



Review

Star-shaped lactic acid based systems and their thermosetting resins; synthesis, characterization, potential opportunities and drawbacks



Arash Jahandideh*, Kasiviswanathan Muthukumarappan

Agricultural and Biosystems Engineering Department, South Dakota State University, PO Box 2120, Brookings, SD 57007, USA

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ABSTRACT

Shortcomings of the conventional PLA synthesis methods have encouraged researchers to investigate on alternative methods for PLA synthesis. Utilization of chain extenders is an effective way to achieve high MW polymers. The concept of using star-shaped resins as the reinforced matrices for biocomposites or in biomedical applications is gaining more and more attention day by day. Star-shaped lactic acid based resins are a class of branched resins with a multifunctional core molecule and lactic acid branches. In order to increase the reactivity of branches, the star-shaped resin oligomers can get end-functionalized which yields in a crosslinkable product. Changing the architecture of a polymer from a linear to a multiarm or hyperbranched one, would change its chemical, diffusional and physical-mechanical properties. This review paper presents the current state and recent advances in the synthesis, characterization, properties and applications of the star-shaped resins made from lactic acid or lactide and multi-hydroxyl core molecules with a focus on the role of the architecture of the polymer on the properties of resins. Rheological, physiochemical and thermomechanical properties of to date synthesized star-shaped resins are compared and discussed. Special emphasis would be made on potential opportunities, probable applications and also gaps and drawbacks concerning these systems. This review aims to provide useful information to help future development of efficient, highly engineered bioresins which can be especially designed for certain applications.

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Abbreviations: LA, lactic acid; PLA, poly lactic acid; S-LA, star-shaped LA based resins; CP, condensation polymerization; ADC, azeotropic dehydration condensation; DP, direct polymerization; ROP, ring opening polymerization; EF, end-functionalization; NMR, Nuclear Magnetic Resonance; DMA, dynamic mechanical analysis; TGA, thermogravimetry analysis; MW, molecular weight; PLEG, poly lactic acid-ethylene glycol; PGA, poly glycolic acid; PEG, poly ethylene glycol; PENTA, pentaerythritol; IT, itaconic acid; MAAH, methacrylic anhydride; MAA, methacrylic acid; TEG, tetra (ethylene glycol); THMP, 1,1,1-tri(hydroxy methyl)propane; DPE, dipentaerythritol; DSC, differential scanning calorimetry; DEA, dielectric analysis; TAN, Total Acid Number; FT-IR, Fourier transform infrared spectroscopy; USDA, U.S. Department of Agriculture; E, modulus of elasticity; UTS, ultimate tensile strength; HRR, heat release rate; FDA, Food and Drug Administration.

* Corresponding author.

E-mail address: arash.jahandideh@sdstate.edu (A. Jahandideh).

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1. Introduction

Different studies have been published on the synthesis of resins from lactic acid (LA) or lactide and branching point molecules. In order to increase the MW of PLA and induce branching points in the structure, different techniques have been employed, including free-radical branching in the presence of epoxides [1], beam irradiation [2], copolymerization with cyclic monomers having hydroxyl groups in the cycle [3] or use of polyfunctional chain extenders. Generally, the star-shaped thermosetting resins are synthesized via a two-step strategy: poly-condensation of LA with the core molecule followed by end-functionalization of the branches. So far, star-shaped LA based resins (S-LA) are synthesized employing core molecules, including ethylene glycol, glycerol xylitol, and pentaerythritol for different applications. The employ of a core molecule in the structure of star-shaped polymers potentially changes the physiochemical properties of the polymer. Compared to linear polymers with the same MW, the star-shaped polymers provide smaller hydrodynamic radius and so, a lower solution viscosity. Star-shaped topology leads to a different chemistry and ease of formulation for various applications. For biomedical application, using a core molecule with adjustable functional groups at the center of the S-LA provides the unique opportunity of designing and controlling over properties of the product. In addition, changing the structure of the polymer from linear to star-shaped results in better control over the synthesis. It is also possible to change the biodegradation rate of the polymer by changing the ratio of the hydrophilic groups to the hydrophobic ones which results in an excellent control over the degradation rate and increase the control over the release of a certain component.

In addition, the core molecule provides reactive sites which can be further used for the addition of a special functional group, e.g. a flame retardant agent, an anti-microbial agent, etc. It is also possible to manipulate the properties of the cross-linked product by changing the nature and the portion of the block units of copolymers of LA and the core molecule. This manipulation could be in terms of changing the hydrophilicity or designing and altering the voids' sizes of the crosslinked polymer's network. For example, by employing longer oligomers, it is possible to increase the size of the microstructural voids in the network and by using hydrophilic monomers, the hydrophilicity of the network can be tailored. Manipulation of both void's size and the hydrophilicity will provide the unique opportunity for designing a polymeric matrix for certain component release or a desired drug delivery with a substantial control over release rate. The employ of multihydroxyl core molecules in the structure of crosslinkable S-LA polymers for biocomposite production has many advantages. A class of employed polyols (e.g. glycerol and xylitol) has biobased sources and are relatively inexpensive; therefore, employ of these molecules in the structure of S-LA reduces the final costs for the produced composites. This structure also provides a better extended network resulting in better thermomechanical properties of the cured resin. In addition, employ of these core

molecules lowers the viscosity of the final crosslinkable resins and enhances the resin's processability, which are of crucial factors in biocomposite manufacturing. Finally, it is believed that the unsaturated branches of the core molecule, increase the hydrophilicity of the produced resin. The higher hydrophilicity, makes the resin more compatible with inexpensive natural fibers and it eventually increases the mechanical properties and lowers the final costs of the biocomposites produced from natural fibers and S-LA thermosets.

Different methods have been introduced for synthesizing and characterizing the S-LA. The differences between the S-LA properties, resulted from employ of different core molecules, different lengths of the LA monomers (or co-polymers) in branches, utilization of different end-functionalization (EF) agents, employing different curing techniques as well as using different curing initiators. Choosing a combination of these factors results in a unique product with specific characteristics which could be suitable for a certain purpose. The concept of using star-shaped resins as the reinforced matrices for biocomposites or in biomedical applications is gaining more and more attention day by day. The increasing number of publications during the recent years, concerning the synthesis and characterization of star-shaped resins for different applications, including biocomposites [4–7], coating [8], biomedical [9,10], drug delivery [11–13], tissue engineering [14], smart packaging, functionalized polymers [15,16] and so on, reflects the growing importance of these new resins. To date, there is no comprehensive study exists on the different synthesis methods and characteristics of the synthesized S-LA.

This review paper presents the recent advances in the synthesis, characterization, properties and applications of S-LA and their thermosetting systems using a multi-hydroxyl clustering core molecule. The synthesis, chemical and thermomechanical properties of S-LAs are assessed. Special emphasis would be made on the potential opportunities, probable applications and also drawbacks concerning the use of the multi-hydroxyl core molecules in the structure of the S-LA. Finally, the limitations and technological gaps of these systems are highlighted. This paper will not address other branched LA based polymers, including dendritic [17], hyperbranched [18], grafted or comb-like polymers [19]; and also, the synthetic fiber reinforcements for bio composites are out of the scope of this paper. In addition, studies on fiber treatment for composite productions are excluded from this review article.

This review paper consisted of four different sections. In the first part, the synthesis of the S-LAs and linear PLA systems are explored. Different synthesis methods of PLA are discussed and currently applied multi-hydroxyl monomers as the core molecule for S-LAs are introduced. The role of EF and attributed methods of end-functionalizing of the branches as well as different methods for curing of the resins are emphasized. In the second part, the characterization of the S-LAs are discussed, including chemical characterization, general properties and thermomechanical properties. In chemical characterization, titration, nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR) of S-LAs are briefly discussed. Special emphasis are made on rheological properties of the star-shaped crosslinkable resins. The general properties section presents the current knowledge on water absorption properties and the biobased contents of the S-LAs. Finally, the thermomechanical properties of the cured resins are discussed based on the reported results of dynamic mechanical analysis (DMA), flexural and tensile analysis. The third part will discuss different applications of these systems, including biocomposites, drug delivery and tissue engineering. In the fourth part, the limitations and future of these systems are discussed.

2. Introduction to PLA synthesis methods

Lactic acid (2-hydroxy propionic acid) exists as the two stereo isomers of L-LA and D-LA, and can be produced via bacterial fermentation of carbohydrates or chemical synthesis. The LA produced by the chemical route is an optically inactive racemic mixture (50/50 L-D) while fermentation-derived LA exists almost exclusively as L-LA [20]. Due to the major limitations of chemical synthesis, the fermentation pathway is often preferred [21,22]. Poly lactic acid (PLA), an aliphatic polyester made up of the LA monomers, is a biodegradable and compostable thermoplastic, which has extensive applications in biomedical fields, including bone fixation, drug delivery and tissue engineering [23]. The applications of PLA are not limited to biomedical field and it has potential to be used in a wide range of applications, including food applications, packaging, furnishings, etc. [22,24].

Synthesis of PLA from LA can follow two different routes of polymerization, condensation polymerization (CP) of LA and polymerization through lactide formation (presented in Fig. 1) [22]. The condensation polymerization route includes direct condensation-polymerization of LA (see Fig. 1, Pathway A) and azeotropic dehydration condensation (ADC) of LA (see Fig. 1, Pathway B). Direct condensation polymerization can occur via melt condensation, interfacial polymerization, solid-phase (state) polycondensation or solution condensation. In the melt condensation, the polymerization occurs in long periods at temperatures about 10–20 °C higher than the resultant polymer's melting point and the consequent water is removed progressively at high temperatures and partial vacuum [22,25], in the interfacial polycondensation, polymerization occurs at the interface of the two immiscible aqueous solutions, and in the solid state condensation, polymerization proceeds at temperatures below the melting points [26,27]. In the solution polymerization method, esterification of monomers happens with the aid of solvents compatible with PLA [28].

The molecular weight of the condensation derived polymer is low, which results in poor mechanical properties [22,25]. In the ADC method, the azeotropic solution and catalysts are employed to produce a high molecular weight PLA. The azeotropic solution helps to reduce the distillation pressure and enables the separation of the PLA from the solvent. In general, PC methods require a good control over the reaction for achieving a PLA with desired MW, and water, as a byproduct of the condensation, must be efficiently removed from the solution for achieving a high MW PLA [29]. In the lactide formation pathway or

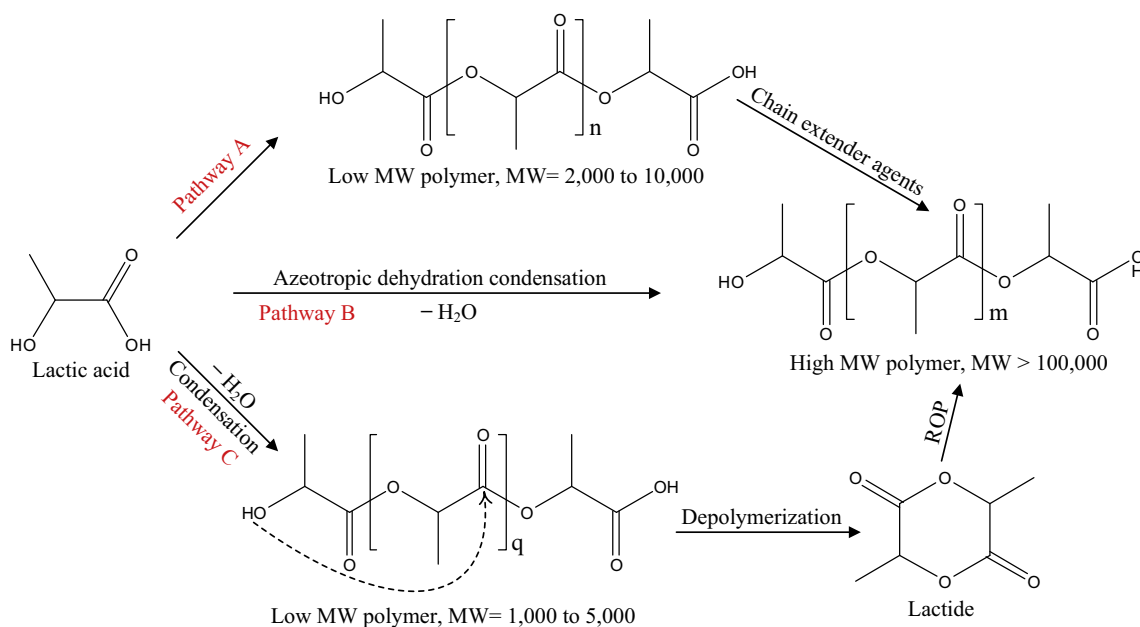


Fig. 1. Synthesis methods for high molecular weight PLA. Condensation/coupling (Pathway A), Azeotropic dehydration condensation (Pathway B) and Ring Opening Polymerization (ROP) of lactide (Pathway C) [25].

ring opening polymerization (ROP) (see Fig. 1, Pathway C), first LA is dimerized to lactide. Adding a proper catalyst at elevated temperatures under vacuum, the PLA is synthesized with relatively high MW. Reaction time, temperature, purity of lactide, control of the backbiting reactions, ring/chain equilibria and type of the employed catalysts are of key parameters in ROP method [30–32]. ROP is the common method currently employed for the synthesis of PLA in the industry. To date, ROP method is the most economically viable and technologically feasible synthesis pathway which yields a high MW PLA. However, the process is believed to be costly, rather slow and complicated and the MW of the produced PLA heavily depends on the type of the employed catalyst. In addition, this method is very sensitive to the presence of the lactide impurities which affects the chain growth by end-capping the LA oligomers and therefore, a rigorous lactide purification step is also required which impose substantial costs to the process [25,31,33–35].

2.1. Synthesis of the PLA by chain extension

In the melt polycondensation, LA is condensate polymerized to yield a low MW brittle glassy polymer. Presence of water, the high viscosity of the polymer's melt, the presence of impurities, low concentration of the reactive groups and occurrence of the unwanted “back biting” reactions which result in lactide formation are of reasons for achieving a low MW polymer [25,36]. Therefore, the resulted polymer is not suitable for any application without further utilization of the chain extenders which are employed to increase the MW of the polymer [25]. Azeotropic condensation-polymerization is also sensitive to the presence of impurities of the supplied LA. The impurities endcap the polymer and limit the chain growth and have a large effect on the MW of the final polymer. In addition, in the azeotropic condensation-polymerization, various diacids, diols or hydroxyl acids interfere with polymerization step and affect the purity of the produced polymer. Residual catalysts in the products is another drawback of this method [25].

On the other hand, the yield and efficiency of ROP method heavily depend on the type of the employed catalyst and the employed polymerization mechanism. Cationic [37], anionic [38] and coordination-insertion [25] are the three mechanisms of the catalytic reactions in the ROP, which are sensitive, complex and expensive [39]. Tin compound catalysts, e.g. tin (II) bis-2-ethylhexanoic acid ($C_{16}H_{30}O_4Sn$, referred to as tin octoate, stannous octoate, octoate or $Sn(Oct)_2$) are the most common catalysts used in the ROP method [40]. It is shown that the rate of chain growth varies greatly, depending on the presence of lactide impurities and also by formation of crystalline phase during polymerization. It is believed that the presence of impurities does not significantly affect the rate of polymerization, but it dramatically reduces the final MW of the polymer. However, carboxylic impurities have an inhibitory effect on the rate of polymerization as well, which could be due to deactivation of the catalyst by forming a complex. Substantial sensitivity of the ROP method to impurities, indicates that a rigorous purification of lactide is required beforehand in those processes which impose substantial costs to the process [25,34].

Shortcomings of the direct condensation methods and the complexity of ROP, encouraged researchers to investigate on alternative methods for PLA synthesis. Utilization of chain extenders is an effective way to achieve high MW polymers. Generally, chain extenders are multifunctional low MW chemicals which are attached to the low MW oligomer and link it into a

polymer with higher MW. The most common chain extenders for polyesters which contain –OH and –COOH groups include diisocyanates, diepoxides, bisoxazolines, dianhydrides and bisketeneacetals [25,34].

2.2. Synthesis of the star-shaped resins

Currently, polymers are designed for a certain application. In order to add especial physio-chemical properties, it is sometimes desirable to change the architecture of the polymer from linear to a star-shaped polymer [15]. Changing the architecture of a polymer to achieve a multiarm or hyperbranched one would change its morphological and physical-mechanical properties [41]. Different methods for achieving star-shaped polymers have been introduced, including employ of multifunctional linking agents or multifunctional initiators [15,42–46]. However, a few studies have been devoted to syntheses of star-shaped polyesters. The early star-shaped polyesters have been synthesized by the reaction of multifunctional hydroxyl compounds and $\text{Sn}(\text{Oct})_2$ using an ROP approach [47,48]. Currently, different polyol molecules with various hydroxyl groups have been employed as the core molecule in S-LA. In the next part of this paper, the recent methods for synthesis of different star-shaped resins using these polyols are explored. In addition, although the two-armed PLA systems, with two hydroxyl groups chain extenders, doesn't have a star shaped architecture and are linear, due to similarities between these systems and other S-LA systems in terms of chemistry, synthesis, physiochemical properties, and applications, the two armed linear PLA systems are also discussed in the next part.

2.2.1. Two-arm linear LA based polymers

Modification of linear PLA is a technique often employed for controlling the degradation rate or increasing the flexibility of the polymers for biomedical application [49]. Poly lactic-ethylene glycol (PLEG) often produced from poly ethylene glycol and poly lactic acid (Fig. 2.1) by direct conjugation method [50]. PLEG has also been synthesized from lactide and ethylene glycol using $\text{Sn}(\text{Oct})_2$ as catalyst at 200 °C [51,52]. Biela et al. employed diethylene glycol and synthesized hydroxyl group terminated $\text{R}-(\text{PLA}-\text{OH})_2$ according to the procedure explained by Arvanitoyannis et al. [53] employing $\text{Sn}(\text{Oct})_2$ as co-initiator. Sealed glass ampules using a standard high vacuum technique were employed for the ROP at 120 °C [54] (Fig. 2.4). Tetra(ethylene glycol), TEG, has also been used as the chain extender and telechelic poly lactides having two CH-OH end groups were obtained. The ratio of LA to TEG was set to 20:1 mol and dry chlorobenzene was added under an atmosphere of dry nitrogen. Reactants were heated up to 120 °C and after 5 min, $\text{Bi}(\text{OAc})_3$ was added – with a ratio of 0.02 mol to mole of TEG [55].

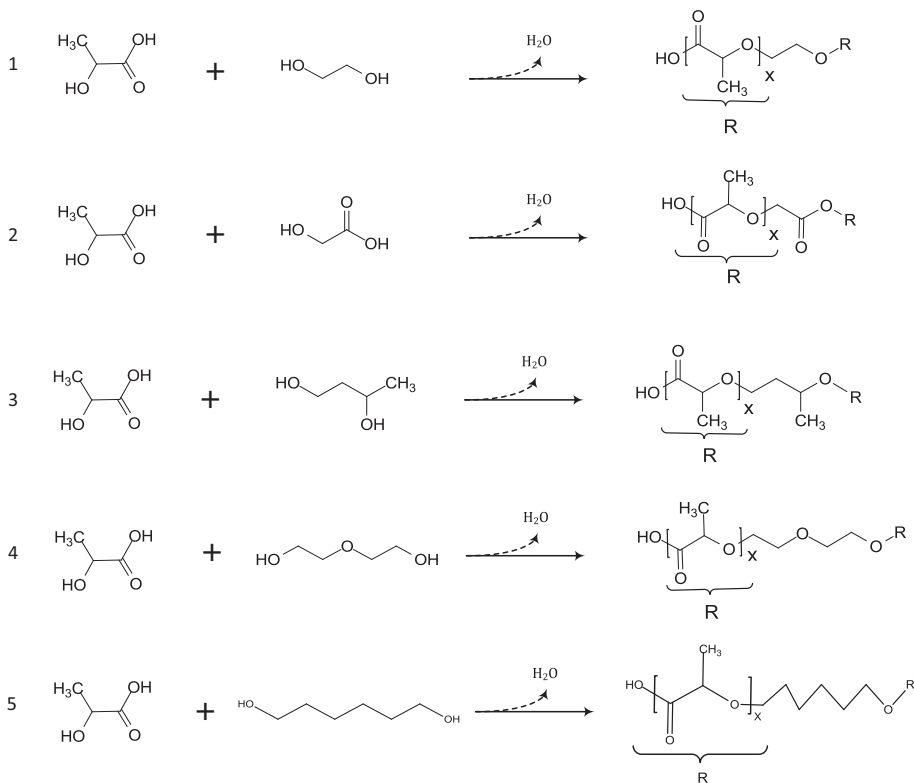


Fig. 2. Synthesis of PLLAs with different chain extenders with two hydroxyl groups. Chain extenders used: (1) ethylene glycol, (2) glycolic acid, (3) 1,4-butanediol, (4) diethylene glycol and (5) 1,6-hexanediol.

The two-armed lactic/glycolic acid polymers (PLGA) have been used to fabricate devices for drug delivery and tissue engineering applications for several decades [56,57] owing to their outstanding biocompatibility and nontoxic and absorbable degradation end-products [58]. Physical properties of PLGA are dependent on multiple factors, including the MW of the polymer, the ratio of lactide to glycolide (or lactic to glycolic acid) in the structure, time of exposure to water and the surface shape [59]. Generally, PLGA are synthesized by the ROP of the lactide and glycolide and common catalysts used include Sn(Oct)₂, tin(II) alkoxides, or aluminum isopropoxide [60,61]. Wang et al. reported the synthesis and characterization of a series of PLGA with various molar ratios of lactic to glycolic acid with various molecular weights, using the ROP method (Fig. 2.2). The PLGA polymers were amorphous, glassy with a T_g, ranged from 21 °C to 52 °C, depending on the MW and the composition [62,63].

Butanediol is also used as the chain extender in the synthesis of the S-LA (Fig. 2.3). The oligomers were polymerized via ROP method from lactide at 160 °C for 3 h. In the presence of 0.02 mol% Sn(Oct)₂ as an initiator, the appropriate amount of the extender to LA molecules were added in which the ratio of the LA monomer to butanediol was varied between 100:12.5 to 100:5 [64]. Wang et al. reported the synthesis and characterization of linear PLA polymers with two arms, using the 1,6-hexanediol and lactide through ROP method at 125 °C (Fig. 2.5). In the reported synthesis method, Sn(Oct)₂ was used as the catalyst [65]. The summary of the synthesis methods is presented in the Table 1.

2.2.2. Core molecules with three hydroxyl groups

Early S-LA polymers with three hydroxyl groups' core molecules were synthesized by reaction of lactide and glycerol by Arvanitoyannis et al. (see Fig. 3.1). The star shaped polymers were synthesized through a ROP method using pressurized ampoules in presence of Sn(Oct)₂ or tetraphenyltin as catalysts at 130 °C in a duration of 4 days. Amorphous polymers obtained when the ratio of lactide to glycerol was below 20:1 (mol:mol) and semicrystalline thermoplast obtained when this ratio was higher than 20:1. In addition, MW of the polymers decreased proportionally to the glycerol content in the polymer [53]. Bakare et al. synthesized a crosslinkable S-LA with glycerol core molecules. The thermoset resins were synthesized in two stages: direct condensation reaction of LA with glycerol and EF of the oligomers with MAAH. Resins with different LA chain lengths of 3, 7 and 10 were synthesized. Condensation reactions performed in the presence of toluene reflux from an azeotropic distillation apparatus as an auxiliary solvent for water removal containing 0.1 wt% of the catalyst, methanesulfonic acid. The temperature was set to 145 °C for two hours, increased to 165 °C for another two hours and to 195 °C for one more hour. For EF, in the presence of 0.1 wt% of hydroquinone as the stabilizer, 3.3 mol MAAH per mole of glycerol was added under a nitrogen atmosphere. The resin was purified from the remained water/toluene and the produced MAA by a rotary evaporator at 13 mbar at 60 °C for 2 h [4]. 1,1,1-tri(hydroxymethyl)propane (THMP) (see Fig. 3.2) has also been used as the core molecule where a three-armed S-LA with three CH-OH end groups was formed. The ratio of lactide to THMP was 20:1 (mol:mol) and dry chlorobenzene was added under an atmosphere of dry nitrogen. The reactants were heated to 150 °C for homogenization before cooling to 120 °C and after 5 min, Bi(OAc)₃ was added with a ratio of 0.02 mol to mole of THMP [54,55]. In another similar study, the same core molecule, THMP, was used with Sn(Oct)₂ as initiator in which lactide was polymerized with the polyol, at 120 °C [16]. In a more recent study, tri(hydroxymethyl)benzene (see Fig. 3.3), used as the

Table 1
Synthesis of multiarm PLA systems.

Chain monomer	Arms	Chain extender/core molecule	Synthesis method	Catalyst	Reaction temperature °C	Ref
Lactic	2	Glycolic acid	ROP	Stannous 2-ethyl-hexanoate	150	[62]
Lactic	2	Glycolic acid	DMC	Tin chloride dehydrate/ p-toluenesulfonic acid	180	[72]
Lactide	2	Glycolide	ROP-A	Fe(acac) ₃ – Fe(OEt) ₃	100–150	[73]
Lactide	2	Ethylene glycol	ROP	Sn(Oct) ₂	200	[51]
Lactide	2	Tetra ethylene glycol	ROP-A	Bi(OAc) ₃	120	[55]
Lactide	2	Diethylene glycol	ROP-A	Sn(Oct) ₂	120	[54]
Lactide	2	Butanediol	ROP	Sn(Oct) ₂	160	[64]
Lactide	2	1,6-hexanediol	ROP	Sn(Oct) ₂	125	[65]
LA	3	Glycerol	PCP	Methanesulfonic acid	145–190	[4]
Lactide	3	Glycerol	ROP-A	Sn(Oct) ₂ -tetraphenyltin	130	[53]
Lactide	3	Tri(hydroxymethyl)benzene	ROP	Sn(Oct) ₂	125	[66]
Lactide	3	THMP	ROP	Bi(OAc) ₃	150	[55]
Lactide	3	THMP	ROP-A	Sn(Oct) ₂	120	[16]
Lactide	4	PENTA	ROP-A	Sn(Oct) ₂	130	[67]
LA	4	PENTA	DCP	Sn(Oct) ₂	180	[8]
Lactide	4	Di(trimethylolpropane)	ROP-A	Sn(Oct) ₂	120	[54]
LA	5	Xylitol	PCP	Methanesulfonic acid	165	[68]
Lactide	5	Xylitol	ROP-A	Sn(Oct) ₂	130	[69]
Lactide	6	Dipentaerythritol (DPE)	ROP-A	Sn(Oct) ₂	120	[54]
LA	6	Dipentaerythritol (DPE)	PCP	Antimony trioxide	150–200	[70]
Lactide	6	Hexa(hydroxymethyl)benzene	ROP	Sn(Oct) ₂	125	[66]
Lactide	13	Poly(3-ethyl-3-hydroxymethyl)oxetane)	ROP-A	Sn(Oct) ₂	120	[54]

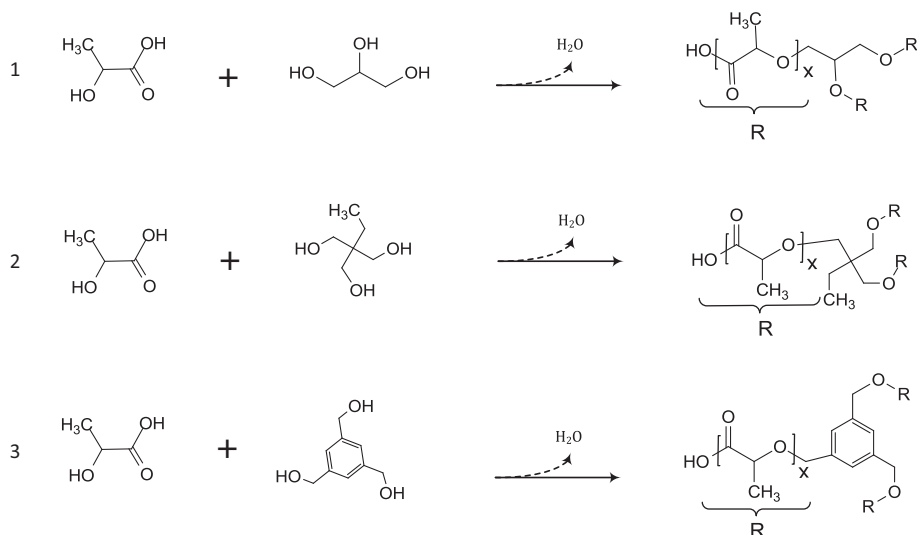


Fig. 3. Synthesis of S-LA with different core molecules with three hydroxyl groups. Core molecules used: (1) glycerol, (2) 1,1,1-tri(hydroxymethyl)propane, (3) 1,3,5-benzenetriol.

core molecule using a $Sn(Oct)_2$ catalyst, for producing S-LA oligomers with 10 lactide monomer units arms. Polymerization reaction was performed at 125 °C for 8 h under nitrogen atmosphere. The precipitation in cold methanol was employed for separation of the polymers from the reactants [66]. The summary of the synthesis methods is presented in the Table 1.

2.2.3. Core molecules with four hydroxyl groups

Kim et al. showed the possibility of the preparation of higher MW S-LA with pentaerythritol (PENTA) (see Fig. 4.1) core molecules. The used catalyst was $Sn(Oct)_2$ and the resulted resin showed a lower intrinsic viscosity compared to those of the linear ones, which confirms the lower viscosity of the star-shaped architecture [47,67]. Åkesson et al. synthesized a crosslinkable resin from LA and PENTA core molecules. The resin was synthesized via direct condensation reaction of LA with PENTA and itaconic acid (IT) followed by the EF of the oligomers with MAAH. At 120 °C, the catalyst, 0.05 wt% of $Sn(Oct)_2$, was added, and the reaction temperature was set to 180 °C. The total polymerization time was 15 h and the resulted product was a yellowish, transparent, rigid, brittle resin. It is assumed that IT was only reacted with one hydroxyl branch of PENTA. For the EF at 100–110 °C, first, 0.1 wt% of hydroquinone was added as the stabilizer and then, 15 wt% of MAAH was added dropwise. The reaction continued at 120 °C for 3 h under nitrogen purge [8]. In another study, Biela et al. synthesized four hydroxyl groups terminated R-(PLA-OH)₄ employing di(trimethylolpropane) (see Fig. 4.2) as the core molecule according to the procedure explained by Arvanitoyannis et al. [53] employing $Sn(Oct)_2$ as catalyst in which sealed glass ampules used for ROP polymerization at 120 °C [54]. The summary of the synthesis methods is presented in Table 1.

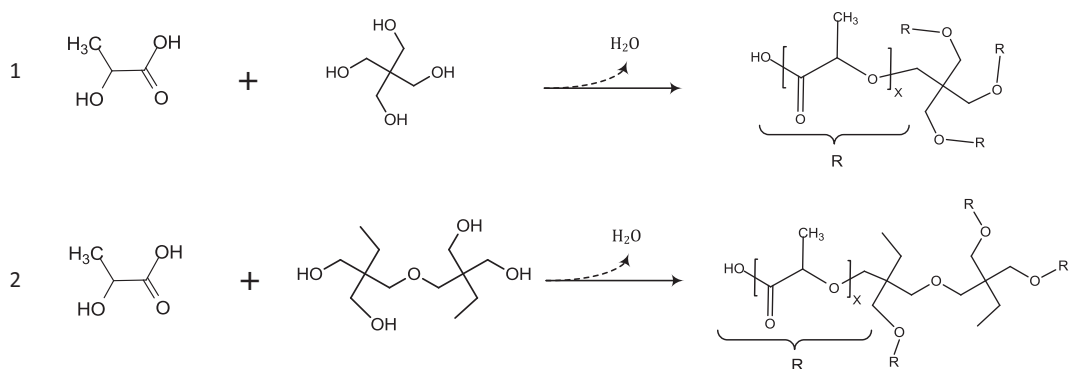


Fig. 4. Synthesis of S-LA with different core molecules with three hydroxyl groups. Core molecules used: (1) pentaerythritol (PENTA) and (2) di(trimethylolpropane).

2.2.4. Core molecules with five hydroxyl groups

In a recent study, the utilization of xylitol (see Fig. 5.1) molecule was examined and evaluated as the core molecule for a crosslinkable S-LA resin. The resin was synthesized via direct condensation reaction of LA with xylitol, in the presence of the toluene reflux from an azeotropic distillation apparatus. 50 g toluene per mole of LA was initially added as an auxiliary solvent for water removal containing 0.1 wt% of the catalyst, methanesulfonic acid. The reaction temperature was set to 145 °C for two hours and then increased to 165 °C for 7 h. The branches were then end-functionalized at 90 °C with methacrylic anhydride (5.5 mol MAAH per mole of LA) in the presence of 1 wt% hydroquinone. Finally, under partial vacuum, the residual toluene and the released methacrylic acid were removed - ~ 10 mbar, 1 h at 60 °C and two hours at 90 °C [68]. S-LA thermoplasts have also been synthesized from lactide and xylitol core molecules. Teng et al. reported synthesizing of S-LA polymers with xylitol core molecules by ROP of the lactide in glass ampoules (see Fig. 5.2). In this method, lactide and xylitol were first transferred in 10 mL ampoules and deoxygenated frozen ampoules were then filled with argon, thawed and immersed in a 130 °C oil bath. After 24 h of polymerization, the products were dissolved in dichloromethane and isolated by vacuum filtration resulting in a white solid powder [69]. The summary of the synthesis methods is presented in the Table 1.

2.2.5. Core molecules with more than five hydroxyl groups

Biela et al. reported the synthesis of S-LA with six hydroxyl groups. The dipentaerythritol (DPE) (see Fig. 6.1) core molecules were used to produce 6 arms S-LA with Sn(Oct)₂ coinitiator using ROP in glass ampoules at 120 °C. The polycondensation method has also been employed by Kim et al. for production of S-LA with DPE core molecules. The polymerization carried out using the antimony trioxid catalysts at 150 °C to 200 °C, under partial vacuum (initially 30 mmHg, reduced to 3–5 mmHg for polycondensation) for 27 h [70]. Kim et al. also assessed the effect of different catalysts including p-Toluene sulfonic acid, Sb₂O₃, SnO, Sn, dibutyl tin oxide, Sn(Oct)₂, tetraphenyl tin, titanium-n-but oxide, titanium isopropoxide and Zr(OBu)₄ on the reaction times, reaction yields and the MW of the synthesized polymers. Perry and Shaver also synthesized and characterized a S-LA, using cyclic hexa(hydroxymethyl)benzene core molecule (see Fig. 6.2) and a Sn(Oct)₂ catalyst with 10 lactide monomer units in arms. Polymerization reaction was performed at 125 °C for 8 h under nitrogen atmosphere [66]. The ROP method with glass ampoules was also employed for synthesizing a 13 arms S-LA polymer with poly(3-ethyl-3-hydroxymethyloxetane) (see Fig. 6.3) core molecule [71]. In this method, Sn(Oct)₂ catalyst was used and polymerization was occurred at 120 °C. The summary of the synthesis methods is presented in the Table 1.

2.3. End functionalization of oligomers

The star-shaped oligomers, resulted from the condensation reaction of LA with a multifunctional hydroxyl core molecule, have reactive groups (either the terminal LA's hydroxyl groups or the core molecules' unreacted hydroxyls) but yet, the groups are not reactive enough for a satisfactory cross-linking or further esterification [8,68]. Esterification of lactic acid oligomers can be promoted by post reaction with brassylic acid, fumaric acid, and acid anhydrides such as maleic and succinic (components with two carboxylic end groups). This modification, results in conversion of the hydroxyl end-groups to carboxyl ones [25,74]. In order to produce a thermoset, capable of efficient crosslinking, branches must be further functionalized- or end capped- with an EF agent. The role of EF is to improve the reactivity of branches, generally by adding carbon-carbon double bonds [64]. Common EF agents, used in the S-LA thermoset systems presented in the literature are MAAH [4,68,75–77] (see Fig. 7.A.1), MAA [7] (see Fig. 7.A.2), IT [7] (see Fig. 7.A.3) and 2-Butene-1,4-diol [78] (see Fig. 7.A.4). The content and the reactivity of the olefinic bonds of the EF molecule are two essential factors in the final crosslinking

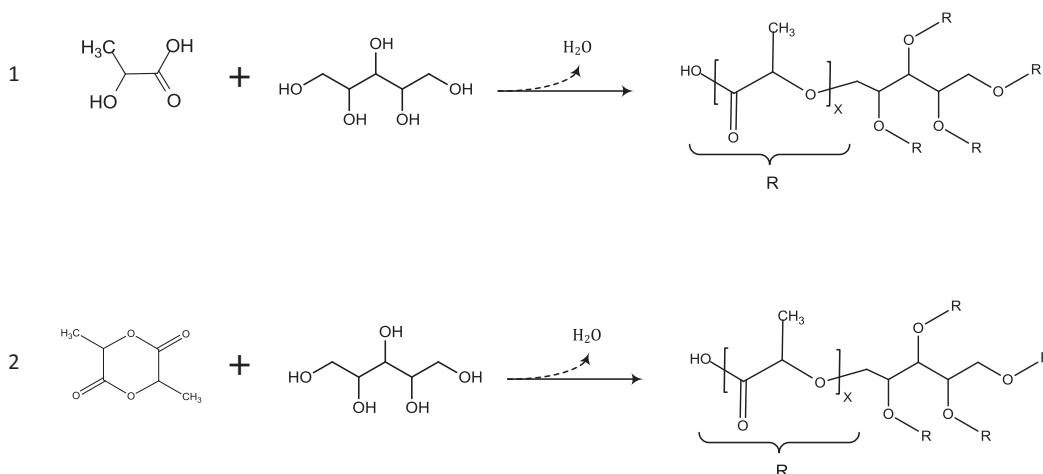


Fig. 5. Synthesis of S-LA with xylitol core molecules with five hydroxyl groups. Using (1) LA and (2) lactide.

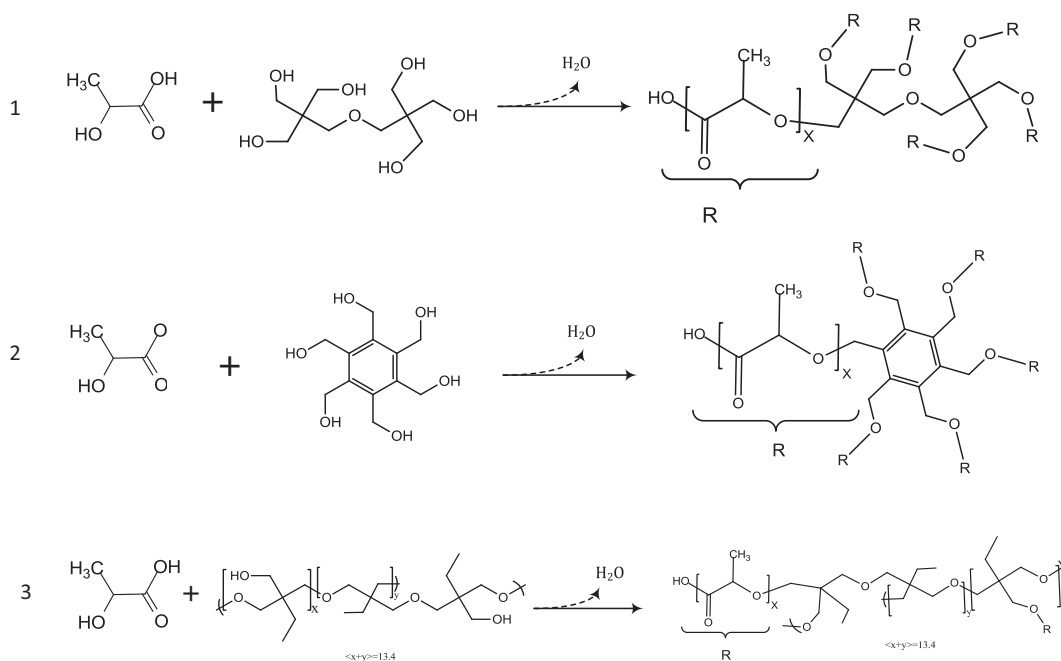


Fig. 6. Synthesis of S-LA with different core molecules with hydroxyl groups > 3. Core molecules used: (1) dipentaerythritol, (2) hexa(hydroxymethyl)benzene and (3) poly(3-ethyl-3-hydroxymethyloxetane).

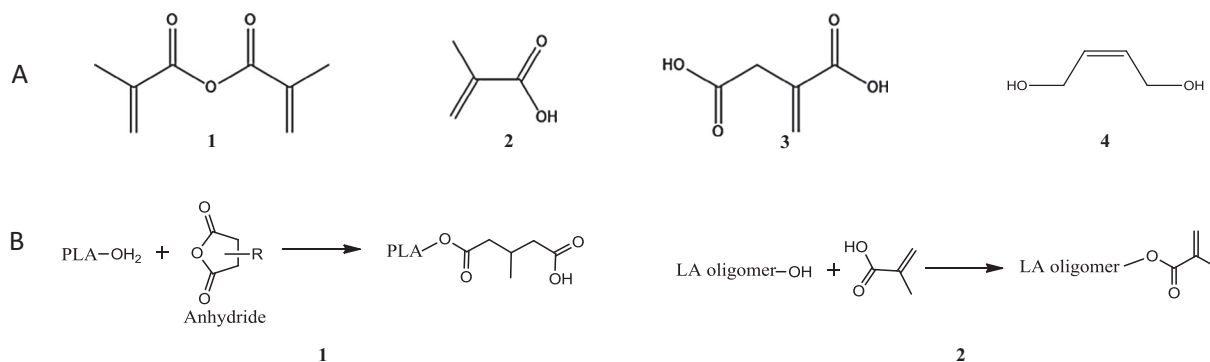


Fig. 7. A. End functionalization agents: A.1.: methacrylic anhydride (MAAH), A.2: methacrylic acid (MAA), A.3: itaconic acid (ITA) and A.4: 2-Butene-1,4-diol. B: End functionalizing reactions. B.1.: PLA esterification promotion functionalization, B.2.: End functionalized LA oligomers capable of free radical crosslinking.

density. Therefore, the two olefinic bonds of the MAAH, bestow a higher reactivity to the molecule and make it more desired for EF purpose, compared to the other EF agents. The schematic of different end-functionalization reactions are presented in the Fig. 7.B. Usually, a stabilizer agent, e.g. hydroquinone, is used to protect the olefinic carbon-bonds during the EF reactions and to avoid subsequent cross-linking reactions and gelation. Generally, EF reactions are sensitive to high temperatures, which induce gelation inside the reactor; therefore, a good control over the temperature is required.

2.4. Thermal curing of the crosslinkable resins

Curing involves the irreversible transformation of the low molecular weight oligomers of a crosslinkable resin into a solid network [79]. The liquid resin is usually composed of several ingredients (e.g. fillers, blowing agents, coupling agents, surfactants, colorants, etc. [80]) with three or more reactive groups per molecule that can react by an external action, such as heating or UV irradiation which results in a tridimensional crosslinked structure [81]. Generally, thermal curing of resins consists of two different stages: the heating period and the curing reaction phase. During the heating phase, the heat is transferred by conduction through the resin which is heated up to a temperature at which the cure reactions start. In the curing reaction phase, the heat evolved from the overall cure reaction zone at a constant temperature which can be described by an

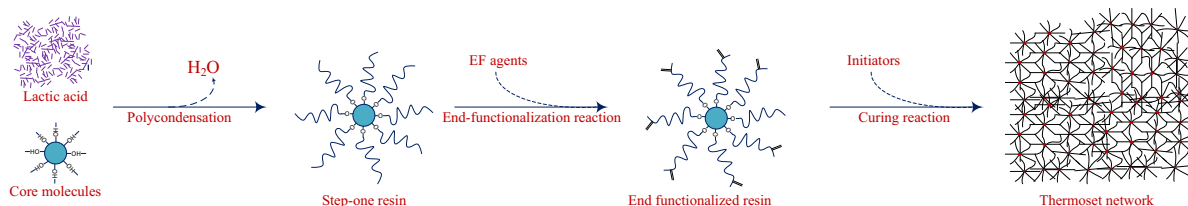


Fig. 8. Reaction Scheme for the two-step synthesis of the S-LA and the thermosetting network.

Arrhenius equation [79]. Often, in the S-LAs, a free-radical polymerization method is employed for curing in which the reaction starts by the assistance of a radical initiator. Common studied initiators for free radical polymerization include benzoyl peroxide [4,22,82], 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane [14], 2-butanone peroxide [64], cobalt naphthenate [15], *tert*-butyl peroxybenzoate [8], N,N-dimethylaniline [5] and *tert*-butyl peroxybenzoate [7,77]. Different factors are involved in free radical curing reactions, including the nature of the initiator, initiator-to-resin ratio, applied heat regimes, retention times and cooling strategies. Often, 1–2 wt% of the initiator is utilized for the thermal curing. Using excess amount of the curing agent or applying high temperatures for curing may result in higher exotherms, faster gelation and more shrinkage due to excessive thermal zoning [68,83]. Fig. 8 presents the reaction schematic for the synthesis steps and the curing reaction.

Differential scanning calorimetry (DSC), Raman spectroscopy, and dielectric analysis (DEA) are of common techniques used for analyzing the curing behavior of the unsaturated polyesters and thermosets [84–87]. The analytical models of cure kinetics have wide applications in numerical simulations of composite manufacturing processes [88–92]. Phenomenological –also called empirical– modeling approach is commonly employed for the analytical expression of the cure kinetics based on an Arrhenius type equation in which the approximated relationship of the curing parameters of the mathematical model are compared with the experimental data [91]. Several phenomenological models are presented in the literature for modeling the curing kinetics of the thermosetting resins [88–92]; however, a few studies performed for the modeling of the curing kinetics of the S-LAs [77,91]. Chang et al. studied the curing kinetics of a set of methacrylated four-armed S-LA systems with PENTA core molecule. The effect of architecture and the LA chain length (with 5–15 LA units) on the curing behavior were investigated using DSC analyzing for non-isothermal and isothermal curing. Chang et al. successfully applied an *autocatalytic* phenomenological model (presented in the Eq. (1)) for the modeling and the parameters of the model were obtained.

$$\frac{d\alpha}{dt} = K\alpha^m(1 - \alpha)^n \quad (1)$$

where α is the *degree of cure* and presents the extent of the curing reaction, K is the *reaction rate constant* which is presented based on an Arrhenius equation, and m and n are the *reaction orders* obtained from the experimental data [77]. The autocatalytic model represents the autocatalytic effect of the curing reactions. This model considers a single rate constant for the reaction and the maximum reaction rate is supposed to take place in the intermediate conversion stage. Their experimental results have shown that the curing time is dependent to the thermal initiation condition and can vary from several minutes to more than an hour. The authors have also reported that changing the LA arm length of the 4-armed S-LA affects the curing process and results in different curing parameters, reaction orders and the evolutions of activation energy [77].

3. Characterization of the S-LA systems

3.1. Chemical characterization

3.1.1. Titration

The condensation retention time is a crucial factor in poly-condensation reactions. On the one hand, insufficient retention time in the reactor results in unreacted reactants and on the other hand, excessive reaction times result in promoting transesterification reactions, which gradually degrades the structure of the oligomers [68]. The progress of the condensation reaction can be evaluated by determination of the *Total Acid Number* (TAN) for residual acidic constituents (carboxyl groups) during the poly-condensation step. According to the ASTM D974-12, the TAN is defined as the quantity of KOH (in mg), required for the titration of 1 g of the sample which is dissolved in a specified solvent system [93]. The samples are diluted in predefined solvent systems, capable of dissolving the S-LA, and then, titrated with a base in the presence of an indicator, e.g. phenolphthalein 1% [94]. The currently used solvent systems for the TAN determination are 1:1 v/v xylene/isopropyl alcohol solutions [4,68,94], acetone [95] and a mixture of toluene and isopropyl alcohol (based on the ASTM D664 and D974-12). The ratio of the *reacted to initial* available carboxylic groups, indicates the degree of completion of the condensation reaction [93]. The titration data for S-LA systems is very rare in the literature. Moreover, the reported conversion rates of the polycondensation reactions for different S-LA systems cannot be directly compared. In other words, the conversion rates of S-LA systems depends on several factors, including the type and the load of the used catalysts, the employed solvents, reaction temperatures and other factors. Bakare et al. showed that the condensation reaction of lactic acid oligomers and

the glycerol core molecules almost starts immediately at 160 °C with methanesulfonic acid as the catalyst [4]; however, using the same polymerization method, the same reaction temperature and the same solvents, Jahandideh et al. reported that reaction of xylitol core molecules with LA oligomers delayed for 100 min. In addition, 95% of conversion achieved after 360 min for glycerol, while 94% of conversion for xylitol S-LA systems achieved after 720 min. Using the same polymerization method, the differences between the conversion rates can be attributed to the differences between the number of hydroxyl groups in the glycerol and xylitol core molecules. Therefore, increasing in the number of the hydroxyl groups of the core molecule in the S-LA architecture results in lower conversion rates, during the polycondensation phase [4,68].

3.1.2. NMR

The Nuclear magnetic resonance (NMR) is a technique frequently used for identifying the chemical structure of the synthesized resins as well as LA chain length in the branches. The ^{13}C NMR data for different S-LA is presented in the literature [4,8,11,12,48,64,68,94,96,97]. Of particular interest is the carbonyl region (160–180 ppm) [5,68]. For neat S-LA, different types of carbonyl bonds are expected, including (a) main-chain carbonyls, (b) LA carbonyl groups adjacent to the ($-\text{O}-\text{CH}_2$) branches of the core molecule, and (c) carbonyls of the LA end-group for unreacted LA. For the end-functionalized resins, signals in the carbonyl area would be broad, because signals for carbonyls of LA next to the core molecule (or next to the end-capping agent) differ from that of LA in chains. In addition, the end-group agent may add other carbonyl bands. The other class of chemical shifts used for characterization, belongs to a carbon atom adjacent to an oxygen atom which is revealed in the range of 60–75 ppm [98]. These CH groups could be (a) in the structure of the core molecule, (b) next to the reacted LA carbonyl groups and an oxygen atom, or (c) adjacent to the hydroxyl end-group. The other expected groups are methyl groups. The LA methyl groups are detected in the 16–22 ppm range [68]. Hydroxyl functionalized end-group of methyl groups are present in the S-LA, but not present in the EF resins. The probable CH_3 groups of the end-capped agent in the resin structure and the olefinic carbon sites of the end-groups are other characteristic signals of the EF resins. Moreover, the NMR technique can also be used for measuring the chain length of the branches [5], the percentage of the LA in forms of reacted with the core molecule as well as the percentage of the LA reacted into free oligomers [4,68].

3.1.3. FT-IR

The Fourier Transform Infrared Spectroscopy (FT-IR) analysis of the S-LA is often performed for verifying the structure of polycondensation resins, the end functionalized resins and also the cured samples. Infrared spectroscopy data of the S-LAs' functional groups is presented in the literature [4,5,8,13,77,96,98–101] and summarized in the Table 2. Different groups might appear in the IR spectra of the S-LA, end functionalized resins and the cured samples. Generally ($-\text{OH}$) Stretch spectra is just presented in polycondensation resins as hydroxyl groups will react with an EF agent during the end-capping reactions. The spectra for ($-\text{C}-$ stretch and bend), ($-\text{C}=\text{O}$ carbonyl stretch) and ($-\text{C}-\text{O}-\text{C}-$ Stretch), generally presented in both neat and crosslinkable S-LA systems. The spectra for ($-\text{C}=\text{C}-$ stretch) and ($=\text{CH}_2$ bending) are just expected in EF resins in which carbon-carbon double bonds are present.

3.2. Thermomechanical properties of the S-LA

The thermomechanical tests currently employed in characterizing thermomechanical properties of the S-LA and their thermosets include DMA tests, tension tests, bending or flexural tests and impact tests. The type of the employed testing methods on the specimen depends on the service expected for the produced thermoset. However, the more testing applied on a specimen, the more information acquired for the intended S-LA. It is believed that the mechanical properties of S-LA is very dependent on the molecular weight and the structure of the network. Generally, employ of a star branching point in the S-LA systems, results in lower melting temperatures (T_m), lower glass transition temperatures (T_g) and lower crystallization temperatures (T_c) for polycondensation resins compared to linear PLA [10]. However, analyzing a series of S-LA systems with flexible polyols (PENTA and diPENTA) and rigid polyols (tri(hydroxymethyl) benzene and hexa(hydroxymethyl)benzene) as core molecules, Perry and Shaver concluded that the length of LA chain primarily determines the physical properties, including glass, melt, crystallization, and decomposition temperatures [66,84]. The lower T_c indicates that the starting points make

Table 2
Infrared spectroscopy data of the S-LAs' functional groups.

Assignment	Peak position (cm^{-1})
$-\text{OH}$ Stretch (free)	3380 [100], 3428 [5], 3491 [96], 3500 [4,5], 3506 [13], 3508 [77], 3520 [99,100]
$-\text{CH}-$ stretch	2870 [13], 2879 [99], 2900 [4], 2994–2943 [96], 2947 [13], 2990 [98]
$-\text{CH}-$ bend	1382–1454 [96], 2947 [13]
$-\text{C}=\text{O}$ carbonyl stretch	1705 [100], 1722 (MAAH) [77], 1734 [13], 1749 [77], 1755 [96], 1757 [5], 1758–1763 [99], 1759 [5]
$-\text{C}=\text{C}-$ stretch	1635 [4], 1638 [77], 1640 [4,5,8]
$=\text{CH}_2$ bending	815 [101], 816 [4,5,77,101]
$-\text{CH}_3$	1453, 2999 [13]
$-\text{C}=\text{O}$ bend	757 [99]
$-\text{C}-\text{O}-\text{C}-$ Stretch	1095–1130 [99], 1170 [13], 1271–1188–1093 [96]
$-\text{CH}$ ring of lactide	932–934 [99]

the material harder to crystallize, while lower T_m indicates that it makes stacking of the polymers more difficult [48,102]. Abiko et al. reported that changing the terminal groups of S-LA systems from hydroxyl to carboxyl groups slightly affects the thermal properties, while it greatly increases the solubility and degradability of these S-LA polymers [97].

Presence of cracks in the casted resins is a common problem in determining the mechanical properties of the casted S-LA thermosets [68]. Therefore, it is very hard to determine the mechanical properties such as flexural and tensile properties of crosslinked resins. However, the viscoelastic properties of the neat S-LA thermosets have been reported in the literature. The viscoelastic properties of the crosslinked S-LA can be acquired by DMA. In DMA, a sinusoidal stress is applied to the specimen and the resulting displacement (strain) is measured. Properties such as storage modulus, loss of modulus, lag phase and T_g are measured with this technique [103]. The storage modulus, which measures the stored energy, represents the elastic characteristic of a polymer. The storage modulus G' is related to the molecular packing density in the glassy state [77,79]; therefore, the higher G' means the better mechanical properties. Jahandideh et al. reported that applying a stepwise curing method for curing of the methacrylated S-LA with xylitol core molecules results in higher G' compared to continuous heating curing method or immediate heating method. Stage curing of crosslinkable S-LA allows gradual solidification and more relaxed state with less built-in stresses and result in lower G' [68,79]. The G' is decreasing upon elevated temperatures when the polymer chain is in the rubbery plateau region [75] due to the free movements of the polymer chains. The same trend was also reported for crosslinkable S-LA resins with different core molecules including glycerol (major changes observed between $\sim 45^\circ\text{C}$ and 80°C), PENTA (major changes observed between 65°C and 105°C) and xylitol (major changes observed between 48°C and 83°C). The loss modulus (G''), measures the energy dissipated as the heat and represents the viscous part. Generally, smaller G'' suggests better mechanical properties and the strong tendency for reversibility in the samples [75] and in the reported crosslinked S-LA thermosets, a rather small and broad loss modulus curve can be seen [68]. At the glass transition temperature, T_g , the G' decreases dramatically while G'' reaches its maximum. The T_g value of polymers and thermoset systems can be reported based on DSC analysis, loss modulus analysis or peak of $\tan \delta$. In order to compare the T_g values of different systems, it is necessary to use the values reported based on the same technique. The T_g of the crosslinked S-LA systems, often presented based on the peak of $\tan \delta$ in DMA curves. The peak of $\tan \delta$ for the linear PLA is reported as $\sim 50^\circ\text{C}$ [104]; however, rather higher T_g values are reported for the crosslinkable S-LA systems. The T_g values reported for crosslinked S-LA systems with glycerol core molecule (LA chain length of 5), PENTA core molecule (LA chain length of 4) and xylitol core molecule (LA chain length of 3) were reported as 83°C , 97°C and 98°C , respectively [4,8,68]. The T_g of the crosslinked S-LA systems is a function of chain length and the number of arms in the cured S-LA. Therefore, a direct comparison between these reported values is not possible, as both the chain lengths and the number of arms differ between these systems; however, all the reported T_g values for the crosslinked S-LA are substantially higher than the T_g value reported for the thermoplastic PLA. In addition, even higher T_g values and consequently better mechanical properties are expected if the reinforcement fibers applied to the crosslinkable S-LA [75,105].

Helminen et al. reported that the crosslinking density of methacrylated S-LA thermosets is increasing with an increase in the number of arms of the core molecule (butanediol, PENTA and polyglycerine used as the core molecules with 2, 3 and 4 arms, respectively) and also, the compressive yield strength will be built up by increasing in the number of arms [64]. The same trend was also confirmed for methacrylated S-LA systems with glycerol and xylitol core molecules with 3 and 5 arms, respectively [4,68].

Jahandideh et al. have shown that in the crosslinked S-LA with xylitol core molecule, different factors affect the final distribution and propagation of cracks, including the mix ratio of the curing agent to the crosslinkable S-LA resin, severity of the mixing, applied mixing method and the mixing temperature. They have shown that cracks can occur, propagate and terminate due to the presence of bubbles in the casted product; however, the crack's problem is fully resolved by changing the mixing method, applying partial vacuum and implementing a stage curing technique for the xylitol S-LA system [68]. The flexural modulus and strength of S-LA with xylitol core molecule with different LA chain lengths of 3, 5 and 7 have also been reported by Jahandideh et al. The authors reported higher flexural strengths for S-LA casted samples with longer LA length chains. However, Chang et al. have reported inferior mechanical properties for S-LA with PENTA core molecule with higher LA chain lengths [77]. The DMA results also provide evidence showing that in crosslinkable S-LA with xylitol core molecule, the short LA chain of three imposes steric hindrance which finally reduces the flexural properties. By increasing the chain length, this hindrance is decreased and flexural properties improved. However, the trend showed that when the chain length is long enough and doesn't impose the steric hindrance, the length of the arms adversely affect the mechanical properties. The same trend was also reported for the tensile strength and the maximum elongation of the crosslinkable S-LA systems [68].

It is believed that the tensile properties of the star-shaped structure are different with that of linear oligomers. The strength can be lower for networks with flexible extension units, or higher for structures with rigid starting points. It is reported that the S-LA systems with high crosslinking density demonstrate similar mechanical properties to those of other biodegradable thermosets; however, longer LA chains will decrease tensile properties [64]. Helminen et al. reported lower tensile strength for linear butanediol-LA systems (despite higher crosslinking density), which was ascribed to the flexible butanediol units used in the structure [64]. However, it is believed that the tensile strength is a function of crosslinking density and generally, a higher crosslinking density results in higher tensile strength for an identical crosslinkable S-LA system [106]. In summary, star branching point in the S-LA systems results in lower T_m , lower T_g and lower T_c compared to linear PLA, while the length of the LA chain in S-LA systems primarily determines the glass, melt, crystallization, and decomposition temperatures. In crosslinkable S-LA systems, the crosslinking density of methacrylated S-LA thermosets is increasing with an

increase in the number of arms of the core molecule and by increasing the arm length, the flexural and tensile modulus are decreased; thus, longer chains results in a reduction in the crosslinking density which leads to an inferior mechanical properties.

3.3. Rheological properties of the star-shaped crosslinkable resins

3.3.1. Viscosity of the resins

Inadequate and poor impregnation of the viscous matrix to fibers is a major problem in the composite manufacturing. It makes the production process to be slow and also reduces the mechanical strength of the product [12,13]. The viscosity is of importance for manufacturing processes, maximizing the production efficiency, improving processability as well as for improving the impregnation efficiency of the matrix to the reinforcement fiber for composite production [107]. It is believed that the linear PLA shows a long Newtonian plateau which is typical in polymers having a linear structure (at low to moderate oscillation frequencies <100 rad/s). For the S-LA systems however, a non-Newtonian behavior has been reported. Also, the S-LA systems show an intensified shear thinning response (similar to comb-like PLA) compared to the linear PLA [10,108]. In composite manufacturing industry, low viscosity of the thermosetting resin is a crucial factor for several processing methods, including vacuum infusion, spray and hand lay-up, filament winding, and pultrusion [8]. Comparably lower viscosities of thermosets, suggest better processability and better impregnation in these systems and make thermosets desirable as a matrix for reinforced composite applications. Generally, the lower the viscosity, the better rheological properties and more desired matrix to be used for reinforced composite applications [91]. For a satisfactory composite manufacturing, Li et al., suggests that the resin flow viscosity needs to be below 5 P (0.5 Pa s) [109]. It is believed that employing a core molecule in the structure of oligomers can reduce the viscosity of the resins. This reduction can be ascribed to the coiling character of polymers [102]; therefore, as the star-shaped polymers have smaller hydrodynamic volume compared to that of linear polymers with the same molecular weight, the viscosity will be lower [15,48,77]. However, the contradictory observations have also been reported by Nouri et al. in which higher viscosity and elastic modulus was observed for branched PLA structures [108]. The viscosity of the S-LA is generally measured based on stress viscometry technique at different temperature intervals. Increasing the length of the LA branches will increase the MW and the viscosity. Bakare et al. reported the same trend for crosslinkable S-LA thermosets with glycerol core molecules with different LA chain lengths in which resins with shorter arms proportionally had lower viscosities. The same trend was reported for the S-LA thermosets resins with xylitol core molecules, and similarly upon increasing the temperature, the viscosity of resins substantially drops down. Low viscosity, even at elevated temperatures (up to curing temperatures), is substantially important as the low viscosity facilitates the impregnation of the resin into the fiber reinforcement at higher temperatures. Table 3 summarizes the viscosities reported for to date synthesized crosslinkable S-LAs.

4. Applications

4.1. Biocomposites

Inexpensive biobased raw material, better environmental profile, low viscosity and better processability of the matrix along with better thermomechanical properties of the produced biocomposites are of advantages expected for the crosslinkable S-LA based composites. To date, composites of crosslinkable S-LA matrix and different reinforcements, including viscose fiber [82], flax fibers [6,7], surface modified cellulose fibers [110] and flax/basalt [6] have been produced. Esmaeili et al. reported rather good mechanical properties for biocomposites made from methacrylated glycerol based S-LA, reinforced by up to 70 wt% regenerated cellulose fiber using different fiber alignments. Using the same matrix, better mechanical properties obtained for unidirectional alignment of the reinforcements (tensile modulus: 11–14 GPa, flexural modulus: 10–11.5 GPa, impact strength: 130–150 kJ/m²) and lower mechanical properties reported for bidirectional and nonwoven fiber alignments [82]. Bakare et al. synthesized a crosslinkable S-LA thermoset with low viscosity from LA, allyl alcohol and PENTA and used it as the matrix for production of biocomposites reinforced with flax and basalt fibers (up to 40 and 60 wt% fiber loads, respectively). Rather good mechanical properties were reported for flax/ballast composites (tensile modulus: 9–14 GPa, flexural modulus: 10–12 GPa, impact strength: 46–54 kJ/m²) and lower mechanical properties reported for

Table 3

The effect of the core molecule and the LA chain length on the viscosity of the crosslinkable S-LA.

Core molecule	LA chain length	End-functionalization	Number of branches	Viscosity at 25 °C Pa s	Viscosity min Pa s	Ref
Unsaturated polyester	–	None	–	0.3	0.1 at 70 °C	[6]
Xylitol	3	MAAH	5	2.97	0.06 at 85 °C	[68]
Pentaerythritol	5	IT-MAAH	4	7000	4 at 80 °C	[8]
Glycerol	3	MAAH	3	1.09	0.04 at 100 °C	[4]
Glycerol	7	MAAH	3	80	0.33 at 100 °C	[4]
Glycerol	10	MAAH	3	900,000	1.05 at 100 °C	[4]
Pentaerythritol	5	MAAH-Allyl alcohol	4	0.02	0.01 at 70 °C	[6]

pure flax composites [6]. Ramamoorthy et al. produced composites from silane and alkali treated regenerated cellulose fibers [111] and methacrylated glycerol S-LA thermosets. Good mechanical properties reported for these biocomposites (tensile modulus: 9.5 GPa, flexural modulus: 6.2 GPa, impact strength: 28 kJ/m² [110]). It has been shown that unsaturated branches of the core molecule increase the hydrophilicity of the produced resin and make it more compatible with inexpensive natural fibers which eventually increases the mechanical properties and reduces the final costs of the biocomposites. However, sometimes a hyper branched core molecule in the structure of the S-LA thermoset can adversely affect the thermomechanical properties, and also it is plausible that unsaturated groups available in the core molecule of the polymer affect the water absorption capacity of the matrix which results in altering the electrical and physiochemical properties of the product.

4.2. Biomedical

4.2.1. Drug delivery

Wide diversity in the chemistry, ease of formulation for various devices, excellent bio-compatibility, biodegradability and desired mechanical strength have introduced a class of FDA approved aliphatic polyesters such as PLA, PGA, and PLGA to be used in controlled release of drugs, especially for cancer therapy [56,96,112–114]. It is believed that the architecture of the polymer, called topology, often influences the physicochemical properties and effects the microsphere preparation and drug delivery properties [3,114]. The polymer architectures plays a crucial role in the drug delivery control and in the fabrication of drug delivery systems; however, it is relatively unfamiliar to pharmacists. Different polymer topologies have been studied for drug delivery, which can be categorized into linear, branched, cross-linked, block, star-shaped and dendrimer topology [50,114–116]. Compared to linear polymers with the same MW, the star-shaped polymers provide a lower solution viscosity. The star-shaped polymers can be synthesized via *arm-first* or *core-first* methods. In the arm-first methods, the linear arms are prepared via a controlled polymerization pathway; then, the chains are reacted with multifunctional terminating agents. The core-first method which is the dominant employed technique, provides a better control over the process and starts with a multifunctional initiator and the propagation of the arms through a controlled polymerization pathway. Research on S-LA polymers as drug vectors seem rather limited so far and the study experience on different PLA architectures and new drug carriers is still quite limited. Thus, so far there are not enough experimental data exists to explain the exact role of polymer architectures on the fate of the conjugated drugs [114]. However, different core molecules have been suggested so far for the drug delivery purposes, including, PEG [48], THMP [16,54], PENTA [67], di(trimethylolpropane) [54], cholic acid [98] and luminescent ruthenium tris(bipyridine) [2].

Different drug carries have been suggested when star shaped polymers are used for drug delivery purpose, including unimolecular micelles and injectable hydrogels (sol-gel transitions). The drug encapsulation capability is an important property when star-shaped architecture polymers are used along with unimolecular micelle drug carrier. When injectable hydrogel drug carriers employed, lower critical solution temperature and gel strength is resulted in star-shaped polymers. The controlling factors for the release rate in star shaped polymers include the dimension of the hydrophobic core, the arm number and the arm length. In the linear two-arm PLA-PEG structure, manipulation of the molecular weights of EG to LA in the structure is an important factor in designing a system with high control over the hydrophilic/hydrophobic balance and core protection [114]. Zeng et al. developed a cholic acid functionalized star-shaped PLGA-b-TPGS for sustained and controlled delivery of docetaxel for treatment of cervical cancer [9]. Choi et al. reported the synthesis of star shaped PEO-PLA polymers by a divergent synthetic method which could be used as the delivery carrier for polypeptide. The authors also reported that the melting point, crystallinity, and phase separation are decreasing with an increase in the degree of branching [48]. Jeong et al. have also shown the capability of employing star-shaped PEO-PLA block copolymers to be used for parenteral injectable drug delivery [117].

4.2.2. Tissue engineering

Tissue engineering aims to apply engineering methods to create artificial substitutes for defective tissues and organs [118,119]. The matrix can be served as a substrate for attachment, grow and migration of cells or can be utilized as a drug carrier to activate cellular function in the region [118,120]. Biodegradable polymers, by providing exogenous matrices suitable for facilitating tissue regeneration, play an important role in most tissue engineering strategies [121]. Successful utilization of biomaterials for tissue engineering is dependent on several factors. The biomaterial must resorb after its service and should provide conditions for sufficient growth rate and effective cell adhesion, while it is -or its degradation materials are-nontoxic, when implanted *in vivo*. The S-LA systems satisfy these needs to some extent. The material which is designed for tissue engineering should also meet certain physical properties, including but not limited to having (a) high porosity ($\leq 90\%$ for providing enough surface area in a 3D structure), (b) minimum diffusional constraints (sufficient to meet the metabolic requirements), (c) sufficient space for extracellular matrix regeneration and (d) adjustable degradation rate (to match the rate of tissue regeneration *in vivo*) [122,123]. The microarchitecture of the device is also of importance as it influences the interconnection between the pores for cell proliferation. In addition, as scaffolds are subjected to remain in intimate contact with the cells for prolonged periods, the influence of the polymeric materials on viability, growth, and function of the attached or adjacent cells is of crucial importance [124,125]. Different biodegradable polymers, including linear PLA, polylactide, polyglycolide and PLG have been employed for cell transplantation or for various tissue regeneration, including bone, cartilage, liver, and skin [121,123]. The mechanical strength and the rate of degradation of the PLG is typically adjusted based on the ratio of lactic to glycolide and polymer's degree of polymerization. Although the polymer blends must be well

optimized by refining their properties to be used for tissue engineering, yet, polymer properties are not the only crucial factors in tissue engineering. The interaction of the cells with the surface of the polymer is another crucial factor and polymers that allow surface modification like PLG are particularly promising for tissue engineering purposes [126].

Go et al. synthesized a heparin-conjugated S-LA by coupling heparin to the S-LA with PENTA core molecules. Authors reported a lower protein adsorption and platelet adhesion as well as higher cell activity on the surface of the S-LA-Hep along with a higher cell spreading area on the surface. These features candidate the S-LA-Hep to be used as blood-tissue compatible materials for implantable medical devices [127]. Cai et al. reported the synthesis of star-shaped polylactide attached to poly (amidoamine) polymers with potentials to be used for hydrophilic drug delivery of growth factor and antibodies in tissue engineering [128]. Cheng et al. also synthesized a functionalized S-LA polymer with a cholic acid core molecule which had better wettability and higher surface energy compared to the linear PLA. These features result in higher cell adhesion and better cell proliferation [129].

5. Perspectives, opportunities and limitations

5.1. Perspectives and opportunities

Substitution of current petroleum-based platforms with renewable-based technologies would be beneficiary in different ways. First, using corn-based LA instead of conventional petroleum based monomers, will reduce the dependency of the national thermosetting plastic industry to the petroleum resources. Thus, in the long term, it will enhance national energy security. Second, compared to petroleum based products, using biobased materials substantially promotes the environmental profile and sustainability of the production chain. In addition, the biodegradability of the products alleviates the carbon footprint and the environmental burdens associated with the final product. Third, using corn-based LA and inexpensive natural fibers as the raw materials subsequently promotes economic diversification in the rural areas. It has been shown that the S-LAs are capable of competing with or even surpassing fossil fuel based resins in terms of cost and eco-friendliness concerns [4,6,7,12,68].

5.1.1. Modifications for biomedical use

Using a core molecule with adjustable functional groups at the center of the S-LA provides the unique opportunity of designing and controlling over properties of the resin. The unsaturated hydroxyl groups of the core molecule ultimately increases the hydrophilicity of the produced resin which makes the resin more compatible with the hydrophilic systems. The privilege of these thermoset systems over other systems is that these resins can be engineered for a certain functionality by changing the chemical structure or altering the crosslinking density. Moreover, by changing the nature and the portion of the block units of copolymers chain, it is possible to further manipulate the polymers properties. This manipulation could be in terms of changing the hydrophilicity properties as well as design and manipulation of the void sizes of the polymer network. In the crosslinkable resin synthesis, the unsaturated carbon bonds are hypothetically added at the end of the LA chain. The end-anchored chains of the crosslinkable S-LA oligomers engaged in the curing reactions during the curing process. Therefore, the chain length of the oligomer is proportional to the length of the microstructural void's edge, and oligomers with longer chains, lead to bigger microstructural void sizes in the network. Thus, by employing longer arms which act as plasticizers, it is possible to increase the size of the voids in the network, and by using hydrophilic monomers in copolymers, the hydrophilicity of the polymer network can be tailored. Manipulation of both void sizes and the hydrophilicity of voids will provide the unique opportunity for designing a polymeric matrix which is specifically designed for a certain chemical component release or a desired drug delivery –based on the drugs chemical structure, molecular weight, polarity, etc. with a substantial control over the release rate. In these systems, the polymer's network can be tailored based on different parameters, including substitution of LA hydrophobic groups with a more hydrophilic group such as glycolic acid, by changing the ratio of the chain extender to the oligomer units or by changing the crosslinking density of the cured thermoset system. Using the short oligomer chains in the network of the polymer leads to a compact network structure and results in greater resistance to diffusion. In addition, by reducing the ratio of the methyl groups to the carbonyl groups in the structure (which results by applying higher ratios of the glycolic acid units to the lactic ones in the PGLA polymer), more hydrophilic structure is achieved.

5.1.2. Smart packaging applications

The S-LA thermosets provide an adjustable polymeric network, which potentially can be tailored for active packaging of products. Active packaging (also called intelligent or smart packaging), means having active functions beyond the inert, passive containment and protection of the product and refers to packaging systems currently employed for foods, pharmaceuticals, and several other types of products [130,131]. Nowadays, PLA is employed as an active packaging material for antibacterial packaging with the ability of the controlled release of the antimicrobial or antioxidant compounds. Antioxidant packaging is a well-known, promising technique for increasing food quality and extending the food production shelf life [131]. The addition of antioxidants to the polymeric packages has two facets. First, available antioxidants in the polymer's formulations protect the ester bonds of the polymer structure from degradation [22,132,133]. Second, it helps in protecting the food contents by migration of antioxidants from the packaging material to the food medium. It is believed that

antioxidant compounds can diffuse and migrate from the packaging material to the food product and help maintain the quality of the food. Previously, antioxidants have been successfully incorporated into different polymeric matrices, including low density polyethylene (LDPE), polyvinyl chloride (PVC) and polypropylene (PP), for various foods [134–136]. The release of antioxidants is a result of the biodegradation of the polymer matrix as well as the diffusion phenomenon [136,137].

5.1.3. Flame retardancy

Many additives have been developed and employed to reduce the risk of fire hazards and to pass safety specifications in polymers. A flame retardant additive reduces the flammability of the product and the smoke generation capability [138,139]. In the S-LA systems, the flame-retardancy feature can be potentially obtained by adding the phosphorus containing groups (or other flame retardant groups) to the structure of the network. In these systems, the core molecule provides different reactive sites (hydroxyls) which may be employed for addition of a special functionality. The other sites which may be used to add a functional group, are the chains. In addition, using an EF agent with groups containing a flame retardant component, can potentially add flame retardancy feature to the S-LA thermosets.

5.2. Gaps and limitations

In this section, shortcomings and gaps of S-LA systems are discussed. S-LA and their composites have been synthesized and employed for several applications for decades. Employing a core molecule makes the structure of these systems more complex compared to the linear thermoplast PLA. Moreover, the combination of different polymerization steps, EF reactions and curing reactions have imposed more complexity to these systems. In addition, numerous applications are considered for these systems, including biomedical applications, adhesives, coatings and biocomposites, and each certain application requires certain characteristics. In order to manipulate the S-LA for a specific desired property, these systems must be thoroughly characterized. Shortcomings and gaps in the different steps must be well studied. The aim of the following section is to discuss drawbacks associated with different steps of preparation and characterization of these systems. These gaps are classified into two categories: the synthesis and manufacturing concerns and the characterizing issues.

Generally, using a core molecule in the structuring of the S-LA imposes more complexity to the system which inevitably leads to comparably poor control over the polymerization. The choice of the core molecule would be one of the most important factors. It can directly effect the crosslinking density, mechanical properties, thermostability, degradation rate and the hydrophobicity of the system. The ratio of the core molecule to the LA monomers is another important factor which affects the crosslinking density and the final properties of the produced network. Too many star points makes the resin brittle and reduces the diffusion rates. The thermostability of the core molecule is of importance, as the synthesis often occurs at high temperatures, and molecules with susceptible bonds can be degraded during the synthesis. Steric hindrance, increased by employing the core molecules with multi-hydroxyl branches and may result in an incomplete reaction of branches with the hydroxyl groups which leaves unsaturated sites in the core molecule. Even if the complete reaction of hydroxyl groups ensured, still the length of chains might vary between oligomers which results in unpredictable mechanical and diffusional properties for the batch-to-batch resins. This is problematic, especially when the resin is expected to be used for drug delivery and biomedical applications. In addition, the polycondensation synthesis pathway, which is commonly employed for the synthesis of the S-LAs, is an energy-intensive step, due to the long reaction times at high temperatures. It also requires large quantities of organic solvents for effective water removal which must be recycled through the azeotropic condensation. This purification and water removal step imposes a substantial environmental load. Thus, there is a need for optimization of the required energy for the synthesis. The energy inputs can be alleviated by optimization of the process and choosing more effective solvents, more efficient catalyst systems or choosing an alternative synthesis method. The EF reaction is the other important synthesis step. Despite the condensation step, the EF reactions occur at moderate temperatures and shorter reaction durations. However, this step requires a crucial control over the temperature as at elevated temperatures, the undesired partial crosslinking happens and the risk of gelation is increased. In this step, in order to avoid unwanted crosslinking, an inhibitor agent is often used for protecting the olefinic carbon bonds. The origin of the EF agents, the presence of releasing products during the reaction, e.g. MAA, the progress of EF reactions and the degradation products are of other concerns, especially when the cured resin is intended to service *in vivo* in biomedical applications. The optimization of the EF reactions would be an obstacle as applying insufficient reaction times and temperatures result in poor crosslinking density and subsequently inferior mechanical properties of the product, and applying excess reaction times and elevated temperatures increase the risk of gelation. Therefore, successful substitution of the nonrenewable EF agents with nontoxic renewable ones is of interest. The rheological properties of these systems are the other hotspot. The rheological properties of the S-LA systems have not been studied intensively in the literature. Although employing a core molecule in the structure of oligomers is believed to reduce the viscosity of the resins [15,77], yet, resulted viscosities are still far from the desired viscosity for manufacturing processes. It is believed that a proportional relationship exists between the MW and the viscosity of these systems [108,140,141]. Employing core molecules with fewer hydroxyl groups, reduction in the LA chain length of branches and an efficient functionalization of the remaining hydroxyl groups can further reduce the viscosity of resins. The curing procedure is also of importance and must be well-optimized as it can affect the properties of the final product. Applying improper curing techniques result in undesired mechanical strength on the matrix [142]. Different factors are involved in the free radical curing reactions which are often employed for curing of the S-LA systems, including the nature of the initiator, *initiator: resin*

ratio, applied heat regimes, retention times and cooling strategies. Using excess curing agent or applying high temperatures for the curing may result in higher exotherms, faster gelation and more shrinkage due to excessive thermal zoning [68,83].

Shortcomings also exist in the characterization methods of these systems. Currently, the titration method is employed for monitoring the progress of the polycondensation step which is based on TAN measurements titration of available acidic groups. The samples are diluted in the predefined solvent systems, capable of dissolving the S-LA, and then titrated with KOH. However, these solvent systems have been optimized for petroleum based materials and might not be capable of efficient dissolving of the high MW oligomers of the S-LA which results in unrealistic high conversion degrees. In addition, comparably more complex structure of these systems makes the interpretation of the FT-IR and NMR analysis hard. Therefore, too many peaks often can be found in the spectra, especially in the carbonyl area of the EF resins, which can obscure the results and make them very hard to interpret. In addition, these techniques provide no solid information about the degree of completion of the polycondensation and EF reactions.

6. Conclusions

The concept of using star-shaped polymers for biocomposites or in biomedical applications is gaining more and more attention day by day. Changing the architecture of the linear PLA to a star shaped one would change the polymer's physico-chemical, mechanical and diffusional properties. For biomedical applications, the star shaped architecture of S-LA provides the unique opportunity to design specific properties such as altering the degradation rate, changing the hydrophilicity and regulation of the drug release rate. The S-LAs are of interest in designing functional polymers as in these systems, the crosslinking density can be altered by changing the length of the LA chains. In addition, reactive sites of the core molecule can be used for addition of a special functionality, e.g. a flame retardant agent, an anti-microbial agent, etc. The crosslinkable S-LA systems also provide several advantages for biocomposite manufacturing including reduced final costs, a better extended network, more compatibility with natural fibers, better thermomechanical properties, lower viscosities and better processability.

Developments in the emerging S-LA systems are spectacular from a technological point of view. However, these systems still suffer from different limitations and technological gaps and have a long way to go. These limitations can be categorized into synthesis deficiencies and characterization gaps. Firstly, employ of a core molecule makes the structure of these systems relatively more complex and reduce the control over the polymerization step. Association of multi-step reactions, including different polymerization steps, EF reactions and curing reactions also impose more complexity to these systems. The steric hindrance, increased by the employ of the core molecule, may result in an incomplete reaction which leaves unsaturated hydroxyl groups in the network. Even if the complete reaction ensured, the risk of inconsistent product still remains as the length of chains cannot be efficiently controlled. The former results in the unpredictable mechanical and diffusion properties of the batch to batch product. The properties of the S-LA is dependent on several factors, including the molecular weight, the architecture of the network, rigidity of the core molecule, length of branches, crosslinking density and the degree of conversion. These interrelated factors, make the optimization and characterization to be complicated and difficult. The tuning of the curing parameters is also a challenge, especially for more complex systems such as industrial formulations. Applying improper curing method results in inferior mechanical properties, higher exotherms, faster gelation and more shrinkage in the cured resins. In addition, the polycondensation synthesis method is known as an energy-intensive step. Large quantities of organic solvents required also impose substantial environmental load. Although these state-of-the-art, adjustable S-LA systems look very interesting and promising for various applications, their usage is limited. Therefore, future use of these systems requires systematic optimization and invention of better characterization methods.

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Arash Jahandideh received his Bachelor in Engineering degree in Chemical Engineering from Isfahan University of Technology in 2010. Then he obtained his Master of Science in Resource Recovery and Sustainable Technology from the University of Borås in 2013. Currently, he is a third year Ph.D. student at the Agricultural, Biosystems and Mechanical Engineering at the South Dakota State University. His research area is the use of renewable resources for the synthesis of biobased star-shaped lactic acid based resins for materials and biocomposites.

Dr. Kasiviswanathan Muthukumarappan, distinguished professor and graduate coordinator in the agricultural and biosystems engineering department at South Dakota State University, has been the principal investigator on several research projects and an advisor to undergraduate and graduate students with academic and research activities. He has authored or coauthored more than 200 peer-reviewed publications and made more than 350 regional, national, and international presentations. He has served in leadership roles on numerous Food and Process Engineering Institute (FPEI) committees and served as FPEI division representative to the Standards council.