	20:0	Saturated
Palmitoleic	Hexadec-9-enoic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	$C_{16}H_{30}O_2$	16:1	Monounsaturated
Oleic	Octadec-9-enoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	$C_{18}H_{34}O_2$	18:1	Monounsaturated
Erucic	Docos-13-enoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	$C_{22}H_{42}O_2$	22:1	Monounsaturated
Linoleic	9,12-Octadecadienoic	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7COOH$	$C_{18}H_{32}O_2$	18:2	Polyunsaturated

	acid				
α-Linolenic	Octadeca-9,12,15-trienoic acid	CH_3-CH_2-CH =CH-CH_2-CH= CH-CH_2- CH=CH$(CH_2)_7$COOH	$C_{18}H_{30}O_2$	18:3	Polyunsaturated
α-Eleostearic	Octadeca-9,11,13-trienoic acid	CH_3-$(CH_2)_3$-CH =CH-CH= CH-CH =CH$(CH_2)_7$COOH	$C_{18}H_{30}O_2$	18:3	Polyunsaturated
Ricinoleic	(9Z,12R)−12-Hydroxyoctadec-9-enoic acid	$CH_3(CH_2)_5CH(OH)CH_2CH$= CH$(CH_2)_7$COOH	$C_{18}H_{34}O_3$	18:1	Monounsaturated
Vernolic	Cis-12,13-epoxy-cis-9octadecenoic acid		$C_{18}H_{32}O_3$	18:1	Monounsaturated

CN : Carbon Number ; DB : Double Bond

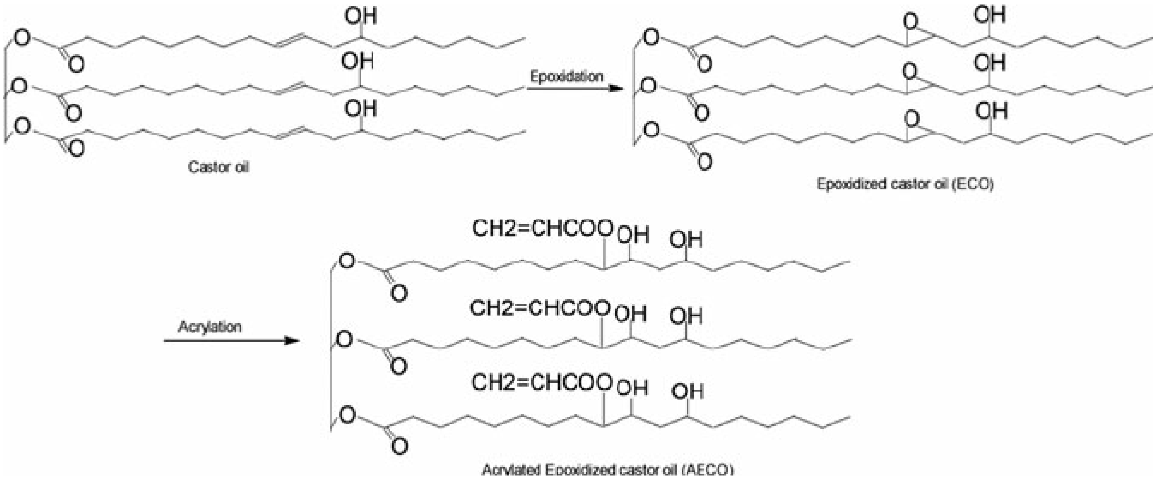
Scheme 4.Common Vegetable Oils and their fatty content

Name	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Arachidic	Oleic	Erucic	Linoleic	Linolenic	Ricinoleic acid
Palm	-	-	-	1.2	41.8	3.4	-	41.9	-	11.0	-	-
Soybean	-	-	-	-	14.0	4.0		23.3	-	52.2	5.6	-
Coconut	6.2	6.2	51.0	18.9	8.6	1.9	-	5.8	-	1.3	-	-
Sunflower	-	-	-	-	6.5	2.0	-	45.4	-	46.0	0.1	-
Rapeseed	-	-	-	-	4	2	-	56	-	26	10	-
Castor	-	-	-	-	1.5	0.5	-	5	-	4	0.5	87.5
Linseed	-	-	-	-	5	4	-	22	-	17	52	-
Naharseed	-	-	-	-	15.9	9.5	-	52.3	-	22.3	-	-
Corn	-	-	-	-	10	4	-	34	-	48	-	-
Olive	-	-	-	-	6	4	-	83	-	7	-	-
Sesame	-	-	-	0.1	8.2	3.6	-	42.1	-	43.4	-	-
Safflower	-	-	-	0.1	6.8	2.3	0.3	12	-	77.7	0.4	-
Almond	-	-	-	-	7	2	-	69	-	17	-	-
Canola	-	-	-	-	4	2	-	62	-	22	10	-
Cod Liver	-	-	-	8	17	-	-	22	-	5	-	-
Cotton Seed	-	-	-	1	22	3	-	19	-	54	1	-
Flax Seed	-	-	-	-	3	7	-	21	-	16	53	-
Peanut	-	-	-	-	11	2	-	48	-	32	-	-

METHODS

It is chemically conceivable to change and transform the triglyceride into the reactive group by means of epoxidation, epoxidation, and metathesis of the double bond, acrylation of epoxies response with maleic anhydride or transesterification. In view of the functional epoxides group on the structure of Epoxidised vegetable oil and moderately high oxirane substance of linseed and soybean oil, presently it is used in appropriate curing agents in order to produce bio-based epoxies system with satisfactory properties (Samarth, 2015, Shakina, 2014). Vegetable oil-based polymers have been developed by free radical, cationic, olefin metathesis, and addition polymerization. The polymers acquired presentation a wide scope of thermo physical and mechanical properties from soft and adaptable rubbers to hard and inflexible plastics, which show guarantee as options in contrast to oil based plastics (Miao, 2014 &Zhang, 2018).

Scheme 5.Epoxidation and Acrylation of Castor Oil



Source: www.researchgate.net

Scheme 6.Production Techniques for Polymer

Technique	Characteristics	Examples
Sheet molding	Fast, flexible,	1-2" SMC automotive body fiber panels
Injection molding	Fast,	high volume Gears, fan blades very short fibers, thermoplastics Resin transfer Fast, complex parts,
Automotivestructural molding	good control of fiber panels orientation	Prepreg tape lay-up Slow, laborious, Aerospace structures reliable, expensive (speed improved by automation)
Pultrusion	Continuous, constant I-beams, columns cross-section parts Filament winding Moderate speed,	Aircraft fuselage, complex geometries, pipes, drive shafts hollow parts
Thermal forming Reinforced thermoplastic	fast, easy repair, joining	All of above (future) matrices

Source: Office of Technology Assessment, 1988

PHYSCIO – CHEMICAL PROPERTY OF THE OIL

Oil properties can be measured by different parameters, including the iodine value, acid value, saponification value, and peroxide value. The degree of unsaturation in oil can be determined by the iodine value. The higher the iodine values are, the higher the unsaturation in the oils is. The determination of the acid value is important for measuring the free fatty acids or acidity present in the oil. Additionally, sometimes, the extent of the polymerization reaction or the desired level of acidity in the sample can be monitored by the same. The chain length or average molecular weight of the fatty acids present in the oil can be determined by the saponification value. The short-chain fatty acids in oil have a higher saponification value, whereas the long-chain fatty acids have a lower value. The peroxide value is required to detect the rancidity or freshness of oil samples. The density of all oils ranges from 0.80 to 0.95 g/cm3, and the specific gravity is around 0.9. All of these properties, directly or indirectly, control the characteristic profiles of polymers produced from vegetable oils (Islam, 2014).

Scheme 7.Iodine Values of Common Vegetable Oils

Name	Iodine Value (g of I_2/100 g)
Castor	102.2
Coconut	15.1
Corn	123.5
Cottonseed	109.4
Linseed	180.0
Palm	43.3
Safflower	134.7
Soybean	128.7
Sunflower	120.0

CHARACTERISATION

Fourier transform of infrared (FTIR) and ^{1}H-NMR spectroscopy are essential techniques for the determination of particular functional groups and the structural elucidation of oil and resin. Some of the important absorption peaks for FTIR spectroscopy and chemical shifts for ^{1}H-NMR of vegetable oil (jatropha)

Scheme 8.FTIR Data for Vegetable Oils

Absorption Band (cm^{-1})	Functionality
3468	-O-H Stretching Vibration
2856-2924	Aliphatic C-H Stretching Vibration
1744	C=O Stretching Vibration of triglyceride esters
1655	C=C Stretching Vibration
1456	C-H Bending Vibration
1162	C-O-C Stretching Vibration of esters
719	Methylene rocking Vibration

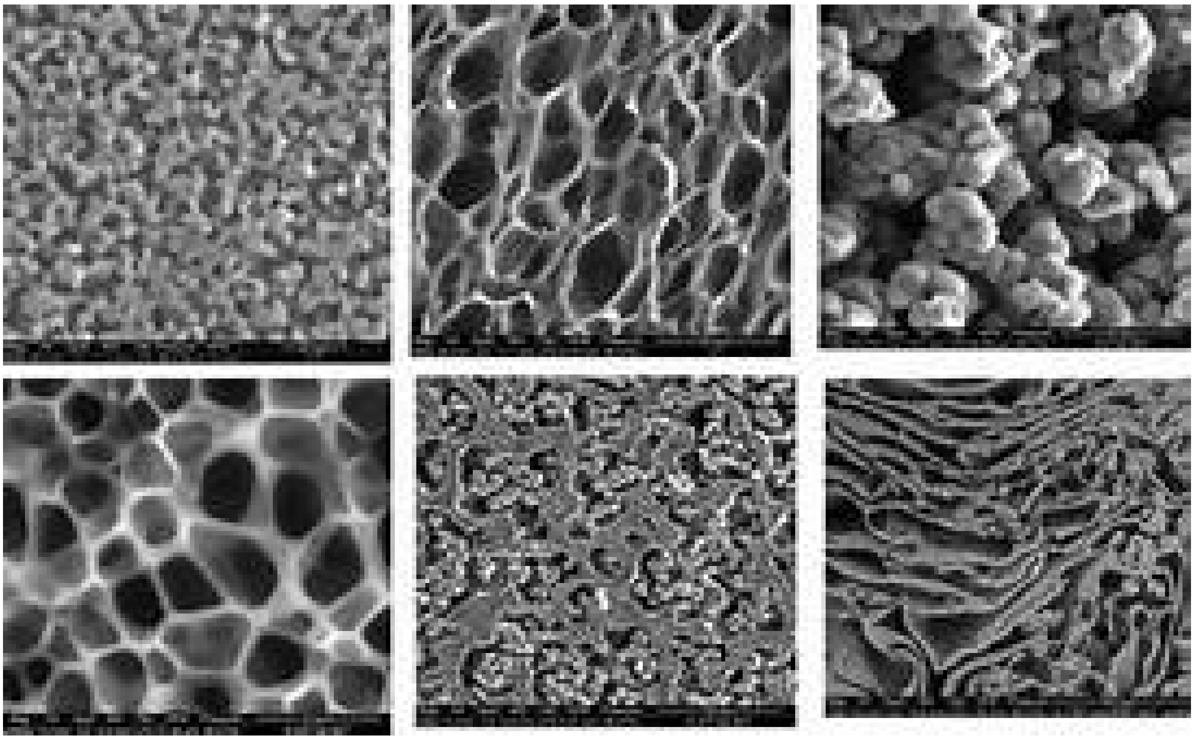
Scheme 9.Some Representative ^{1}H-NMR Shift Values for Vegetable Oil

^{1}H chemical shift (ppm) protons	
0.87-0.89	Proton of terminal methyl groups
1.60	Protons of initial -CH_2- groups
2.01-2.05	Allylic protons of CH_2
2.30-2.32	α Protons of ester group
2.75-2.78	CH_2 of double allylic proton
4.15-4.28	Protons of glyceride moieties
5.32-5.35	Protons of the -CH=CH- moieties

SURFACE MORPHOLOGY OF POLYMER

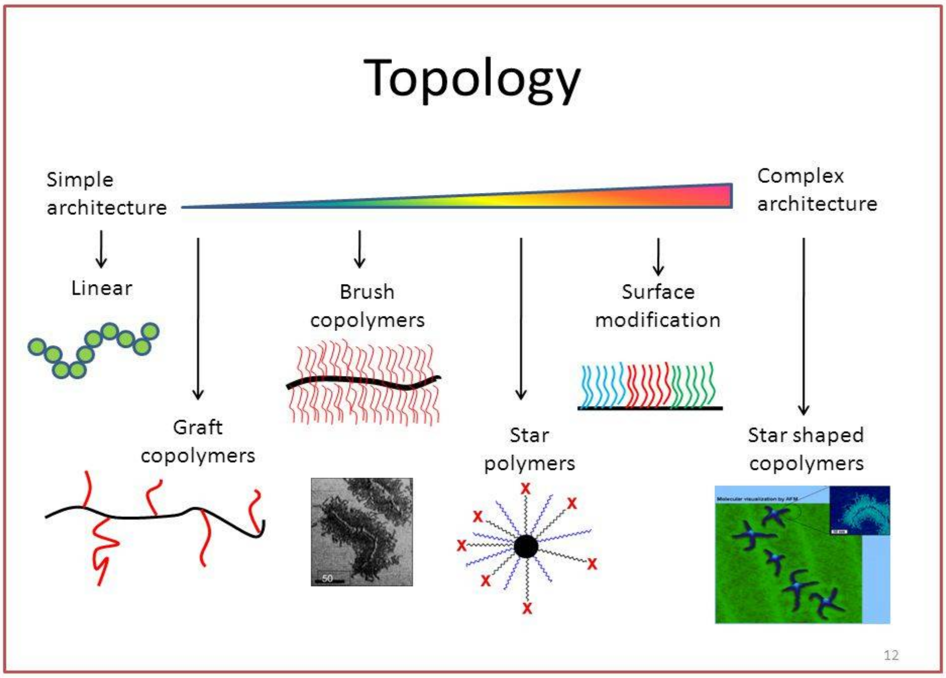
Molecular weight of the polymer can be determined using GPC. Characterisation and structure elucidation can be analysed by UV, FT-IR and NMR spectroscopy. Surface morphology is studied using SEM and DSC. The thermal and mechanical properties of the polymer can be measured using TGA, DTA, DMA and the bio degradability of the polymers can be tested using ASDM and strum test.

Scheme 10.SEM of Polymer Networks and Gels



Source: www.imc.cas.cz

Scheme 11.Topology of polymer



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RECYCLABLE POLYMERS

Currently available polymers are mostly non bio degradable and so affect the eco system. In order to protect the nature most of the countries are recycling the used polymers.

Scheme 12.Recycling Codes for polymeric Materials in the United States

Number	Abbreviation	Polymer
1	PET or PETE	Polyethylene Terephthalate
2	HDPE	High-density Polyethylene
3	V or PVC	Polyvinyl Chloride
4	LDPE	Low-density Polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	Polycarbonate

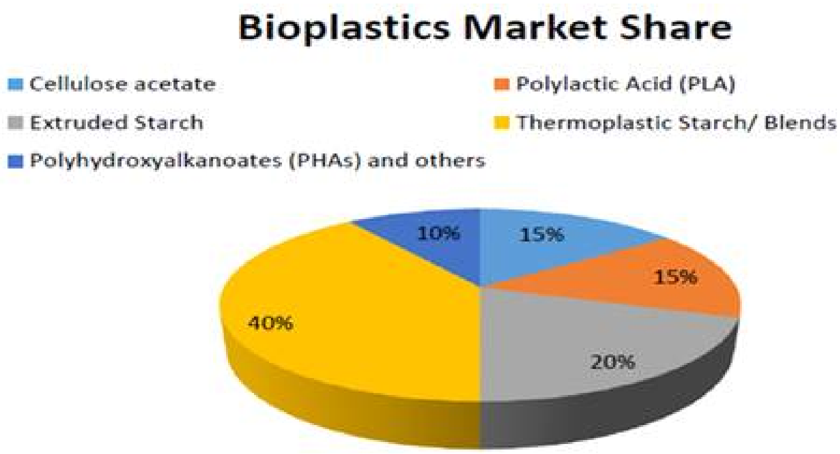
BIODEGRADATION

Polymer degradation can be considered as a number of processes, such as physical disintegration, chemical reaction resulting small molecules and degradation by biological mechanisms. Only polymers that can degrade in nontoxic by products without causing environmental pollutions can be called biodegradable polymers.

DE MERITS

Over usage of edible oil may affect the food chain. The over production of non edible plant oils and the impact of additional pesticides, fertilizers, and the cultivation of more land is detrimental enough to outweigh the benefits of biodegradable plastics have a negative impact on the environment. This has spurred research into a number of possible alternative materials including waste wood pulp and wood pieces from paper mills (Bendale, 2018).

Scheme 13.Bioplastics Market Share



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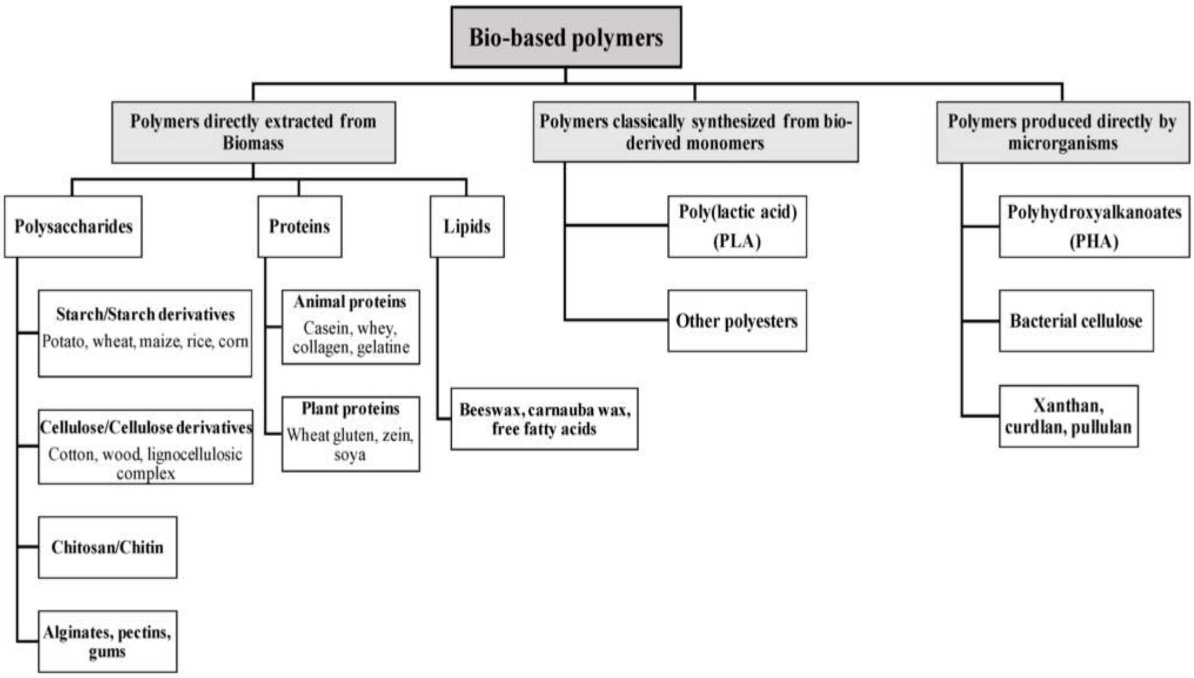
APPLICATIONS

Polymers are having potential applications in the field of medicine and agriculture like PSA-Pressure Sensitive Adhesive, agricultural mulch, anti bacterial sensors in medical devices, bio plastics, lubricants, bio fuel, paint and varnishes decorative, industrial laminates, electrical insulating, encapsulating materials, pesticides, wax compounding adhesives, lacquers, Foundry resins, fungicides, biomaterials, anti termite treatment of timber. Some typical applications of plastics include packaging, textiles, coatings, automobile components, biomedical devices and household items (Farmer, 2015; Belgacem, 2008). Our dependence on plastics keeps increasing, but the fossil fuel is depleting. It is proposed that all petroleum resources will be exhausted within the next one hundred years (Liu et al., 2014).With the rapidly growing market of flexible electronics and sensors, there is a pressure to move toward environmentally friendly products and biomedical materials (self-healing properties) for health monitoring applications (Hong, et al, 2012; Eissen, 2002).

BIO-BASED POLYMERS IN MEDICINE

Natural polymers are becoming increasingly important in the field of tissue engineering. Marine-derived natural polymers have been used for the development of suitable biocompatible composite scaffolds for use in bone tissue regeneration. They are composed of bioactive compounds as well as biorestorable materials, which can mimic the natural function of bone and activate *in vivo* mechanisms for bone regeneration.

Scheme 10.Classification of Bio-based polymers



Source: www.mdpi.com

CONCLUSION

The future of polymer depends on renewable resources especially vegetable oils. Which is non toxic, easily available, low cost, ability to undergo versatile organic reactions and easily biodegradable. The majority of the biodegradable materials presently available on the market are based on natural polymers, for example, collagen and synthetic polymers such as poly (esters). Advances in synthetic organic chemistry and novel bioprocesses are utilized for the improvement of a wide scope of novel polymeric materials as the possibility of creating transient embeds and medication delivery vehicles. The accomplishment of the biodegradable nature of the polymers can be specially craft or change existing biomaterials to accomplish suitable biocompatibility, degradation, and physical properties to inspire ideal biological responses.

Different functionality and the chain length make the oil to show potential properties. Because of the highly hydrophobic nature of triglyceride molecules, the development of waterborne polymeric materials (latexes in particular) from plant oils has been challenging. Other than that plant oil based polymers are the sustainable feedstock of future plastics. Novel polymer materials are expected in future.

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