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Acrylation of biomass: A review of synthesis process: Know-how and future application directions

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Abstract

Over the years, eco-friendly raw biomass is being investigated to develop novel green monomer and oligomer components for sustainable polymer materials synthesis. The use of naturally obtained biomass can reduce the dependence on petrochemical suppliers and the impact of petroleum prices. Polymer materials obtained from biomass are a competitive alternative comparing with those made from petrochemicals. Domestically and industrially used vegetable oil derivatives are considered widely available, while cellulose derivatives are the most abundant natural polymers. Biobased acrylic polymers developed from vegetable oils and cellulose are very popular nowadays. Using acrylic derivatives of vegetable oils and cellulose as naturally obtained materials leads to long-lasting biopolymers with a wide range of high exploitation properties and applications. The characteristics of vegetable oil- and cellulose-based acrylate resins of high-biorenewable carbon content are suitable for industrial application, while their role is still underestimated. A brief analysis of biomass-derived biopolymer resin compositions, properties, and applications is critically outlined herein.

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Keywords

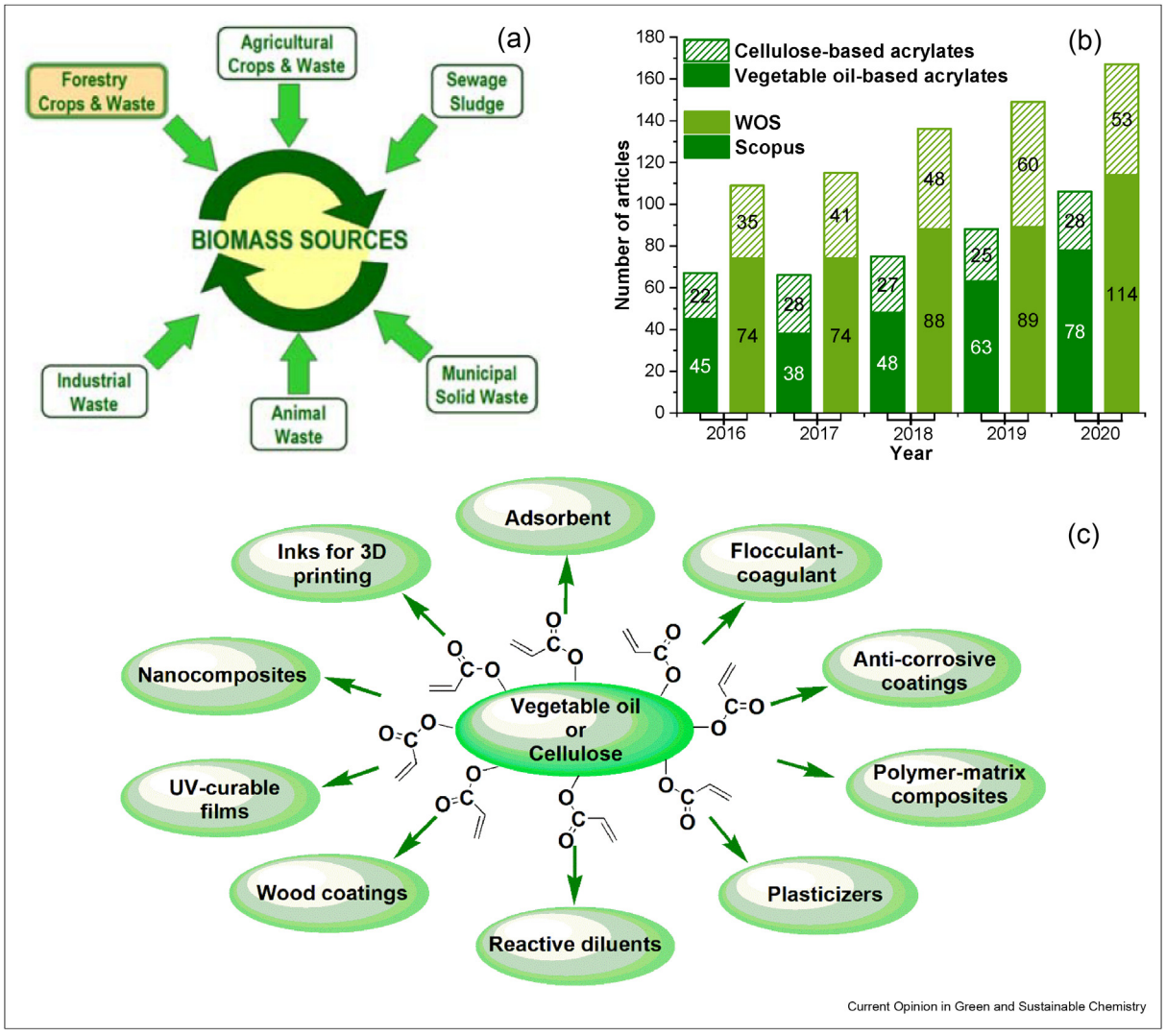
Acrylate bio monomer, Vegetable oil, Cellulose, Polymerization.

Literature analysis of acrylated biomass derivatives

The number of applications of diverse polymeric materials continues to increase. The common polymers and polymer composites are derived from petroleum reserves, meaning an alternative source for these materials is still demanded [1,64]. To overcome the drawbacks of petroleum-based polymers, renewable bio-based resources, for example, biomass, have begun to attract much attention. Figure 1 (A) from M. E. Fortuna et al. article lists the most relevant biomass sources are "forestry, agricultural, industrial, animal and municipal solid waste and sewage sludge," which ensure vast availability of the biomass [2]. Due to their broad availability and modification possibilities, the biomass of cellulose and natural oils from forestry and agricultural crops are of extra interest for the reviewed acrylation process. Cellulose is the most abundant biological macromolecule found in plants, marine animals, fungi, and algae, where it acts as the structural component in cell walls [65,66]. Mainly cellulose consists of D-anhydroglucopyranose ($C_6H_{11}O_5$) linear, chemically polar chains with β-(1, 4)-glycosidic bonds, with polymerization of approximately 10,000. Although cellulose has been widely used in polymer acrylate matrix primarily as a reinforcing filler without additional modification [3], developing more sustainable cellulose-based biomaterial products requires novel ways to modify this renewable biomass. Vegetable oils are mainly triacylglycerols (92%–98%); the number of carbon atoms, double bonds (unsaturation), and functional groups differ in fatty acids. The consumption of seed oils has increased where saturated palmitic acid (16:0), stearic acid (18:0), monounsaturated oleic acid (18:1), the polyunsaturated linoleic (18:2) and α-linolenic (18:3) acids (x:y stands for chain carbon atoms: number of unsaturation) are the most used ones. The active groups in triacylglycerols are double bonds, allylic carbons, ester groups, and alpha to the ester group. The reactivity of various groups in the long chains is relatively low [4,**5].

An intensive investigation has also been performed to develop sustainable polymer materials from vegetable oils in the last decade, considering the growing price of petroleum-based resources and environmental contamination [6]. Moreover, methods for obtaining polymers from vegetable oils meet the principles of "green chemistry," such as design for degradation, pollution prevention, energy efficiency, and use of renewable feedstocks [7]. Using newly formed vegetable oils resins, biopolymers with a wide range of improved physical performance have been developed [8]. Photo-induced polymerization initiation triggered by light

Figure 1



The most relevant sources of biomass **(a)** [2], the number of articles reporting biobased acrylic polymers from 2016 to 2020 **(b)**, application of vegetable oil- and cellulose-based polymers containing acrylate functionality **(c)**.

radiation occurs too slowly for the neat vegetable oils, and it is not suitable for commercial application to obtain any polymer materials. For this aim, the oils are being modified, introducing more active functional groups [9] and some formulations with more reactive comonomers are also investigated [10*]. Modified vegetable oils can undergo radical polymerization, although polymerization can also occur via an ionic mechanism [7,11–13]. Acrylates and methacrylates are among the most reactive monomers suitable for UV-initiated photopolymerization [7,12,13]. Furthermore, acrylation or similar functionalization reactions are the most common means to introduce polymerizable groups to the vegetable oils molecules [14,*15].

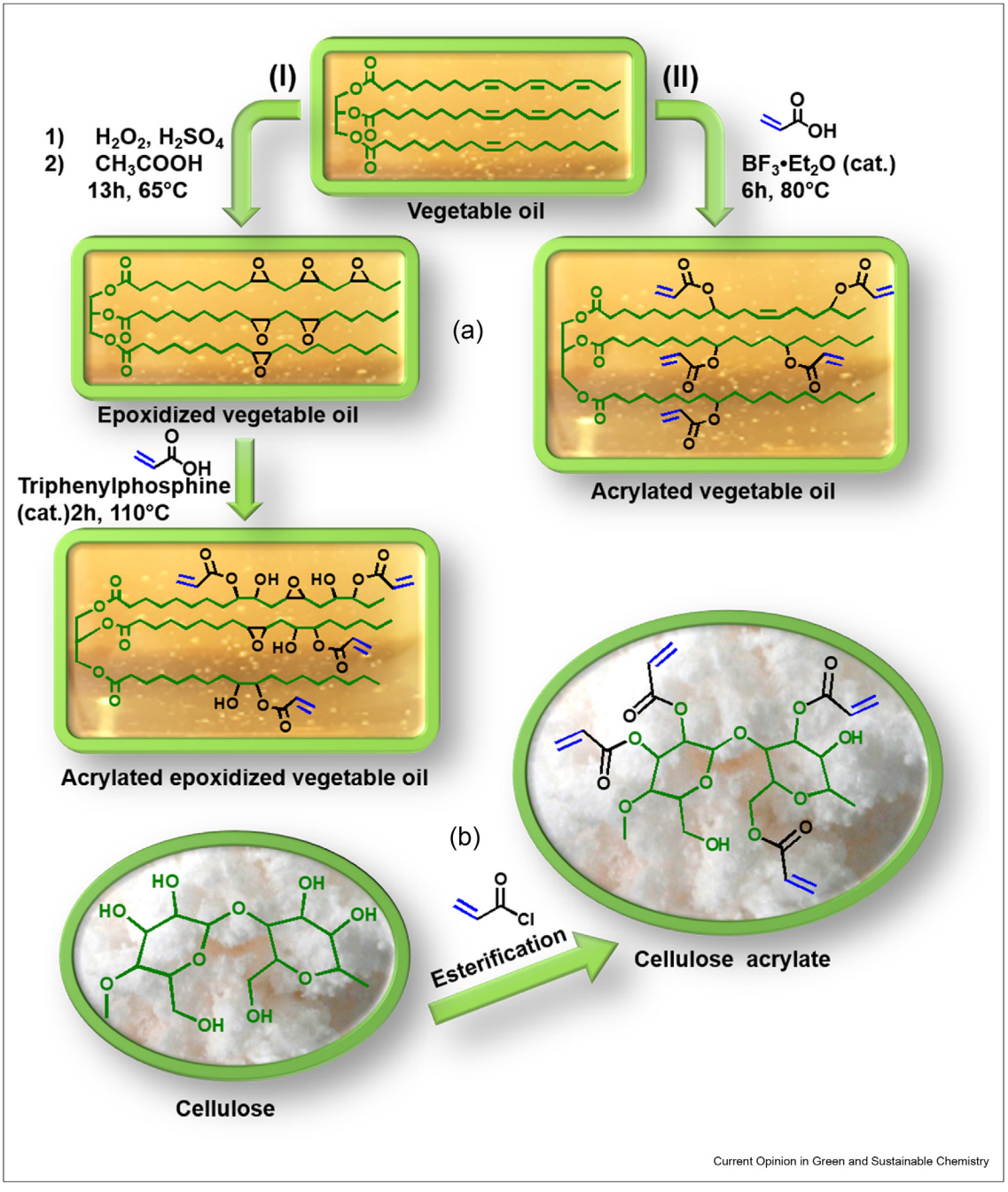
The number of articles reported from Scopus (Elsevier) and Web of Science (Clarivate Analytics) indexing databases of vegetable oil and cellulose acrylate polymer is represented in Figure 1 (B) (August 2021). The keywords used in the search were “cellulose, acrylate, polymer” for cellulose-based acrylates and “oil, acrylate, polymer” for vegetable oil-based acrylates. Nevertheless, the number of articles in 2016 reporting vegetable oil-based acrylic polymers and their derivatives are only 45 and 74 from Scopus and WOS databases, respectively, which mostly describe acrylated epoxidized soybean oil (AESO) and castor oil (CO) derivatives. In contrast, cellulose-based acrylic polymers are about 22 and 35, including acrylate-grafted cellulose. The total number of

publications tends to increase every year, 2020 showed that the absolute number of publications doubled.

Biomass acrylation and formulation

Figure 2 (A) (I) shows that acrylation of vegetable oils usually proceeds via a two-step process: (1) epoxidation of double bonds [16], followed by (2) oxirane ring-opening that has been extensively reported by the reaction of methacrylic acid with epoxidized soybean oil, linseed oil [17], sucrose soyate [18], etc. Lately, different vegetable oil-based acrylate prepolymers were obtained using one-step synthesis Figure 2 (A) (II) through the acrylation of vegetable oil with acrylic acid under the catalysis of $BF_3 \cdot Et_2O$, including palm, olive, peanut, rapeseed, corn, canola, and grapeseed oils [19**]. The advantages of the reaction are simple operation, mild

Figure 2



Vegetable oil acrylation via two-step (I) and one-step (II) synthesis methods **(a)**, cellulose acrylation via esterification **(b)**.

Table 1

Characterization of biopolymers derived from vegetable oils containing acrylate entities.

Acrylate bio-sourced	Composition	Tensile strength (MPa)	Elongation at break	Thermal properties, °C	$T_{degradation}$, °C	T_g, °C	E'_{25} (MPa) (storage modulus at RT)	Application function	Ref.
Cardanol oil	Adding 95% cardanol oil acrylate to AESO led to:	Increase from 1.66 to 11.13	Decrease from 7.92% to 5.06%	T_{max} changed from 363.4 to 337.8 and 445.2	$T_{5\%}$ increase from 229.8 to 275.0	Increase from 25.0 to 58.7	Increase from 146.7 to 460.7	UV-curable reactive diluent	[25]
	Adding 30% cardinal acrylate to castor oil-based polyurethane acrylate led to:	A decrease from 10.4 to 5.3	Decrease from 10.2 to 25.3	–	–	Increase from 2.1 to 22.4	Increase from 34.9 to 73.5		[26]
Castor oil	Adding 40% castor oil acrylate to AESO led to:	An increase from 3.2 to 5.9	–	–	$T_{5\%}$ increase from 311.9 to 312.2	Increase from 12.9 to 15.6	Increase from 77.4 to 262	UV-curable reactive diluent	[28]
	Polyurethane acrylate oligomer based on castor oil	–	–	–	–	65.6	–	A degradable ingredient	[29]
	Adding 60% of castor oil acrylate to bifunctional aliphatic polyurethane acrylate led to:	An increase from 1.7 to 6.1	Decrease from 25.8 to 7.0	Decrease from 426.7 to 407.6	$T_{5\%}$ decrease from 223.3 to 216.3	A rise from −14.7 to 0.1	–	Crosslinking agent in UV-curable materials	[30]
Acrylated epoxidized soybean oil	AESO:isobornyl methacrylate (60:40)	257.2	8.5	-	$T_{10\%}$ = 308	60.8	13.63	Crosslinking agent in UV-curable resin	[33]
	AESO: methacrylic ester (70:30)	19.0	12.8	-	$T_{10\%}$ = 353	24.3	9.67		[33]
	AESO: tetrahydrofurfuryl acrylate (70:30)	24.4	10.5	-	$T_{10\%}$ = 345	4.6	10.44		[33]
	AESO: tetrahydrofurfuryl methacrylate (70:30)	110.2	16.1	-	$T_{10\%}$ = 351	43.7	13.34		[33]
	AESO:2-hydroxyethyl acrylate (20:80)	17.91	–	–	–	–	–	Biocompatibility and crosslinking agent in 3D printing ink	[35]
Linseed oil	Increasing linseed oil acrylate (from 30% to 70%) and decreasing reactive diluent (from 40% to 0%) led to:	Decrease from 13.62 to 6.54	Decrease from 3.76 to 9.	–	$T_{10\%}$ decrease from 307.8 to 275.8	Decrease from 78.9 to 54.7	Decrease from 722.4 to 370.2	Crosslinking agent in UV-curable materials	[36]
Sesame oil	Adding 50% of the total mass of sesame oil acrylate to maleated castor oil led to:	–	–	T_{peak} increase from 402 to 409	$T_{10\%}$ increase from 326.0 to 341.2	An increase from 71 to 73	–	Crosslinking agent in thermosets	[37]

conditions and atom economy. Mudri et al. used multiple step approach for Jatropha oil-based polyurhane acrylate synthesis [20]. Jatropha oil was initially epoxidized and hydroxylized, followed by isocyanation step with isophorone diisocyanate and 2,4-toluene diisocyanate, with and without dibutyltin dilaurate catalyst respectively, to obtain Jatropha oil-based polyurethane acrylates. Pengsong et al. have went even further with green synthesis approach and developed one-pot and solvent-free synthesis [21]. Castor oil-based polyurethane acrylic resin was synthesized from castor oil, isophorone diisocyanate, hydroxyethyl acrylate and isobornyl acrylate. The synthesis involved two steps, each only 3 h and mild conditions where temperature did not exceed 78 °C.

Acryloyl chloride is a popular reagent to obtain cellulose with acrylate entities, as shown in Figure 2 (B). The vinyl groups can be introduced via esterification between acryloyl chloride and hydroxyl groups of the cotton and jute cellulosic fibers [22*]. Commonly, partly acrylation reaction conversion is received. The isocyanate is proposed to substitute the residual hydroxyl groups of cellulose, obtaining the cellulose esters [23]. Most recently Chen et al. used three step synthesys where through oxidized hydroxypropyl cellulose esterification Ox-HPC methacrylate ester was obtained [24]. Ox-HPC methacrylate ester maintained previous hydrogel printability properties and showed promise in 3D printing, photo-patterning, and tissue engineering. Functionally important acrylic entities that are incorporated in cellulose are summarized in Table 2. The primary application of the modified cellulose is the filler for polymer biocomposites but new prospects in 3D printing are emerging.

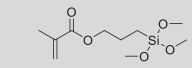
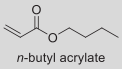
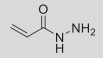
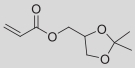
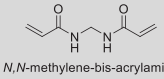
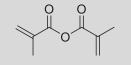
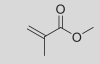
Different vegetable oils containing acrylate entities have been investigated and summarized in Table 1 to adjust the physical properties demanded on the material end application. UV-curable cardanol oil acrylate demonstrated the best reactive diluent properties compared with petroleum-based acrylic monomers [25]. Reactive diluent cardinal acrylate was also used in castor oil-based polyurethane resins, improving bio-based content and reducing volumetric shrinkage [26]. Castor oil is a hydroxyl-containing trifunctional vegetable oil that is easily converted into an acrylate derivative. In the 2020 L. Meng et al. study [27], castor oil-based acrylate was used to prepare a polymer network with covalent connections with the SiO_2 network. The novel hybrid system is considered an excellent wood coating, decreasing elongation at break from 301% to 32%. A more complicated two-step method was used to create a polyfunctional castor oil-based acrylate monomer to replace petroleum-based monomers in UV-curable coatings. Castor oil acrylate showed improved adhesion, better compatibility with acrylated epoxidized soybean oil (AESO) prepolymer and inhibited volumetric shrinkage than petroleum-based monomer [28]. Castor oil acrylate affected glass transition temperature (T_g) for urethane acrylate/ZnO nanocomposite material reaching T_g up to 70 °C [29]. Good compatibility was achieved between castor oil-based hyper-branched acrylate as a reactive diluent, polyurethane acrylate, and acrylic monomer. At the same time, the coatings were exposed to acidic and alkaline media. The highest chemical resistance was achieved using 40% castor oil-based acrylate, with only 2% weight loss after contact with NaOH [30].

AESO has attracted considerable interest in polymer materials for many years; there is no wonder that its commercial form is available under the trademark *Ebecryl 860* [31]. Such AESO-based polymers offer a competitive solution to replace petroleum-derived polymeric materials in the polymer industry. Mechanical characteristics of AESO polymer prepared by molding stereolithography (SLA) and digital light processing methods (DLP) have been evaluated and compared with commercial 3D printing resin [31,32]. The synthesized polymers exhibited thermal decomposition temperature at the weight loss of 10% above 300 °C and showed very high-tensile strength values. Interestingly, two similar polymeric resins, methacrylic ester AESO and tetrahydro furfuryl acrylate AESO, with the most deficient mechanical properties, also showed the highest biodegradability [33]. AESO-based UV-curable waterborne polyurethane pigment print adhesive is proposed for the textile industry considering the surprising increase of water absorption with the higher AESO content in the resin [34]. Nanocomposite containing AESO blended with 2-hydroxyethyl acrylate has excellent biocompatibility for bone tissue engineering applications [35].

Acrylated linseed oil resin was found suitable processing properties and a viscosity of 803 mPa s. As described before, the 2.5-functional acryl groups were introduced in the fatty acid molecules by one-step method [36]. Novel vegetable oil-based miscible thermoset acrylate blends were made using sesame oil-derived acrylate. A conclusive comparison of the obtained products was evaluated by sustainability, preparative and performance factors, showing renewable sources as a good alternative for petroleum-based materials [37]. On the other hand, jatropha oil as a non-edible oil suits its use in non-food industries, potentially using an anti-corrosive coating. Cured jatropha oil-based epoxy acrylate resins filled with ZnO nanoparticles showed high resistance toward the corrosive environment. It was carried out by salt spray test in 5-wt% NaCl solution for 792 h. Moreover, incorporating ZnO revealed any effects on the decomposition of polymer resin formulation [38].

Table 2

Functions and parameters of polymer materials derived from cellulose containing acrylate entities.

Acrylate entities in cellulose	The function of incorporated acrylate entities in cellulose	Parameters	Application	Ref.
 γ-methacryloxypropyl trimethoxysilane	To obtain better dispersibility and hydrophobicity	High surface tension Thermal stability Low viscosity (16.2–29.7 mPa s) Good acid/alkali resistance Oil and water repellency	Paper cultural relic protective coatings	[39]
 *n*-butyl acrylate	To increase the hydrophobicity and flexibility of macromolecule	Optimum adsorption parameters: pH: 5; contact time: 360 min, adsorbent dosage: 4 g/100 mL and initial metal ion concentration: 125 mg/L	Adsorbent for removal of Pb(II) from wastewater	[40]
 hydrazidoacrylate	To provide strong electrostatic, hydrogen bonding and chelating interactions	The maximum adsorption capacity of 457.6 at 25 °C	Adsorbent for removal of Cr(VI) from wastewater	[41]
 solketal acrylate	To improve the moisture absorption properties	Increase of hydrophilic characteristics	For dryness applications	[42]
 *N,N*-methylene-bis-acrylamide  acrylic acid	To enhance degradation of the copolymer Serves as macro-radical receptor	Water absorbency in distilled water - 165 g/g (Hydrogel swelled in distilled water up to 165 times its dry weight)	Biodegradable hydrogel composites. Agricultural applications – to form a slow-release fertilizer and soil conditioning	[43]
 acrylamide	To enhance solubility in water To improve the ability of flocculation of cellulose to remove turbidity of cationic colloidal systems and removal of heavy metal ions	Flocculating capacity to heavy metals ions removal ($qeCu^{2+}$ = 400 mg/g) and to cationic colloidal systems clarification (99% to $Fe(OH)_3$) at pH 7. High negative charge density (–50 mV)	As a heavy metal ion flocculant and cationic colloidal systems clarifying agent. Ecofriendly, low-cost, non-toxic, and water-soluble flocculant-coagulant in water treatment at the industrial level	[44]
 acryloyl chloride	To provide three-dimensional crosslinked networks, thereby inhibiting melt dripping	Cellulose acrylate char yield increase from 0 to 20–30% compared to cellulose	Halogen-free, anti-dripping, easy-to-process, flame-retardant and transparent coating for protecting flammable materials from fire (such as books, buildings, furniture)	[45]
 methacrylic anhydride	To incorporate photocurable functional groups	Degree of substitution = 0.6, (25% of the hydroxyl groups present in the CMC were e grafted with a methacrylic group) Gel point (from photorheology) in less than 2 s	Bio-based photocurable hydrogel ink for light-assisted 3D printing technology. Biomedical application field	[*46]
 methyl methacrylate	To improve mechanical and thermal properties of 3D SLA, printed resin	Increase of tensile strength to 38.3 MPa Increase of tensile modulus to 3.07 MPa	Polymer engineering. 3D SLA printing technique	[47]

Applications of acrylated biomass

Modified vegetable oil and cellulose applications includes adhesives [48], polymers [8], inks [49], nanocomposites matrix [50] and coatings [51] (Figure 1 (C)). The main advantages of these resources for polymeric materials are low costs and sustainability aspects—low ecotoxicity and low hazardous to humans [52*]. Commonly oil component develops a polymer matrix, while cellulose is applied as a reinforcing filler [50]. While, the modified cellulose can also be the matrix

itself containing nanofillers [46]. Wood protective modified vegetable oil coatings are being developed for physicochemical and fungal resistance. Linseed oil acrylate has high—wood-bonding adhesive strength but lower self-bonding cohesive strength [53]. Shear strength and adhesive bonds strongly depend on wood type, considering cellulose and hemicellulose percentage, stiffness and wood porosity. Wood adhesive from acrylated linseed oil could be used in exterior grade material due to its resistance to water [48].

Other types of biomass like aliphatic biomass used in the acrylation process include renewable glycidyl methacrylate, succinic acid and itaconic acid. They produce materials of high-tensile strength of 31—45 MPa and glass transition temperature of 140—183 °C from glycidyl methacrylate/succinic acid and glycidyl methacrylate/itaconic acid, respectively [54]. Liu et al. used acrylic acid as a grafting monomer for corn starch biobased backbone. Gel-like starch-g-poly(acrylic acid) superabsorbent polymer with urea obtained in one-step synthesis absorbed water 2704 times its own dry weight in distilled water [55]. A perspective acrylate from nonedible lignocellulosic biomass was obtained through enzyme-catalyzed transglycosylation. Saccharide acrylate was synthesized from cotton and after reaction two products were detected—the primary product 2-(β-glucosyloxy)-ethyl acrylate and the minor product 2-(β-xylosyloxy)-ethyl acrylate [56]. 2-octyl acrylate and isobornyl methacrylate monomers were derived from castor oil and pine resin respectively, containing biobased content of about 70%. These new waterborne pressure-sensitive adhesives were made via environmentally friendly free-radical emulsion polymerization. The presence of isobornyl methacrylate significantly increased shear resistance and work of adhesion [57].

As acrylic functional groups are incorporated into cellulose molecules to obtain light reactivity properties and meet many applications. These monomers, oligomers, and polymer resins are widely applied due to their excellent ability to cure under ultraviolet (UV) and visible (VIS) lights by creating stable chemical crosslinks. UV-curable resin research and commercial application have expanded rapidly due to their advantages over traditional solvent evaporation and thermal two-component hardening methods, including very rapid curing, high-cost performance, energy-saving and friendliness to the environment [58].

Cellulose acrylate derivatives have found some applications to coat pharmaceutical dosage forms in textile, construction, electronic and automotive industries (Table 2) [*46]. Derived cellulose crosslinking has been widely investigated and reported since 1961 and is highly important for progress in new material formulations [59]. Qian et al. extensively researched a novel solid—solid phase-changing material from cellulose acrylate and poly(*n*-alkyl acrylate) [60]. Synthesized material melting enthalpies and transition temperatures were sensitive to the molecular weight of the components, thus opening possibilities to tune for good thermal and shape stability. UV-curable formulations for coating application containing modified cellulose and AESO were prepared by Auclair et al. [61], who proposed modification reaction with acryloyl chloride, using a 1-methylimidazole catalyst and 1,4-dioxane solvent. Cellulose modification positively affected the mechanical properties of the coatings.

He et al. wrote that hydroxyacrylate-melamine matrix mixed with 0.5 wt% CNC showed the hydrogen bonds formed in the interface, which improve application possibilities for corrosion resistance coatings [62]. Chen et al. reported a CNC—Br macroinitiator obtained grafting PMMA with cellulose, resulting in composite with increased strength, stiffness, mechanochemiluminiscent emission, and profound application in energy conversion [63].

Acrylates formulated on cardanol, castor, soybean, linseed, and sesame oils are proposed extensively in UV-curable resins. In contrast, cellulose acrylates find their application as fillers, sorbents and clarifying agents to remove heavy metal ions in water. Applying acrylates as an additive in polymer composites technology can enhance the overall thermal stability, chemical resistance, and mechanical properties of the material for a specific application.

Conclusions and remarks

2016—2020 literature analysis shows that the acrylic entities in vegetable oils primarily function as photocurable groups. Furthermore, fillers of cellulose-based acrylates can enormously enhance the developed biopolymers' hydrophobicity, mechanical, and thermal properties. However, despite the fact, that the end product of acrylation is obtained using biomass, the synthesis route primarily implies petroleum-based reagents, such as acryloyl chloride and acrylic acid. Almost all of those reagents and solvents used are far from being environmentally friendly and even present hazards for human health. Further investigations should focus on implementing and optimizing greener synthesis pathways for biomass acrylation, solving ecological and hazards concerns, for example, the enzymatic catalysis paths or more one-pot solvent free synthesis. The next-generation biomass synthetic conversion pathways could reach high-acrylation reaction conversions within mild process conditions and decrease commercial process costs and environmental impact.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could

have appeared to influence the work reported in this article.

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** of outstanding interest

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