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The use of renewable feedstock in UV-curable materials – A new age for polymers and green chemistry

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ABSTRACT

This review aims to cover the state of the art of renewable feedstock use in materials production using photopolymerization processes. This area of investigation is an emerging field of research, and it combines biosourced molecules with a cheap and rapid radiative processing method that avoids any emission of volatile organic compounds. The main classes of naturally occurring molecules and macromolecules such as lipids, amino acids, carbohydrates, polyenes, etc. are detailed. The way they are used or integrated in photopolymerizable systems are described in relation to their applications: coatings, biomaterials, biodegradable drug delivery systems, microelectronics or optoelectronics. This critical review takes into account the reactivity of the various compounds as well as their cytotoxicity, biodegradability and finally their end uses.

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Abbreviations: 5-CAGA, 5-ring membered cyclic acetalglycerin acrylate; 6-CAGA, 6-ring membered cyclic acetalglycerin acrylate; AEMA, Aminoethylmethacrylate; API, Acrylatedpolyisoprene; BMA, *n*-butyl methacrylate; CCCA, Cyclic carbonate carbamateacrylate; DAAm, *N,N*-dimethylacrylamide; DMAc, Dimethylacetamide; DMAP, N,N-dimethylamino pyridine; DMF, Dimethylformamide; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DMSO, Dimethylsulfoxide; DS, Substitution degree; ECLO, Epoxidized cyclohexene-derivatized linseed oil; ECM, Extracellular matrix; EDC, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimidehydrochloride; ENLO, Epoxynorbornene linseed oil; EO, Epoxidized oil; EPI, Epoxypolyisoprene; ESBO, Epoxidized soybean oil; ESO, Epoxidized sunflower oil; F, Phenylalanine; GCA, Glycerin carbonateacrylate; GMA, Glycidyl methacrylate; HA, Hyaluronic acid; HBA, Hyperbranched acrylate; HEMA, 2-hydroxyethyl methacrylate; HMPP, 2-hydroxy-2-methylphenyl-1-propanone (Darocur® 1173); hMSC, Human mesenchymal stem cells; HPN, Hybrid polymer network; I, Isoleucine; iBMA, Isobutyl methacrylate; IEMA, 2-isocyanatoethylmethacrylate; IPN, Interpenetrating polymer network; K, Lysine; L, Leucine; LbL, Layer by layer; LCST, Low critical solution temperature; LMOGs, Low molecular weight organogelators; LO, Linseed oil; M, Methionine; MA, Methacrylic anhydride; MAG, Monoacylglycerol (monoglyceride); MDI, Methylene bis(4-phenylisocyanate); MMA, Methyl methacrylate; NELO, Norbornenylepoxidized linseed oil; NHS, *N*-hydroxysuccinimide; NIPAAm, *N*-isopropylacrylamide; NMA, *N*-methylolacrylamide; NMP, *N*-methyl-2-pyrrolidone; NR, Natural rubber; NVP, 1-vinyl-2-pyrrolidinone; PBS, Phosphate buffer solution; PDMS, Polydimethylsiloxane; PEG, Poly(ethylene glycol); PEGDA, Polyethylene glycol diacrylate; PI, Polyisoprene; PLLA, Poly(L-lactide); PNIPAAm, Poly(*N*-isopropylacrylamide); PUR, Polyurethane; RAFT, Reversible addition-fragmentation chain transfer polymerization; SA, Succinic anhydride; SBO, Soybean oil; SIPN, Semi-interpenetrating polymer network; SMCs, Smooth muscle cells; SolA, Solketalacrylate; T, Threonine; TAG, Triacylglycerol (triglyceride); TDI, Toluene diisocyanate; TEC, Thiol-ene coupling; TEOS, Tetraethylorthosilicate; TPGDA, Tripropylene glycol diacrylate; V, Valine; VA-086, 2,2′-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide]; VAPG, Valine-alanine-proline-glycine; W, Tryptophan.

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1. Introduction

The increasing number of research studies devoted to the development of biosource-based materials reveals the great potential of renewable raw molecules and their ability to substitute for petrochemical-based materials. The construction of biorefineries and the availability of molecules such as glycerin derived from biodiesel production are a great evolution of the chemical industry. Until now, only a few examples of biosourced polymers have been available, and the famous polyamide 11 is synthesized from castor oil, a vegetable oil also used in the preparation of polyurethanes. In recent years, there has been a real explosion in the number of studies on the development of materials derived from biomass. Typical monomers such as acrylic acid, epichlorohydrin and acrylonitrile can be now produced from biosourced feedstock. The industrial production of "green" polyethylene in Brazil proves that this is not just a trend but a "mutation" in polymer chemistry. Moreover, this industrial revolution should enable agricultural revitalization in certain countries, thanks to the added value of agricultural products.

This mutation, which started one decade ago, must be followed by a real strategy concerning the economic constraints of this approach. The best example addresses the peculiar case of lipids, which are currently used for human and animal food and have recently been employed in the production of biodiesel. This continuous growth of lipochemistry activities will promote competition among the different end uses of vegetable oils (in some countries, mainly human nutrition).

Nevertheless, some non-edible oil species may be a non-competitive alternative to this situation. Other biomass deposits, such as algae, lignins, celluloses, polysaccharides and vegetable proteins, are easily affordable precursors of carbon with unlimited deposits and very easy access thanks to worldwide production. These carbon sources can be extracted from some industrial by-products and wastes (wood, wood pulp, starch, etc.) whose actual valorization is not secured. Developments based on these by-products will undoubtedly be of great interest because they are not competing with raw materials devoted to nutrition. Biosourced materials are rarely used just after harvest or extraction and often need preliminary treatments (purification, chemical or enzymatic modifications, etc.) to access reagents usable in the elaboration of polymers and polymeric materials. Linseed oil is a rare oil variety that can be used in its native form, as its polymerization occurs under oxygen and UV irradiation without any preliminary modification.

To modify biosourced raw materials to make them usable as reagents in material production will be the great challenge for chemical engineering and biotechnologies during the next decades. Some recent promising results open the way in the field of vegetable oil modification (epoxidation) and enzymatic degradation of starch to produce various monomers (succinic acid, glycolic acid, etc.).

The use and purification of biomass can be satisfying if environmentally friendly processes limiting the production of wastes and the emission of volatile organic compounds (V.O.C.) are involved. In the same way, materials processing should require low temperature and energy-efficient processes. For instance, UV radiation is a simple and convenient form of energy and does not require expensive devices. Thanks to its high output, this special polymer processing method is enjoying a new expansion and is applied at the industrial scale for inks, curable resins and also in various high-added-value products such as liquid crystal polymers and non linear optics. Liquid resins can be converted into solid resins in a few tenths of a second, making this process very attractive to the scientific community for the past three decades. The