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Polymer Resins Synthesized via the Michael 1,4-addition from Tall Oil Fatty Acids Using Various Epoxidation Techniques

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ABSTRACT

Studies on the use of renewable materials for various applications, including polymers, have gained momentum due to global climate change and the push towards a circular economy. In this study, polymer resins were developed through Michael 1,4-addition. The precursors were synthesized from tall oil-based acetoacetates derived from epoxidized tall oil fatty acids or their methyl esters. Two different epoxidation methods were employed: enzymatic epoxidation of tall oil fatty acids and ion-exchange resin epoxidation of tall oil fatty acid methyl esters. Following oxirane opening and transesterification with trimethylolpropane, further esterification or transesterification was carried out to obtain the acetoacetates. These synthesized acetoacetates were then reacted with acrylates of various functionalities to obtain polymer resins with differing degrees of crosslinking. The developed polymer resins were characterized using differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetric analysis. The results indicated that the glass transition temperature and storage modulus of the polymer resins were significantly influenced by both the functionality of the acrylates used and the epoxidation technique employed. Higher acrylate functionality resulted in increased stiffness, while enzymatic epoxidation enhanced the polymer's mechanical properties, nearly doubling the storage modulus, achieving approximately 470 MPa, compared to the ion-exchange resin technique. Therefore, selecting the appropriate acrylate functionality and epoxidation method could tailor the mechanical properties of the polymer resins.

KEYWORDS

Tall oil fatty acids; bio-based resin; enzymes; epoxidation; enzymatic; ion resin; Michael 1,4-addition

Nomenclature

DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
E^ETOFA	Epoxidized tall oil fatty acids via enzymatic epoxidation
E^ETOFA_TMP	Polyol synthesized from E^ETOFA through oxirane ring-opening, followed by transesterification with trimethylolpropane
E^ETOFA_TMP_AA	Acetoaceate obtained from E^ETOFA_TMP, subsequently reacted with tert-butyl acetoacetate
E^{IR}TOFA	Epoxidized tall oil fatty acids with ion-exchange resin
E^{IR}TOFAME_TMP	Polyol synthesized from E^{IR}TOFA through oxirane ring-opening, followed by transesterification with trimethylolpropane

$E^{IR}TOFAME\_TMP\_AA$	Acetoacetate obtained from $E^{IR}TOFAME\_TMP$ reacted with tert-butyl acetoacetate
HDODA	Hexanediol diacrylate
PETA	Pentaerythritol tetraacrylate
TGA	Thermal gravimetry analysis
T_{max1}	The first maximum of DTG peaks
T_{max2}	The second maximum of DTG peaks
TMG	1,1,3,3-tetramethylguanidine
TMP	Trimethylolpropane
TMPTA	Trimethylolpropane triacrylate
$T_{m5\%}$	Temperature at a weight loss of 5%
$T_{m10\%}$	Temperature at a weight loss of 10%
TOFA	Tall oil fatty acids
TOFAME	Tall oil fatty acids methyl ester
T_{onset}	Onset temperature

1 Introduction

The increasing environmental challenges of climate change and resource depletion have underscored the urgency for sustainable development practices. Renewable materials have emerged as a critical component in this paradigm shift, offering a viable alternative to traditional, fossil-based resources. The concept of a circular economy, which emphasizes resource efficiency, waste reduction, and the continual use of resources, has gained significant traction globally [1,2]. In Europe, stringent directives and regulations, such as the European Green Deal and the Circular Economy Action Plan, drive the transition towards sustainable materials and processes [3]. Developing and utilizing renewable materials, including those used to produce polymers, are integral to achieving these ambitious environmental goals and fostering a resilient and sustainable future [4].

Renewable sources have evolved significantly, starting from the first generation, which competes with the food industry, to the fourth generation, which includes genetically modified resources [5]. Tall oil, a byproduct of the Kraft pulping process in the paper industry, stands out as a promising second-generation bio-based material. Unlike first-generation bio-based materials that compete with food resources, tall oil derives from waste streams, making it a more sustainable option. Rich in fatty and resin acids, tall oil can be refined into valuable chemicals and materials [6,7], including adhesives [8,9], coatings [10], surfactants [11,12], rigid foams [13,14], and various types of films and resins [15,16] such as polyesters, polyethers, polyurethanes, polyamides, epoxy resins, alkyd resins [6], polyacrylates [17] and resins obtained via Michael 1,4-addition [18].

Polymer resins derived from tall oil fatty acids (TOFA) exhibit a wide range of thermal and mechanical properties. The glass transition temperature of polyester urethane films from TOFA has been reported at around 60°C, which is lower than that of poly (urethane amides) at approximately 65°C. The modulus of elasticity for these materials varies between 0.5 and 1.0 GPa, and they remain thermally stable up to 225°C [16]. TOFA-based alkyd resins and alkyd–acrylate copolymers have a glass transition temperature of around 40°C [15]. Hyperbranched alkyd resins from TOFA, as reported by Murillo et al., display a glass transition temperature ranging from −50°C to −5°C and a thermal decomposition temperature between 253°C and 296°C [19]. Rodriguez-Tobias et al. studied poly(acrylate)s synthesized from fatty acid-based methacrylate monomers, including TOFA. The resulting acrylic paints and coatings, demonstrated excellent drying times. However, their mechanical performance—particularly in terms of flexion, impact resistance, and adhesion—was moderate to poor. The glass transition temperatures of these coatings ranged from ~53°C to ~69°C [17]. TOFA-based polymer resins obtained via Michael

1,4-addition have shown glass transition temperatures between 21°C and 63°C, Young's modulus ranging from 8 MPa to 2.7 GPa, and thermal stability up to 300°C [18]. In the realm of sustainable polymers, resins produced via Michael 1,4-addition represent a notable advancement. This chemical process involves the reaction between an electron-deficient olefin and a nucleophile, typically an amine or thiol, resulting in a robust network of cross-linked polymers [20]. TOFA can be employed as precursors to obtain polyols after epoxidation and esterification. Further acetoacetylation gives acetoacetates as Michael donor. Reacted with various acrylates, cross-linked polymers can be obtained. The versatility of Michael 1,4-addition allows for the incorporation of various bio-based monomers, enhancing the material properties and expanding their application range [21]. By leveraging bio-based inputs and innovative chemical processes, the development of sustainable polymers continues to progress, offering significant potential for reducing environmental impact and advancing green chemistry.

In the chemical route for Michael donor and/or acceptor synthesis from TOFA, epoxidation is required. This process can be achieved through various techniques. Enzymatic epoxidation utilizes specific enzymes to catalyze the reaction, providing a mild and environmentally friendly approach [22]. Ion exchange resin epoxidation employs ion exchange resins to facilitate the process, offering a reusable and efficient method [23]. Traditional chemical epoxidation methods, such as using peracids or hydrogen peroxide, are also widely used. Additionally, a methylation step can be introduced before epoxidation to enhance the process. Each technique presents distinct advantages, allowing for selection based on the desired efficiency, environmental impact, and application requirements [24,25].

This study aimed to develop polymer resins via Michael 1,4-addition using TOFA, which were modified through two distinct chemical routes. The first route involved the enzymatic epoxidation of TOFA, followed by oxirane ring opening and esterification with trimethylolpropane (TMP). The second route started with the methylation of TOFA, followed by the epoxidation of the resulting TOFA methyl esters (TOFAME) using ion exchange resin, and subsequent oxirane ring opening and transesterification with TMP. A comprehensive comparison of these methods was conducted, focusing on the resulting polyols and polymer resins. The study discussed the efficiency, environmental impact, and evaluated material properties of the polyols and resins obtained from each method, providing insights into how various epoxidation techniques influence the production of sustainable polymer resins from TOFA.

2 Materials and Methods

2.1 Materials

The primary bio-based raw material for acetoacetate synthesis was TOFA, with an acid value of 198 mg KOH/g and an iodine value of 155 g I_2/100 g. Sourced from Forchem Oyj (Rauma, Finland), it comprised over 96% fatty acids, with less than 2% rosin and unsaponifiables. TOFA consists mainly of oleic and linoleic acids with small amounts of other fatty acids [6,26]. Key reagents included Candida antarctica lipase B (Novozym® 435, Novozymes A/S, Bagsvaerd, Denmark) used for enzymatic epoxidation, and methanol (≥99.8%) from Riedel-de Haen (Seelze, Germany) for methylation reactions. The choice of Novozym® 435 for TOFA epoxidation was driven by its excellent selectivity in catalyzing epoxidation reactions. It efficiently targets the double bonds in fatty acids, converting them into epoxides with minimal side reactions. Additionally, its effectiveness under mild conditions and its alignment with green chemistry principles made it the preferred choice for this process [27,28].

Additional materials, including hydrogen peroxide, sulfuric acid, trimethylolpropane (TMP), Amberlite® IRC120 H, tert-butyl acetoacetate (98%), were purchased from Sigma-Aldrich, and tetrafluoroboric acid solution was obtained from Alfa Aesar (Kandel, Germany).

Polymer resins were developed from the synthesized acetoacetates using difunctional hexanediol diacrylate (HDODA), trifunctional trimethylolpropane triacrylate (TMPTA), and tetrafunctional

pentaerythritol tetraacrylate (PETA) in the presence of catalyst 1,1,3,3-tetramethylguanidine (TMG), all received from Sigma-Aldrich without further purification.

2.2 Synthesis of Michael Donors

Acetoacetates were prepared using two distinct routes. In the first approach, TOFA was epoxidized enzymatically using Novozym® 435, followed by oxirane ring-opening with TMP. The resultant polyol was further acetoacetylated with tert-butyl acetoacetate. The synthesis pathway for acetoacetate via enzymatic epoxidation is presented in Fig. 1.
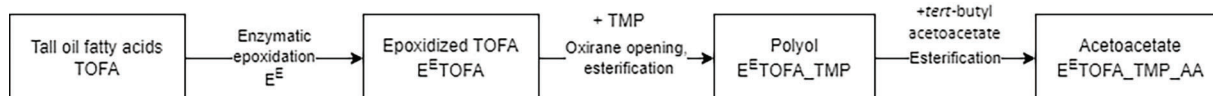
Figure 1: Synthesis pathway for acetoacetate via enzymatic epoxidation of TOFA

The second route involved methylating TOFA, epoxidizing the methyl ester using ion-exchange resin, and completing the transesterification with TMP before acetoacetylation. A schematic representation of this synthesis pathway can be found in Fig. 2.
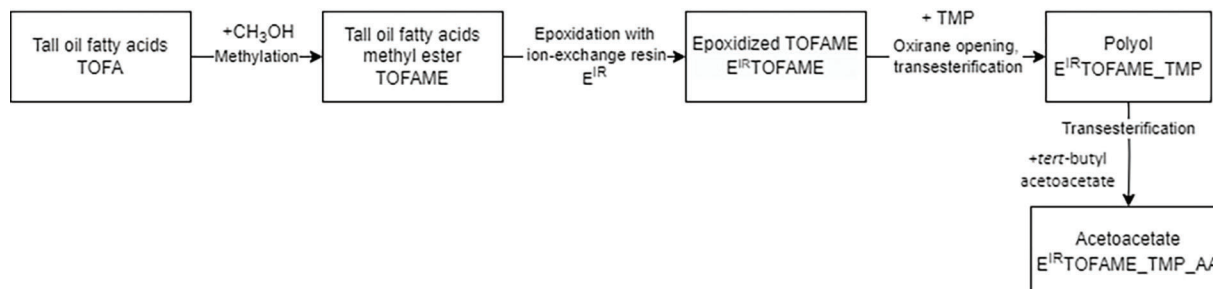
Figure 2: Synthesis pathway for acetoacetates via ion-exchange epoxidation

Details on enzymatic epoxidation can be found in the study by Abolins et al. [29], and for a more comprehensive description of the methylation of TOFA and ion-resin epoxidation refer to the study by Polaczek et al. [30]. E^ETOFA or E^{IR}TOFAME was subjected to a reaction with TMP in the presence of tetra-fluoroboric acid solution as a catalyst. Oxirane ring-opening occurred at 120°C, while for esterification/transesterification, the temperature was elevated to 200°C. A full description of synthesis is given in the work by Abolins et al. [29]. Obtained polyols (E^ETOFA_TMP and E^{IR}TOFAME_TMP) were further reacted with tert-butyl acetoacetate at 120°C temperature for 4 h to yield acetoacetates, abbreviated E^ETOFA_TMP_AA and E^{IR}TOFAME_TMP. For additional details, refer to the study by Pomilovskis et al. [31].

2.3 Polymerization

Synthesized acetoacetates E^ETOFAME_TMP_AA or E^{IR}TOFAME_TMP_AA served as Michael Donors, while acrylates (HDODA, TMPTA, and PETA) with varying functionalities acted as Michael Acceptors. A total of six polymer resin samples were produced and subsequently characterized. Polymerization was carried out with a 1:2 molar ratio of acetoacetate to acrylate groups, employing 1% (by total mixture mass) of TMG as a catalyst. After mixing, the solution was centrifuged for 1 min to remove any air bubbles, ensuring a homogeneous polymer monolith formation.

2.4 Characterization

The acid value of polyols was determined following the ISO 2114:2000 standard [32], while hydroxyl value was assessed according to the ISO 4629-2:2016 standard [33]. Moisture content was evaluated using Karl Fischer titration. Polymer resin characterization involved differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) in compression oscillation mode, and thermogravimetric analysis (TGA). Detailed descriptions of the characterization methods are provided in Table 1. The glass transition temperature was derived from DSC data, in compliance with ISO 11357-2 [34]. All data analysis was performed using OriginPro 2022b (version 9.9.5.171).

Table 1: Characterization of polymer resins

Method	Equipment	Specimens	Description of method
DSC	Mettler Toledo DSC 823e	m = 5 ± 0.5 mg	Heating: 25°C to 180°C; Cooling: to −50°C; Heating: −50°C to 180°C; Heating rate: 10°C/min
DMA	Mettler Toledo DMA/SDTA861e	D = 13 ± 0.2 mm, H = 7 ± 0.2 mm	Temperature: −100°C to 180°C; Heating rate: 3°C/min; Frequency: 1 Hz; Amplitude: 30 μm; Maximum force: 5 N
TGA	Discovery TGA (TA Instruments)	m = 10 ± 0.5 mg	Temperature: 30°C to 700°C; Heating rate: 10°C/min; Atmosphere: N_2

3 Results and Discussion

3.1 Polyols and Corresponding Acetoacetates

Two bio-based polyols were synthesized from TOFA via distinct pathways: the first involved enzymatic epoxidation followed by oxirane opening and esterification, while the second pathway employed methylation followed by ion-exchange epoxidation, and subsequent oxirane opening and transesterification. An alternative epoxidation method could involve direct TOFA epoxidation with an ion-exchange resin. In this study, methylation of TOFA was chosen due to the possibility of reducing the formation of dimers and trimers during the synthesis process, as no free acid groups are available for dimerization and trimerization reactions [30]. However, a disadvantage of this approach is the additional methylation step in the synthesis process and the use of acetic acid. Acetic acid as a low-molecular organic acid opens oxirane rings and esters are formed. In contrast, enzymatic epoxidation reduces the formation of low-molecular-weight by-products but enzymes cost more. The chemical structures of the raw materials, polyols, and the subsequently synthesized acetoacetates are shown in Fig. 3.

Table 2 compares the characteristics of synthesized polyols and their corresponding acetoacetates. It reveals that the polyol synthesized via the enzymatic epoxidation method (E^ETOFA_TMP) has a higher hydroxyl value than the polyol synthesized through ion-resin epoxidation (E^{IR}TOFAME_TMP). Both polyols have similar acid values and water content. Both were effective in reacting with *tert*-butyl acetoacetate to form acetoacetates. Due to the higher hydroxyl value of the enzymatically derived polyol, the resulting acetoacetate exhibits a higher acetoacetate group content.

3.2 Polymer Resins

The acetoacetates obtained were used as Michael donors and reacted with acrylates (HDODA, TMPTA, and PETA) to produce six different polymer resins. The corresponding Michael acceptors and Michael donors, along with the designations of the polymer resin samples, are presented in Table 3.
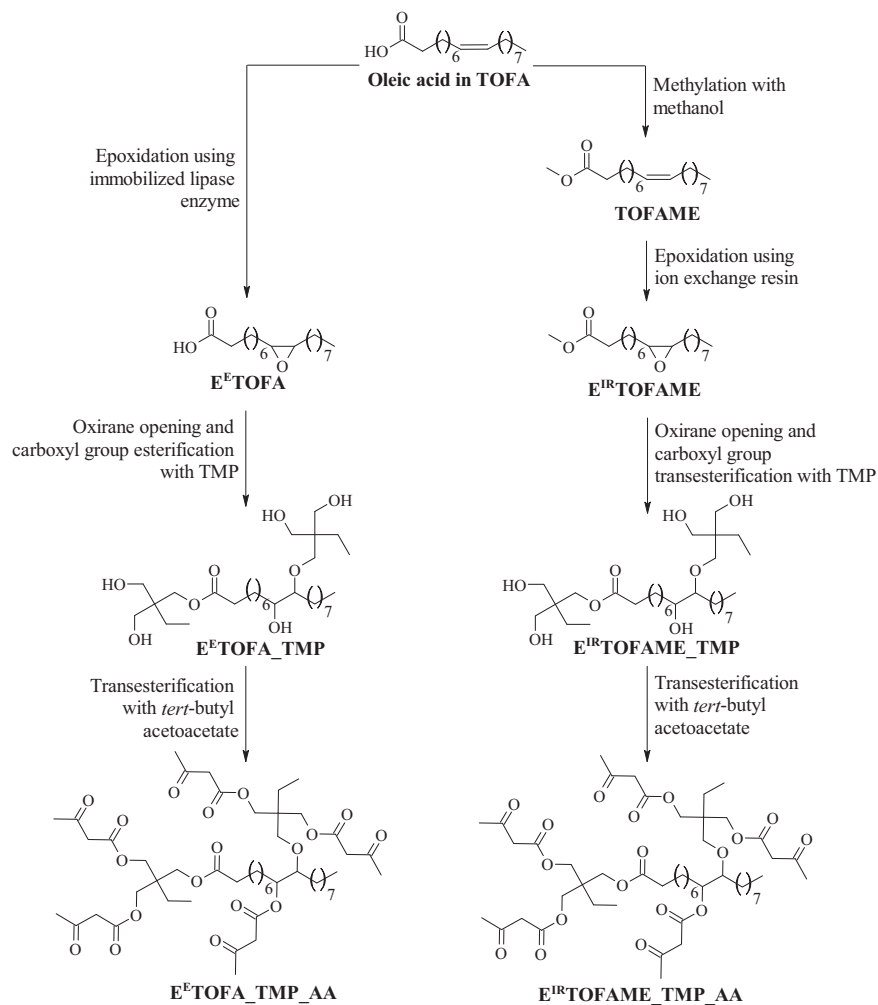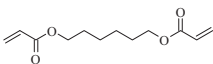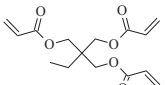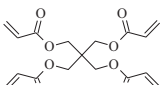
**Figure 3:** Synthesis pathways of polyols and acetoacetates from TOFA with chemical structures

Table 2: Characteristics of tall oil-based polyols and corresponding acetoacetates

Polyols		
Parameters	E^{E}TOFA_TMP	E^{IR}TOFAME_TMP
OH value, mg KOH/g	482 ± 3	430 ± 1
Acid value, mg KOH/g	9.1 ± 0.1	9.2 ± 0.3
H$_2$O content, %	0.046 ± 0.004	0.050 ± 0.003
Acetoacetates		
Parameters	E^{E}TOFA_TMP_AA	E^{IR}TOFAME_TMP_AA
Acetoacetate group content, mol/100 g	0.492 ± 0.003	0.474 ± 0.007

Table 3: Chemical structures of Michael acceptors and designation of polymer resin samples based on combinations between Michael acceptors and Michael donors

Michael acceptor	Michael donor	
	E^{E}TOFA_TMP_AA	E^{IR}TOFAME_TMP_AA
HDODA (f = 2)	E^{E}TOFA-HDODA	E^{IR}TOFAME-HDODA
TMPTA (f = 3)	E^{E}TOFA-TMPTA	E^{IR}TOFAME-TMPTA
PETA (f = 4)	E^{E}TOFA-PETA	E^{IR}TOFAME-PETA

The schematic chemical structure of the obtained polymers is shown in Fig. 4. R^1 and R^2 correspond to the respective Michael acceptor and Michael donor listed in Table 2, thus generating six unique polymer resin structures.

R^1 - respective Michael donor moiety
R^2 - respective Michael acceptor moiety
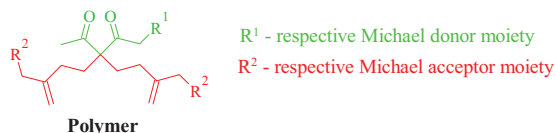
Polymer

Figure 4: Schematic representation of the polymer backbone with R^1 and R^2 moieties corresponding to Michael donors and acceptors

DSC, DMA, and TGA were employed to characterize the thermal and mechanical properties of obtained polymer resins. The DSC results, presented in Fig. 5, indicate that the glass transition temperature increases with the functionality of the acrylate used in the polymer resin synthesis. For samples where enzymatic epoxidation was used in synthesis pathways, glass transition varied from 26°C to 72°C. In the case of samples derived from ion-exhange resin epoxidation technique—glass transition temperature increased from −5°C to 62°C. It can be seen that E^{E}TOFA samples (Fig. 5a) show higher glass transition than E^{IR}TOFAME samples (Fig. 5b).

The glass transition temperatures identified from the tan δ curves presented in Fig. 6 are higher than those determined by DSC, but they exhibit the same trend.

Curves of storage modulus (E') are shown in Fig. 7. Storage modulus increases with the functionality of the acrylate used in the polymer resin synthesis. Higher functionality of acrylate leads to a denser crosslinked network in the polymer. This denser network enhances the rigidity and mechanical strength, thereby increasing the storage modulus. When comparing different epoxidation techniques, the enzymatic epoxidation method results in polymer resins with significantly higher storage modulus, nearly double, compared to ion-exchange resin method. This can be attributed to the more efficient and controlled

formation of epoxy groups, leading to better crosslinking and, consequently, a stiffer polymer network. The ion-resin method might produce polymers with some degree of irregularity in epoxy group distribution, leading to less optimal crosslinking and lower storage modulus and glass transition temperature.
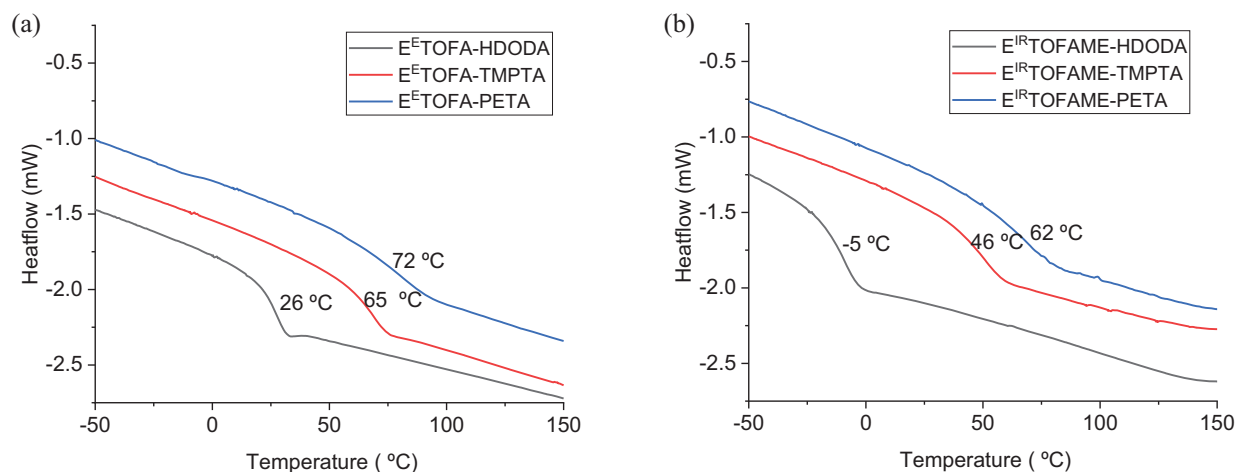

Figure 5: DSC curves and glass transition temperatures of polymer resins: a—polymer resin samples obtained from E^ETOFA, b—polymer resin samples obtained from E^{IR}TOFAME
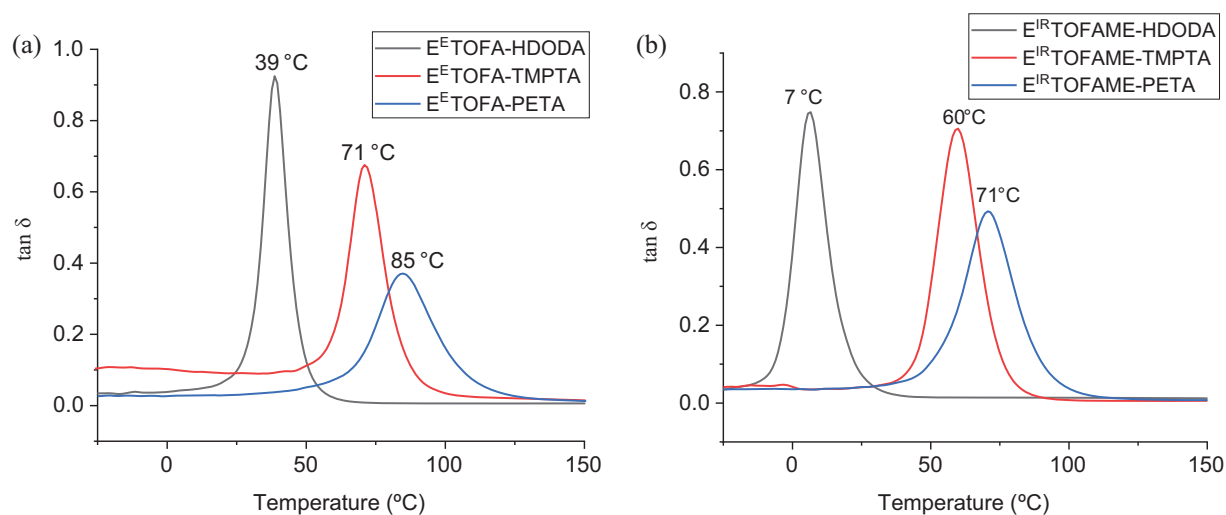

Figure 6: Tan δ curves from DMA analysis and corresponding glass transition temperatures: a—polymer resin samples obtained from E^ETOFA, b—polymer resin samples obtained from E^{IR}TOFAME

Thermal stability was assessed using TGA, with TGA and derivative thermogravimetry (DTG) curves shown in Fig. 8. Characteristics of thermal stability-onset temperature (T_{onset}), the temperature at a weight loss of 5% and 10% ($T_{m5\%}$ and $T_{m10\%}$), the weight of the solid residue remaining at 700°C (residue), and maximums of DTG peaks (T_{max})—are presented in Table 4.

Thermal degradation of developed polymer resins occurs in one main step in the temperature range from 300°C to 500°C. E^{IR}TOFAME_HDODA shows an additional peak at 180°C in the DTG curve. The

differences in thermal stability are minimal, with the polymer resins synthesized with HDODA showing a slightly lower T_{onset} and a lower T_{max1} in the DTG curve. Additionally, the polymer resin obtained with HDODA exhibits an additional peak shoulder at approximately 445°C (for E^{E}TOFA-HDODA) and 455°C (for E^{IR}TOFAME-HDODA) in the DTG curve. For the other samples, a single main degradation peak is observed at approximately 370°C–378°C, corresponding to the degradation of the polymer network. The residue at the final temperature (700°C) increases as the functionality of the acrylate used in the synthesis increases. The thermal degradation pattern of developed resins is similar to the degradation behavior observed in other polymer resins synthesized via 1,4-Michael addition [18,21]. Additionally, these resins exhibit higher thermal stability than pure epoxy resins (T_{onset} < 360°C [35,36]), conventional polyurethanes (T_{onset} < 215°C [37,38]), and poly(methyl methacrylate) films (T_{onset} < 245°C [39,40]), demonstrating superior thermal stability properties.
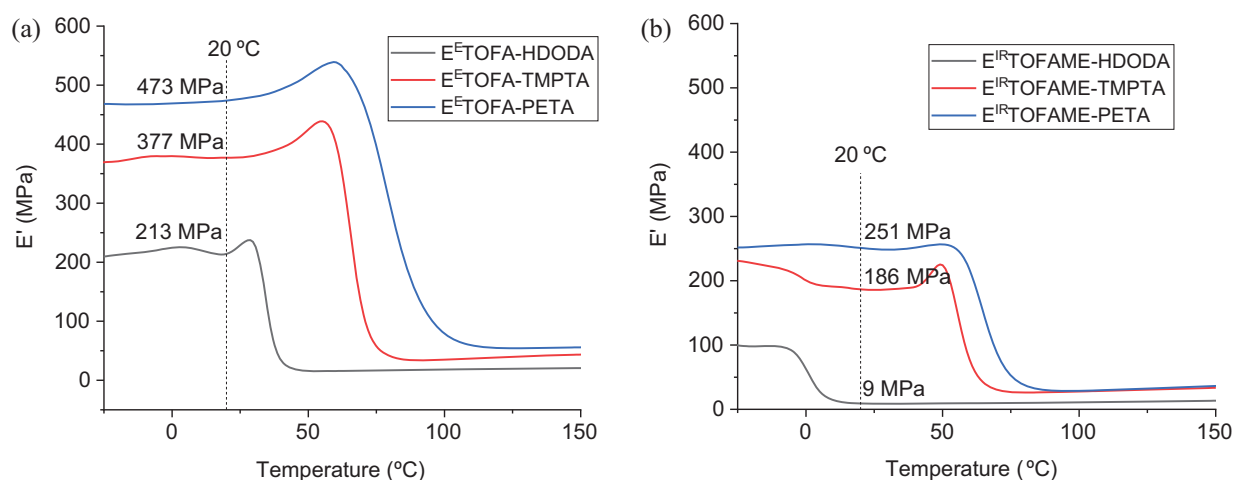

Figure 7: Storage modulus curves from DMA analysis, including storage modulus values at 20°C temperature: a—E^{E}TOFA samples, b—E^{IR}TOFAME samples
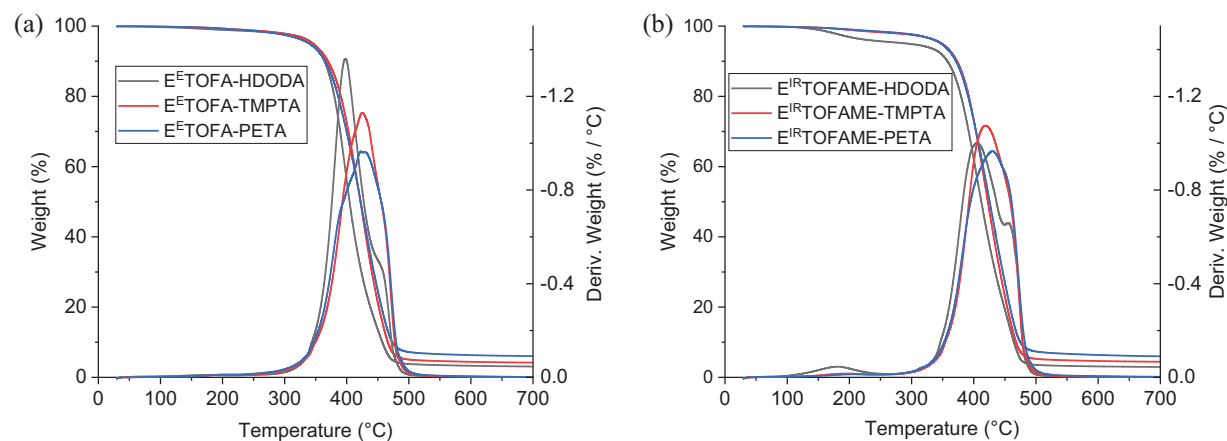

Figure 8: TGA and DTG results: a—E^{E}TOFA samples, b—E^{IR}TOFAME samples

Table 4: Thermal properties of polymer resins

Acrylate used in synthesis	E^ETOFA polymer samples			E^{IR}TOFAME resin samples		
	HDODA	TMPTA	PETA	HDODA	TMPTA	PETA
T_{onset}, °C	368	378	370	363	376	375
$T_{m5\%}$, °C	345	345	340	295	349	348
$T_{m10\%}$, °C	364	370	365	358	373	372
Residue, %	3.1	4.2	6.1	3.0	4.5	6.0
T_{max1}, °C	368	425	423	406	419	430
T_{max2}, °C	442	–	–	458	–	

4 Conclusions

Six polymer resins were synthesized from tall oil fatty acids-based acetoacetate and acrylates with varying functionalities. For the polyol synthesis necessary for acetoacetate synthesis, two epoxidation techniques were employed: enzymatic epoxidation and ion-exchange resin epoxidation. Polymerization was carried out via the Michael 1,4-addition at room temperature. The obtained polymer resins were characterized using DSC, DMA, and TGA.

The glass transition temperature and storage modulus of the polymer resins were significantly influenced by both the functionality of the acrylates used and the epoxidation technique employed. Higher acrylate functionality resulted in increased stiffness, while enzymatic epoxidation enhanced the polymer's mechanical properties by nearly doubling the storage modulus compared to the ion-exchange resin technique. Thermal stability was similar across all six samples, although the polymer resin obtained with HDODA exhibited slightly lower thermal stability.

Depending on the application, selecting the appropriate acrylate functionality and epoxidation method can tailor the mechanical properties of the polymer. For instance, applications requiring high stiffness and mechanical strength would benefit from high-functionality acrylates and enzymatic epoxidation techniques.

Author Contributions: The authors confirm contribution to the paper as follows: study conception and design: Ralfs Pomilovskis, Arnis Abolins; data collection: Ralfs Pomilovskis, Arnis Abolins; analysis and interpretation of results: Ralfs Pomilovskis, Arnis Abolins, Aiga Ivdre; draft manuscript preparation: Aiga Ivdre, Ralfs Pomilovskis, Arnis Abolins. All authors reviewed the results and approved the final version of the manuscript.

Availability of Data and Materials: The data that support the findings of this study are available from the corresponding author, Aiga Ivdre, upon reasonable request.

Ethics Approval: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest to report regarding the present study.

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