

1 *Conference Proceedings Paper*

## 2 **Photocross-linked bio-based polymers for potential** 3 **application in optical 3D printing**

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10 **Abstract:** Acrylated epoxidized soybean oil (AESO)-based resins were developed as a biobased  
11 resin for potentials application in optical 3D printing. AESO was photocross-linked with myrcene  
12 (MYR) and vanillin dimethacrylate (VDM) or divinylbenzene (DVB, for comparison) in the presence  
13 of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator. The higher amount of myrcene  
14 in the compositions resulted better homogenization and lower viscosity, though prolonged  
15 photocross-linking reaction and reduced mechanical and thermal properties of the synthesized  
16 polymers. The used aromatic compounds (VDM or DVB) improved mechanical and thermal  
17 properties of cross-linked polymers. Replacing DVB with VDM in the systems led to the higher  
18 photocross-linking rate and higher yield of insoluble fraction. The resin composed of only plant-  
19 derived monomers AESO/MYR/VDM, molar ratio 1:1:3, was indicated as a suitable renewable  
20 photoresin for potential application in optical 3D printing.

21 **Keywords:** biopolymers; renewable polymers; cross-linking; photopolymerization; thermosets.

### 22 **1. Introduction**

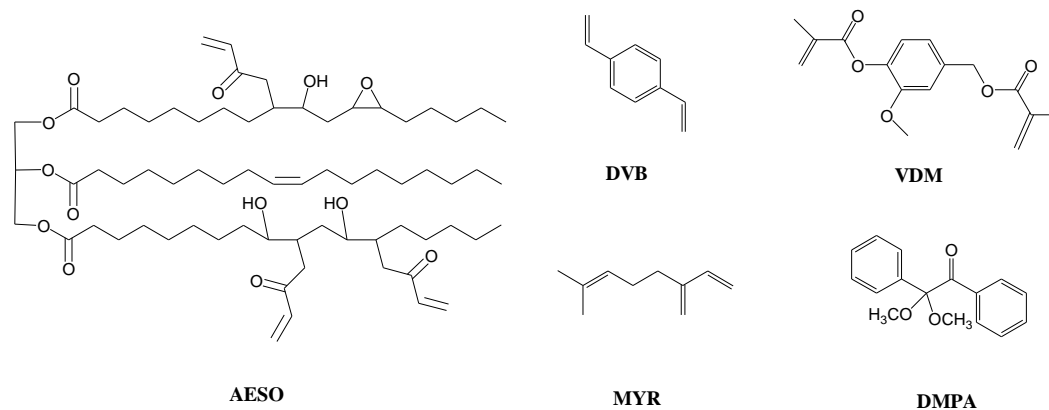
23 In recent years, additive manufacturing or 3D printing gained a lot of interest as a highly  
24 accurate, fast, and low raw material using technology [1]. Optical 3D printing is a  
25 photopolymerization method employing UV/VIS light to polymerize photosensitive resin layer by  
26 layer. Synthetic acrylates are the most frequent choice in optical 3D printing due to their relatively  
27 low cost and high light sensitivity [2].

28 As a replacement of petroleum-derived monomers, renewable raw materials such as natural oils  
29 are one of the most promising starting materials for polymer synthesis. Acrylated epoxidized  
30 soybean oil (AESO) could be easily cross-linked by UV/VIS light using an appropriate photoinitiator  
31 [3]. Though, due to poor mechanical properties of AESO polymers predetermined by fatty acid long  
32 aliphatic chains, various petroleum-derived aromatic comonomers such as styrene, divinylbenzene  
33 (DVB), dicyclopentadiene acrylonitrile and others are added [4,5]. Vanillin dimethacrylate (VDM) or  
34 methacrylated vanillin alcohol, which can be produced from lignin, is a considerable candidate to  
35 replace petroleum-derived aromatic compounds due to its high reactivity [6].

36 Synthetic reactive diluents are often used to reduce the high viscosity (19000-31000 cP/mPa·s) of  
37 AESO [7] and to improve properties of cross-linked polymer. Natural compound myrcene (MYR), a  
38 component of the essential oils of several plants, including bay, mango and others [8], could replace  
39 the petroleum-derived reactive diluents due to the very low viscosity [9] and the presence of three  
40 reactive double bonds, one of which is conjugated.

41 In this study, the resins composed of commercially available AESO, DVB, and MYR were  
42 photocross-linked in various ratios. Plant-derived VDM was used as a replacement of DVB (Figure  
43 1). The investigation of photocross-linking kinetics of the designed resins was carried out by real-

44 time photorheometry for the first time. The dependency of photocross-linking rate and properties of  
 45 the cross-linked polymers on the resin composition was determined. The resin composed of only  
 46 plant-derived monomers, AESO, MYR, and VDM, showed characteristics suitable for potential  
 47 application in optical 3D printing.



48 **Figure 1.** Chemical structure of acrylated epoxidized soybean oil (AESO),  
 49 divinylbenzene (DVB), vanillin dimethacrylate (VDM) and 2,2-dimethoxy-2-phenylacetophenone  
 50 (DMPA).

## 51 2. Materials and Methods

### 52 2.1. Materials

53 Acrylated epoxidized soybean oil (AESO, an average number of acryloyl groups per molecule calculated  
 54 from 1H-NMR spectrum is 2.7 and 0.3 of epoxide groups), myrcene or 7-methyl-3-methylene-1,6-actadiene  
 55 (MYR), divinylbenzene (DVB), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from  
 56 Sigma-Aldrich. Chloroform was purchased from Chempur. Vanillin dimethacrylate was purchased from  
 57 Specific Polymers. All materials were used without further purification.

### 58 2.2. Preparation of Cross-Linked Polymers

59 Curing formulations were prepared by mixing adequate amounts (Table 1) of AESO, MYR, and aromatic  
 60 compound (DVB or VDM) at 40 °C with magnetic stirrer. 3 mol. % of photoinitiator DMPA was added.  
 61 Prepared resins were poured into a tablet-shaped (∅ 15 mm, h 3 mm) Teflon mold and irradiated with Helios  
 62 Italquartz, model GR.E 500 W lamp which intensity was 310 mW·cm<sup>-2</sup> at the distance of 15 cm until hard  
 63 polymer tablets were formed.

### 64 2.3. Soxhlet Extraction

65 The yield of insoluble polymer fraction (YIF) was determined by Soxhlet extraction. Samples of prepared  
 66 polymers were wrapped into a filter package and put into a Soxhlet apparatus. Extraction was performed with  
 67 chloroform for 24 h. Extracted polymer specimens were dried under vacuum to constant weight. The amount  
 68 of insoluble fraction was calculated as the difference of the sample weight before and after extraction.

### 69 2.5. Kinetics of Photocross-Linking

70 The investigation of photocross-linking kinetics was carried out as reported earlier [10].

### 71 2.6. Thermal Analysis

72 Glass transition temperature ( $T_g$ ) of the photocross-linked polymers was estimated by differential scanning  
 73 calorimetry (DSC). The measurements were performed on a Perkin Elmer DSC 8500 apparatus with heating-  
 74 cooling-heating rate of 10 °C·min<sup>-1</sup> under nitrogen atmosphere (nitrogen flow rate 50 ml·min<sup>-1</sup>). The  $T_g$  value  
 75 was taken as the middle point in the heat capacity step of the glass transition.

76 Thermogravimetric analysis (TGA) measurements of prepared polymers were performed on a Perkin  
 77 Elmer TGA 4000 apparatus in the temperature range from room temperature to 800 °C at a heating rate of 20  
 78 °C·min<sup>-1</sup> under nitrogen atmosphere (nitrogen flow rate 100 ml·min<sup>-1</sup>).

### 79 2.8. Mechanical Testing

80 Mechanical properties of the photocross-linked polymer tablets were estimated by compression test on a  
81 BDO-FB0.5TH (Zwick/Roell) testing machine as reported earlier [10].

### 82 3. Results

#### 83 3.1. Real-time Photorheometry

84 In this study, AESO was used as the main component which is easily UV/VIS-curable biobased material.  
85 Synthetic cross-linking agent DVB was used to improve mechanical properties of polymer. As an alternative  
86 for DVB, the plant-derived bifunctional VDM was used. MYR was used to control mixture viscosity and  
87 dissolve solid components. The images of photocross-linked polymer tablets are presented in Figure 2. Due to  
88 three double bonds, MYR acts as a reactive diluent, which connects into polymer network [11]. 3 mol. % of  
89 DMPA was used to initiate the photopolymerization of biobased resins.

Table 1. Compositions of photo-resins

Resin	MRM <sup>1</sup> , AESO:MYR: Aromatic compound	Used aromatic compound
S1	1:1:1	DVB
S2	1:3:1	DVB
S3	1:5:1	DVB
S4	1:1:1	VDM
S5	1:3:1	VDM
S6	1:5:1	VDM
S7	1:1:3	DVB
S8	1:1:5	DVB
S9	1:1:3	VDM
S10	1:1:5	VDM

<sup>1</sup> Molar ratio of monomers

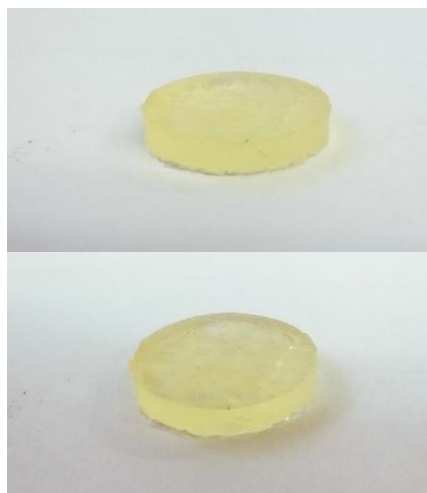
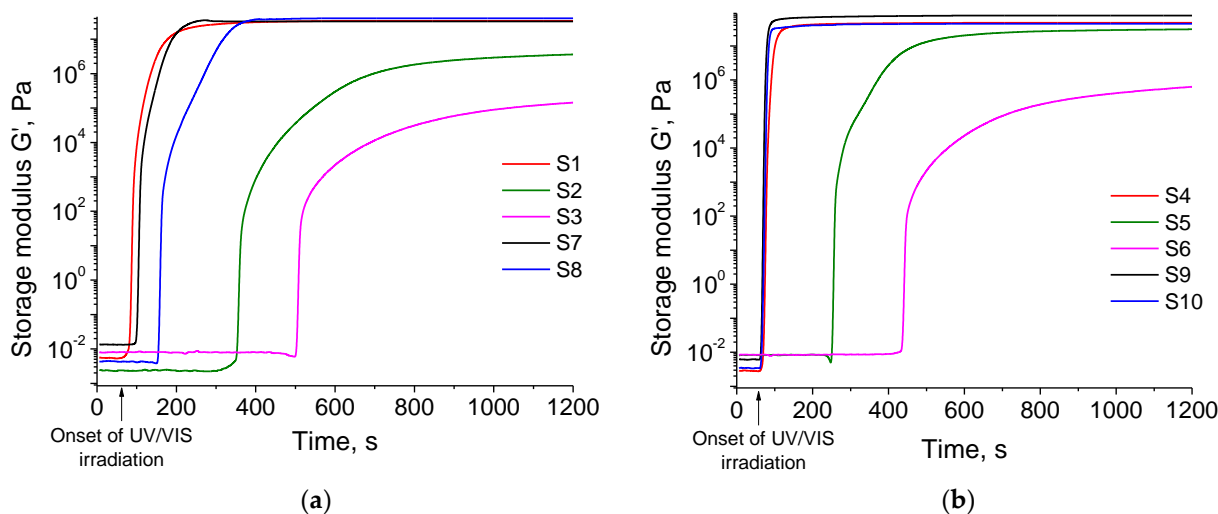


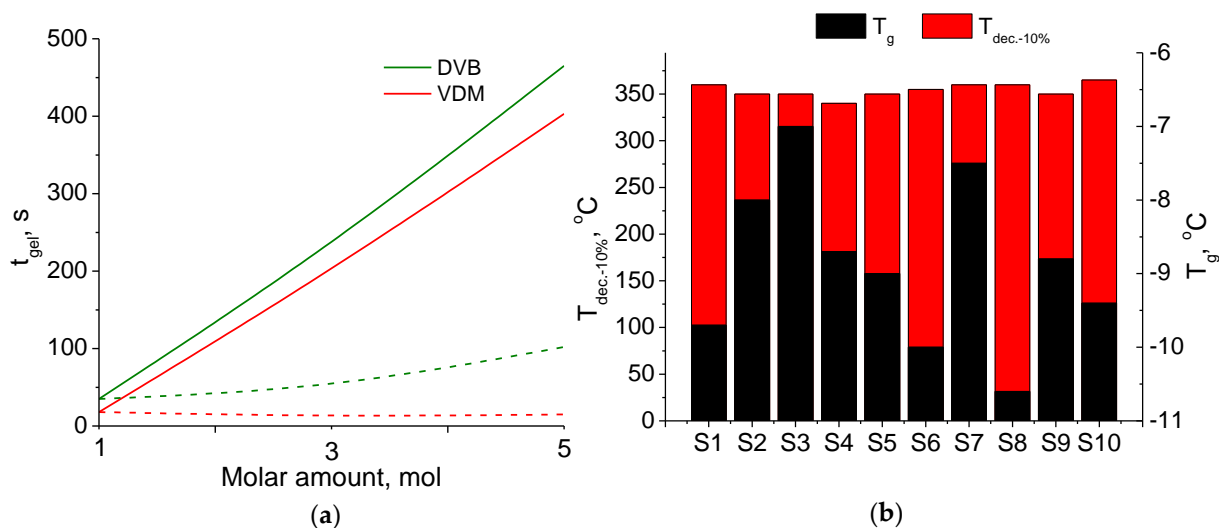
Figure 2. Photocross-linked polymer tablets of S2 (top) and S4 (bottom) (a); Compositions of photo-resins (b).

90 Ten different designed resins (S1-S10 Table 1) were investigated to determine the influence of their  
91 composition to the reaction rate and properties of the resulting polymers. The kinetics of photocross-linking of  
92 resins S1-S10 was monitored by the real-time photorheometry. Storage modulus  $G'$  and gel time ( $t_{gel}$ ) were  
93 measured. Time dependencies of storage modulus  $G'$  of the resins are shown in Figure 2.



94 Figure 2. Time dependencies of storage modulus  $G'$  of the resins with different aromatic compounds: DVB (a) and  
95 VDM (b).

96 It was observed, that resins with higher amount of MYR showed significantly lower values of  $G'$  and  
 97 highly increased  $t_{gel}$  (Figure 3a). A slow formation of soft and rubbery polymer confirmed the widespread MYR  
 98 usage in small amounts as comonomer to adjust elastomeric properties as a soft block [12]. Comparing resins  
 99 with higher amount of MYR and different aromatic compounds, resins **S1-S3** containing plant-derived VDM  
 100 showed the higher photocross-linking rate than those containing petroleum-derived DVB (**S4-S6**). Moreover,  
 101 the resins with VDM showed the higher  $G'$  values than those with DVB corresponding to better mechanical  
 102 properties of the first polymers.



103 **Figure 3.** The dependency of the gel time ( $t_{gel}$ ) of the resins with different amounts of MYR (solid) and aromatic  
 104 compound (dashed) (a); Thermal properties of cross-linked polymers (b).

105 Resins with higher amount of aromatic compound showed higher maximum values of  $G'$  indicating the  
 106 formation of more rigid cross-linked network. It was observed that resins with higher amount of DVB indicated  
 107 extensively prolonged gel time, though higher values of  $G'$  were monitored as well. This confirmed the DVB  
 108 effectiveness as comonomer improving mechanical properties of the polymer [13], despite the long induction  
 109 period.

110 It was determined, that VDM was more efficient aromatic compound comparing to DVB, due to the  
 111 improved  $t_{gel}$  and higher  $G'$  values. Short gel time of the resins with VDM indicated high photosensitivity of  
 112 the compound, which is one of the most important features for optical 3D printing [14]. The resin with 3 mol%  
 113 of VDM (**S9**) showed the shortest  $t_{gel}$  (12 s) and the highest values of  $G'$  ( $7.78 \cdot 10^7$  Pa).

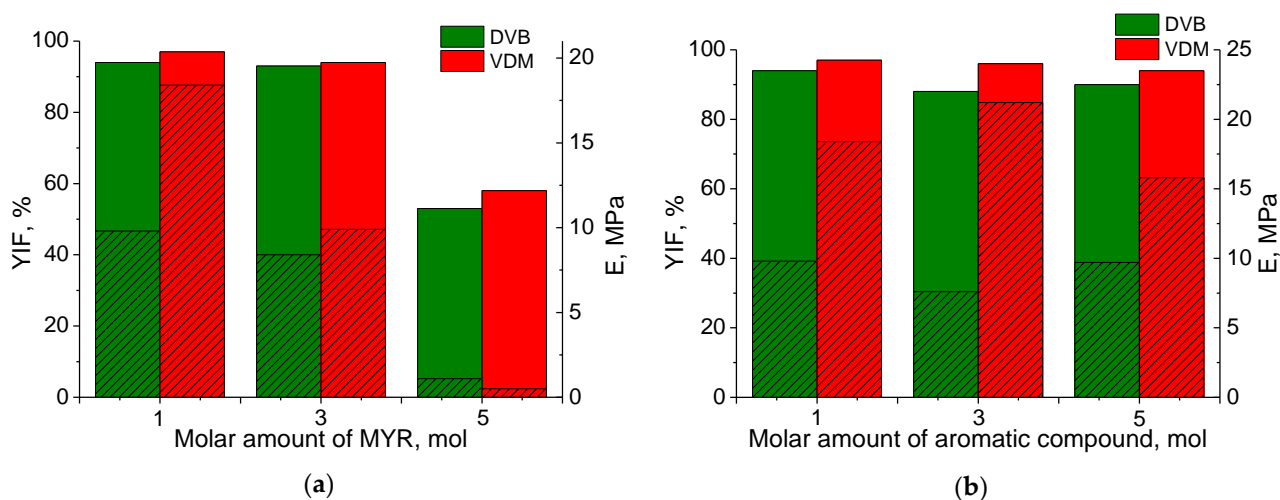
### 114 3.2. Characterization of photocross-linked polymer structure

115 Formed cross-linked polymer structure was confirmed by Soxhlet extraction. The yields of insoluble  
 116 fraction (YIF) of the cross-linked polymers were in the range of (53-99) % (Figure 4). It was observed that  
 117 polymers with higher amount of MYR caused lower YIF values of the cross-linked polymer confirming the  
 118 formation of MYR linear and/or branched polymer chains [15]. The higher YIF values of the photocross-linked  
 119 polymers with VDM fragments were observed compared to those with DVB fragments. This could be explained  
 120 by the acrylate ability exhibit high reaction rate and high values of YIF [16]. However, no significant influence  
 121 of the amount of aromatic component to the yield of insoluble fraction of the synthesized polymers was  
 122 observed.

### 123 3.2. Thermal properties

124 DSC confirmed that all synthesized photocross-linked polymers were amorphous materials. The values of  
 125 the glass transition temperatures ( $T_g$ ) of biobased polymers varied in the range of (-10.6 - -7) °C. (Figure 3b),  
 126 which were caused by the flexible chains of AESO and MYR. Due to the cross-linked structure, the solid state  
 127 of synthesized polymers at room temperature was observed. TGA confirmed that the photocross-linked

128 polymers exhibited high thermal stability. The 10 % weight loss temperatures ( $T_{\text{dec-10\%}}$ ) of all photocross-linked  
 129 polymers were in the close range and varied from 340 °C to 365 °C (Figure 3b).



130 **Figure 4.** The dependency of the Young's modulus (E) (striped) and yield of insoluble fraction (YIF) (solid) of the  
 131 polymers with different amounts of MYR (a) and aromatic compound (b).

### 132 3.2. Mechanical properties

133 The mechanical properties of the synthesized cross-linked polymer samples were investigated by the top  
 134 pressure test. It was determined that the value of the Young's modulus decreased when the higher amount of  
 135 MYR was added to the resin (Figure 4). This significant reduction of E was caused by the formation of soft and  
 136 flexible MYR chains followed by the formation of the lower amount of cross-links and leading to the loss of  
 137 polymer stiffness [17]. It was observed that the higher value of the Young's modulus was reached when the  
 138 higher yield of insoluble fraction was determined. Photocross-linked polymers with VDM fragments showed  
 139 the higher values of the Young's modulus compared to the polymers with DVB fragments, what could be due  
 140 to the higher values of YIF.

## 141 4. Conclusions

142 The novel cross-linked polymers were synthesized from acrylated epoxidized soybean oil, myrcene and  
 143 divinylbenzene or vanillin dimethacrylate by UV/VIS photopolymerization. It was determined that  
 144 photopolymerization rate and properties of the cross-linked polymers were highly depended on the resin  
 145 composition. It was observed that even though myrcene reduced the resin viscosity, it also significantly  
 146 prolonged the photocross linking reaction, and impaired mechanical properties of synthesized polymers. The  
 147 replacement of petroleum-derived aromatic component divinylbenzene by plant-derived vanillin dimethacrylate  
 148 led to the faster photocross linking reaction, improved mechanical and thermal properties of polymers. The  
 149 resin composed of only plant-derived monomers, acrylated epoxidized soybean oil, myrcene, and vanillin  
 150 dimethacrylate, molar ratio 1:1:3, showed the most favorable properties and was selected as a potential  
 151 renewable photoresin for application in optical 3D printing.

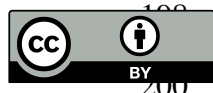
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154 **Author Contributions:** J.O. and M.L. conceived and designed the experiments, analyzed the data; M.L.  
 155 performed all experiments and characterizations. All of the Authors contributed to writing the manuscript.

156 **Conflicts of Interest:** The authors declare no conflicts of interest.

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