

1 *Conference Proceedings Paper*

2 **Vanillin acrylate-based photocross-linked polymers:** 3 **synthesis and investigation of properties**

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10 **Abstract:** Cross-linked polymers were obtained by photopolymerization of vanillin derivatives
11 (vanillin dimethacrylate and vanillin diacrylate) using ethyl(2,4,6-
12 trimethylbenzoyl)phenylphosphinate as photoinitiator. The changes of rheological properties were
13 examined during the curing process under ultraviolet/visible radiation. The influence of solvent,
14 amount of photoinitiator, and vanillin derivative to cross-linked polymer properties and reaction
15 rate was investigated.

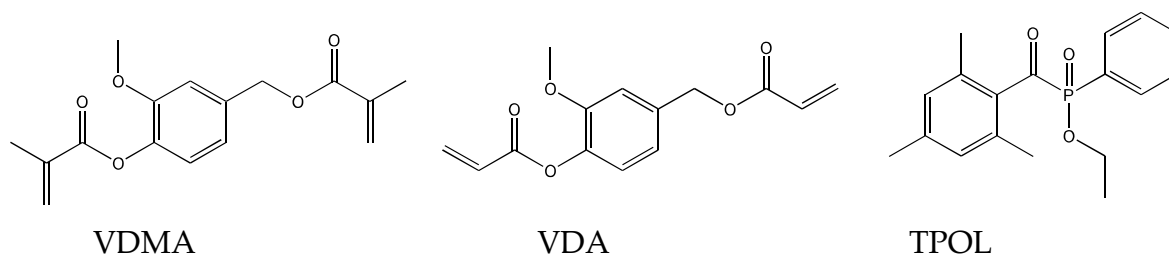
16 **Keywords:** vanillin dimethacrylate; vanillin diacrylate; photopolymerization.

18 **1. Introduction**

19 Vanillin produced by chemical modification of lignin is considered as natural vanillin and is 250
20 times cheaper than synthetic vanillin. Due to aromatic structure it could be able to replace widely
21 used petro-based aromatic monomers [1]. Photopolymerization engendered high interest both in
22 academia and in industry due to the considerable practical and economic benefits. Advantages of the
23 photopolymerization are following: high reaction speed, low energy consumption, high efficiency,
24 low volatile organic compound emission, and the large number of applications in not only
25 conventional areas such as coatings, inks, and adhesives, but also in high-tech domains, such as
26 microelectronics, optoelectronics, laser imaging, stereolithography, and nanotechnology [2-3].

27 In this study, cross-linked polymers were obtained by photopolymerization of vanillin
28 diacrylate (VDA) or vanillin dimethacrylate (VDMA) using ethyl(2,4,6-
29 trimethylbenzoyl)phenylphosphinate (TPOL) as photoinitiator (Figure 1.). TPOL was selected due to
30 the liquid form at room temperature and the high reaction rate [10]. Real-time photorheometry was
31 used to evaluate the influence of selected vanillin derivative, amount of photoinitiator, and the
32 presence of solvent to rigidity and photocross-linking rate of resulting polymers. Thermal properties
33 were investigated by differential scanning calorimetry and thermogravimetric analysis.

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Figure 1. Structure of vanillin dimethacrylate (VDMA), vanillin diacrylate (VDA) and ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate (TPOL)

40 2. Experiments

41 2.1. Materials

42 Ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate (TPOL) was purchased from Fluorochem.
 43 Vanillin diacrylate (VDA) and vanillin dimethacrylate (VDMA) were purchased from Specific
 44 Polymers. Dichloromethane (DCM) was purchased from Reachem Slovakia. All these materials were
 45 used as received.

46 2.2. Real-time photorheometry

47 UV/Vis real-time photorheometry curing tests were performed with resins containing 1 mol of
 48 vanillin derivative (VDMA or VDA) and 1, 3 or 5 mol.% of photoinitiator (TPOL) (Table 1) on a
 49 MCR302 rheometer from Anton Paar equipped with the plate/plate measuring system. The detailed
 50 description can be found in a previous publication [4].

51 **Table 1.** Composition of the resins C1-C9

Resin	Vanillin derivative	Amount of photoinitiator TPOL, mol.%	Solvent
C1	VDA	1	-
C2	VDA	1	DCM
C3	VDMA	1	DCM
C4	VDA	3	-
C5	VDA	3	DCM
C6	VDMA	3	DCM
C7	VDA	5	-
C8	VDA	5	DCM
C9	VDMA	5	DCM

52 2.3. Preparation of cross-linked polymer specimens

53 The resins, containing vanillin derivative (VDA or VDMA), a minimal amount of DCM and 1, 3
 54 or 5 mol.% of TPOL were stirred at room temperature (25 °C) with a magnetic stirrer until
 55 homogenous phase was reached. Then homogenous resins were poured into a Teflon mold and cured
 56 for 1-4 min under the Helios Italquartz UV lamp (model GR.E 500 W) with UV/Vis light at intensity
 57 of 310 mW/cm².

58 2.4. Characterization of thermal properties

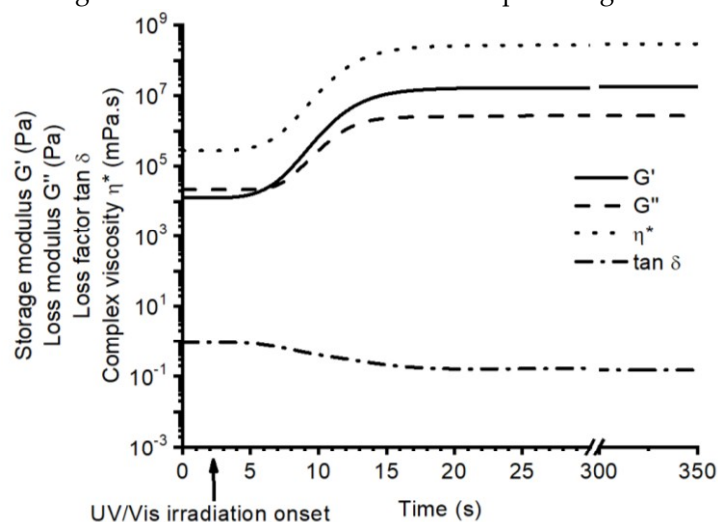
59 Differential scanning calorimetry (DSC) measurements were performed on a DSC 8500
 60 apparatus (Perkin Elmer, Llantrisant, UK), thermogravimetical analysis (TGA) was performed on

61 a TGA 4000 apparatus (Perkin Elmer, Llantrisant, UK). The detailed description can be found in a
 62 previous publication [5].

63 3. Results

64 3.1. Monitoring of photocross-linking kinetics by real-time photorheometry

65 Due to illumination of the photosensitive reaction mixture, G' , G'' , and η begin to increase
 66 rapidly due to the growth of polymer chain and the formation of polymer network. As the
 67 photopolymerization proceeds, G' increases faster and acquires higher values than G'' . Such a sudden
 68 increase in G' occurs due to the formation of polymer network, during which a high-viscosity
 69 Newtonian fluid turns into a solid elastic material. This phase transition is characterized by the point
 70 of intersection of G' and G'' , which is called a gel point. Subsequently, G' and G'' continue to increase
 71 as the reaction proceeds. Lower values of G'' compared to G' indicate higher elastic properties of the
 72 formed polymer network. The decrease in $\tan\delta$ during the crosslinking reaction indicates that the
 73 polymer becomes a solid elastic body. Figure 2 shows the evolution of storage modulus G' , loss
 74 modulus G'' , loss factor $\tan\delta$, and complex viscosity η^* of the VDA-based resin C4 during UV/Vis
 75 irradiation. [6]. The rheological characteristics of all tested samples are given in Table 2.



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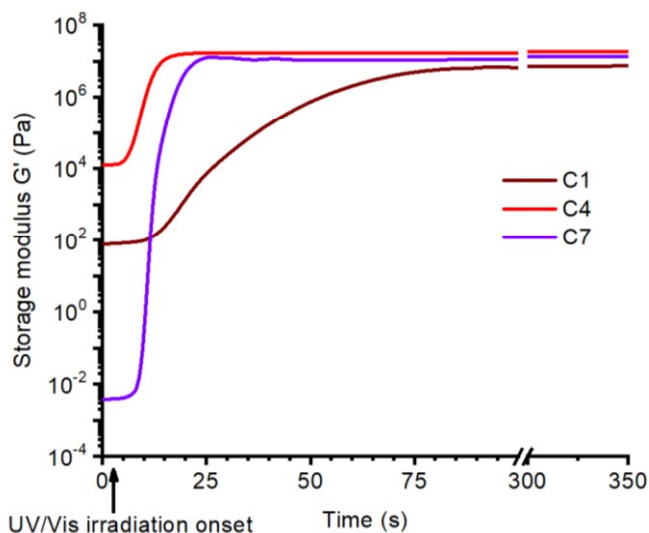
77 **Figure 2.** Dependencies of storage modulus G' , loss modulus G'' , loss factor $\tan\delta$, and complex
 78 viscosity η^* of the resin C4 on irradiation time

79 **Table 2.** Rheological characteristics of the resins C1-C9

Resin	Storage modulus G' , MPa	Complex viscosity η^* , mPa.s	Loss modulus G'' , MPa	Gel point ^a t_{gel} , s
C1	7.35	0.15	6.34	10
C2	13.40	0.22	2.35	20
C3	13.00	0.21	1.65	6
C4	18.10	0.29	2.70	6
C5	11.30	0.18	1.64	12
C6	18.20	0.29	2.94	5
C7	13.30	0.23	5.78	10
C8	14.50	0.23	2.02	14
C9	19.80	0.32	3.36	6

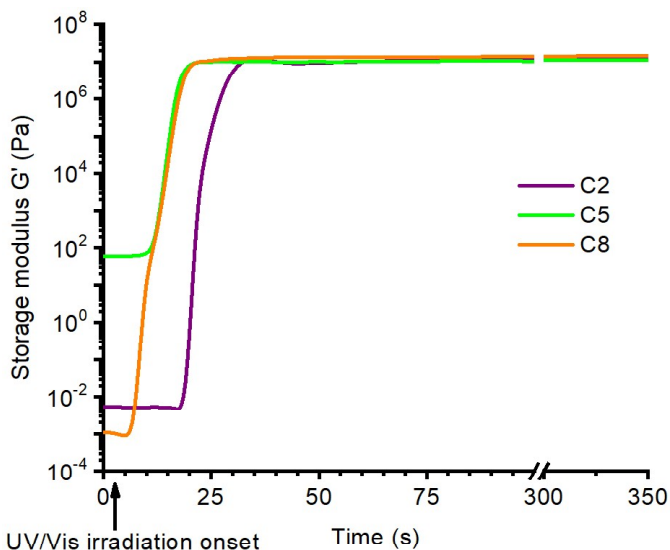
80 a- calculated from the UV/Vis irradiation onset.

81 Comparing the shape of the storage modulus curves of the resins with different concentration of
 82 photoinitiator, the highest final rigidity and the fastest photocross-linking was demonstrated by the
 83 resin C4 with 3 mol.% of TPOL in the VDA-based resins without solvent series (C1, C4 and C7) (Figure
 84 3.).



85
 86 **Figure 3.** Dependencies of storage modulus G' of the VDA-based resins C1, C4 and C7 with different
 87 amount of photoinitiator on irradiation time

88 The presence of solvent had the higher influence to the photocross-linking rate than the concentration
 89 of photoinitiator. In VDA-based resins with solvent series (C2, C5 and C8), the photocross-linking
 90 rate of resins with 3 mol.% and 5 mol.% of TPOL (C5 and C8 respectively) was similar and faster than
 91 that of the resin C2 with 1 mol.% of TPOL, although the more rigid polymer was obtained from the
 92 resin C8 (Figure 4.).

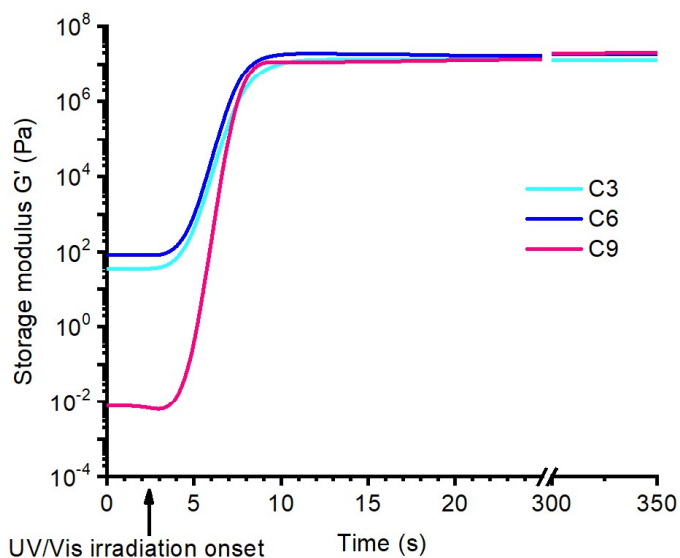


93
 94 **Figure 4.** Dependencies of storage modulus G' of the VDA-based resins C2, C5 and C8 with different
 95 amount of photoinitiator on irradiation time

96 In VDMA-based resins with solvent series (C3, C6 and C9), the photocross-linking rate did not
 97 depend on the concentration of TPOL, although the more rigid polymer was obtained from the resin

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C9 with 5 mol.% of TPOL (Figure 5). Comparing the gel points (t_{gel}) of the resins (Table 2), the t_{gel} was reached the fastest when 3 mol.% of photoinitiator was used in the case of all resin series.



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Figure 5. Dependencies of storage modulus G' of the VDMA-based resins C3, C6 and C9 with different amount of photoinitiator on irradiation time

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103 3.2. Thermal properties of photocross-linked polymers

104 Thermal characteristics of the photocross-linked polymers C4-C6 were obtained DSC and TGA
105 experiments. Vanillin-based polymers are amorphous materials, only the glass transition
106 temperature is visible in DSC curves. Polymer C5 demonstrated the lowest glass transition
107 temperature (63 °C). Polymers C4 and C6 demonstrated similar glass transition temperature 87 °C
108 and 86 °C, respectively. The glass transition temperatures of obtained vanillin-based polymers are
109 similar to the acrylate resins based on natural phenolics, which were presented as candidate materials
110 for stereolithography (79 °C) [7].

111 Thermogravimetical analysis was used to investigate thermal decomposition of vanillin-based
112 polymers. The temperature of 10 % weight loss ($T_{dec.-10\%}$) was the highest for VDA-based polymer C4
113 (350 °C). C5 and C6 polymers, which were prepared with DCM, both demonstrated lower
114 temperature of 10 % weight loss (330 °C and 340 °C, respectively). $T_{dec.-10\%}$ of obtained vanillin-based
115 polymers is similar or even slightly higher than $T_{dec.-10\%}$ of some acrylated epoxidized soybean oil
116 based polymers (297 - 356 °C) tested in optical 3D printing [8].

117 4. Conclusions

118 Novel vanillin acrylate-based cross-linked polymers were obtained by the photopolymerization of vanillin
119 diacrylate and vanillin dimethacrylate using ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate as photoinitiator.
120 Investigation of photopolymerization kinetics revealed that no use of solvent and usage of 3 mol.% of ethyl(2,4,6-
121 trimethylbenzoyl)phenylphosphinate increased polymer rigidity. Photopolymerization was the fastest when 3
122 mol.% of photoinitiator were used. Vanillin dimethacrylate-based systems showed lower values of gel point and
123 polymerized faster than vanillin diacrylate-based systems. Polymers with the fragments of vanillin diacrylate
124 without solvent performed higher values of thermal stability. The designed vanillin-based compositions could
125 be used as photosensitive resins in optical 3D printing.

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128 **Author Contributions:** J.O., A.N. and G.M. conceived and designed the experiments, analyzed the data; A.N.
129 performed all experiments and characterizations.

130 **Conflicts of Interest:** The authors declare no conflict of interest.

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