

Article

Effects of the Amount and Type of Diol Ring Openers on the Properties of Oligolactide Acrylates for UV-Curable Printing Inks

Santi Kulsiriswad¹, Kawee Srikulkit^{1,2} and Onusa Saravari^{1,*}

¹ Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand; santi.kulsiriswad@gmail.com (S.K.); kawee.s@chula.ac.th (K.S.)

² Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

* Correspondence: sonusa@chula.ac.th; Tel.: +66-2218-5544

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Abstract: This study aimed to synthesize low viscosity oligolactide acrylates for UV-curable inks from oligolactide diols. Firstly, low molecular weight oligolactide diols were prepared by ring opening reaction of L-lactide with diols. Oligolactide acrylates were then synthesized by functionalizing the oligolactide diols with acrylic acid. In this study, three diol ring openers having short and long alkyl chain length were used to investigate the effects of the amount and type of diols on the properties of the oligolactide acrylates. The obtained oligomers were characterized, and the viscosities of oligolactide acrylates were measured. Results showed that oligolactide acrylates were successfully synthesized in all cases of ring openers, as confirmed by ¹H-NMR (proton nuclear magnetic resonance spectroscopy) and FTIR (Fourier transform infrared spectroscopy). An increase in the alkyl chain length of the ring openers resulted in oligomers with lower viscosity and a decrease in T_g . Following that, the obtained oligolactide acrylates were employed for the formulation of UV-curable screen printing inks and their properties were investigated. Results showed that the inks formulated from oligomers with lower molecular weight exhibited better ink flow. Additionally, all ink films cured by UV radiation were very flexible with excellent adhesion, high impact resistance, and excellent water resistance.

Keywords: oligolactide; acrylate; UV-curable; printing ink

1. Introduction

Acrylate oligomers are the main vehicles found in the formulation of UV-curable screen printing ink. These types of oligomers contain the acrylate functional group, which exhibits the highest reactivity compared to other ethylenically unsaturated groups in terms of free radical polymerization [1]. Typically, acrylate oligomers are synthesized from conventional synthetic oligomers such as oligoester and oligourethane containing hydroxyl end groups. Such a hydroxyl end group is able to react with acrylic acid to yield an oligomer possessing vinyl double bonds. At present, the conventional synthetic oligomer starting materials are generally manufactured from petroleum which is a non-renewable resource. To date, researches of UV-curable printing inks are focused on exploitation of renewable resources, particularly vegetable oils [2–4].

Poly lactide is a polyester polymer made from lactic acid, which is produced from renewable resources such as tapioca starch, corn starch, or sugarcane. This environmentally friendly polymer has been widely used in medical and pharmaceutical applications because of its biocompatibility and biodegradability [5]. Referring to previous papers, poly lactides containing vinyl end groups were

synthesized and their thermal or UV curing behaviors were investigated [6,7]. As far as an application in UV-curable screen printing inks is concerned, ink formulation with low viscosity is desirable. To obtain low viscosity ink formulation, acrylate monomers are usually employed [8]. Apart from being diluents, these monomers play an important role in improving the coating properties of ink such as flexibility, adhesion, etc. [9]. Unfortunately, due to their high molecular weights, polylactide acrylates are too viscous to be diluted by reactive monomers and to be applied by the screen printing process. Therefore, oligolactide acrylates could possibly be used for the replacement of polylactide acrylates in this case.

Starting oligolactides can be synthesized by ring opening polymerization of lactide monomers or by depolymerization of polylactide such as glycolysis [10]. The ring opening polymerization is preferable when compared to other routes because the reaction consumes low reaction temperature and short reaction time. By carefully controlling reaction parameters such as the type and the amount of the ring openers, reaction time, and temperature, the low molecular weight oligolactides can be synthesized. Using a suitable polyol molecule as a ring opener, oligolactide with only hydroxyl end groups—oligolactide diol—can be obtained [11–14]. The oligolactide diols can be further functionalized with acrylic acid, resulting in oligolactide acrylates. The functionalization is an esterification reaction between hydroxyl groups of oligolactide diols and carboxylic groups of acrylic acid. The reaction is conducted in the presence of an acid esterification catalyst and a polymerization inhibitor under azeotropic distillation [15]. The acrylic acid is employed in excess in order to drive the reaction forward. The acrylic acid residue in the oligomers can be removed by washing with dilute caustic soda. However, the acid residue remains in most cases and emulsions which are difficult to separate are also formed during the washing process [16]. Preferably, the acrylic acid residue is converted into acrylate monomer by neutralizing with chemicals. Neutralization of the acid residue by reacting with epoxy compounds is preferred since the neutralization products can be further employed for ink formulation without removal [17]. Our previous study showed that an oligolactide acrylate prepared by functionalization of an oligolactide diol synthesized from the ring opening reaction of L-lactide with 1,6-hexanediol in melt reaction condition can be used in UV-curable application [14].

Therefore, the purpose of this research was to investigate the effects of the amount and type of diol ring openers having different alkyl chain length on the properties of the obtained oligolactide acrylates. The oligolactide diols were firstly synthesized by ring opening reaction of L-lactide with three types of diol ring openers in solution reaction condition. After that, the oligolactide diols were functionalized with acrylic acid and the residual acrylic acid was neutralized with diglycidyl ether of bisphenol A. Screen printing inks were then formulated from the obtained oligolactide acrylates and the properties of ink films achieved by UV-curing were tested and compared with that prepared from a commercial polyester diacrylate oligomer (EB524).

2. Materials and Methods

2.1. Materials

The L-lactide monomer, Puralact B3, was kindly provided by Purac (Thailand) Ltd. (Rayong, Thailand), and 1,4-butanediol (BD) by Catalite Co., Ltd. (Bangkok, Thailand). 1,6-hexanediol (HD), 1,10-decanediol (DD), tin(II) 2-ethylhexanoate (stannous octoate), acrylic acid (AA), p-toluenesulfonic acid monohydrate (p-TSA), tert-butylhydroquinone (DBHQ), and tributylamine (TBA) were purchased from Sigma Aldrich (St. Louis, MO, USA). Diglycidyl ether bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 190 g/eq was purchased from Brenntag Ingredients (Thailand) Company Limited (Public) (Bangkok, Thailand). Toluene was purchased from Union Petrochemical PCL (Bangkok, Thailand). Hexanediol diacrylate (HDDA) and triphenylphosphine oxide (TPO) were purchased from Innovachem Co., Ltd. (Bangkok, Thailand). A mixture of Oxy-phenyl-acetic acid 2-[2-oxo-2-phenyl-acetoxy-ethoxy]-ethyl ester and Oxy-phenyl-acetic acid 2-[2-hydroxy-ethoxy]-ethyl ester (Irgacure 754) was purchased from Merit Solution Co., Ltd. (Bangkok, Thailand). A polyester

diacrylate oligomer (EB524) was kindly given from Behn Meyer Chemicals (T) Co., Ltd. (Bangkok, Thailand). Polyether-modified polydimethylsiloxane (BYK-333) was purchased from Colossal International Co., Ltd. (Bangkok, Thailand). Carbon black (Printex 25) was purchased from Jebsen & Jessen Technology (T) Ltd. (Bangkok, Thailand). All materials were used as received without further purification.

2.2. Synthesis of Oligolactide Diols (OL-OHs)

Oligolactide diols were synthesized by ring opening reaction of L-lactide and three kinds of aliphatic diol ring openers: BD, HD, and DD. The amounts of the ring openers, as illustrated in Table 1, were controlled in order to obtain oligolactide diols with the molecular weight of 900, 1200, and 1500 g/mol. The synthesis commenced by adding predetermined amounts of L-lactide and a ring opener into a 250-mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer, a nitrogen gas inlet tube, a Dean–Stark separator (Sigma Aldrich, St. Louis, MO, USA), and a condenser. Toluene 10% *w/w* of the total weight of L-lactide and a ring opener was then filled in to the flask. The temperature was raised to 160 °C and the mixture was refluxed under stirring for 15 min. The mixture was then cooled to 80 °C and stannous octoate 0.1 mol % of L-lactide was added. The temperature was raised to 125 °C and the mixture was stirred at this temperature for 8 h [12]. The obtained samples were labelled according to their theoretical molecular weight. For example, an oligolactide diol produced from BD having theoretical molecular weight of 900 g/mol is designated as BDOH-900.

Table 1. Formulations of the as-synthesized OL-OHs.

Sample	L-Lactide (g)	Diol (g)	Stannous Octoate (g)	Toluene (g)
BDOH-900	100.00	11.11	0.28	11.11
BDOH-1200	100.00	8.11	0.28	10.81
BDOH-1500	100.00	6.38	0.28	10.64
HDOH-900	100.00	15.07	0.28	11.51
HDOH-1200	100.00	10.86	0.28	11.09
HDOH-1500	100.00	8.58	0.28	10.86
DDOH-900	100.00	24.07	0.29	12.41
DDOH-1200	100.00	16.96	0.28	11.70
DDOH-1500	100.00	13.12	0.28	11.31

2.3. Synthesis of Oligolactide Acrylates (OL-As)

UV-curable oligolactide acrylates were synthesized by functionalizing OL-OHs obtained from the previous step with AA at hydroxyl to carboxyl ratio of 1:1.25. AA was added into a 250-mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer, a nitrogen gas inlet tube, a Dean–Stark separator, and a condenser. The stoichiometric amount was calculated from the theoretical molecular weight of each OL-OH. Subsequently, p-TSA (1% *w/w*), DBHQ (0.1% *w/w*), and toluene (35% *w/w*) were added into the flask. The mixture was heat to 130 °C under nitrogen blanket for 16 h. After that, the solvent and unreacted acrylic acid was removed by distillation under reduced pressure at 25 inHg at 130 °C for 2 h [15]. The amount of residual acrylic acid in each OL-A was determined by acid value determination according to ASTM D1639 [18]. The residual acrylic acid was neutralized by reacting with DGEBA (equimolar amount of residual AA) using tributylamine as a catalyst at 110 °C for 4 h. Acid values of the OL-As after neutralization were also determined. The obtained samples were labelled according to their original oligolactide diols. For example, an oligolactide acrylate produced from BDOH-900 is designated as BDA-900, and its neutralized acrylate is designated as BDAN-900.

2.4. Characterization of Oligolactide Diols (OL-OHs) and Oligolactide Acrylates (OL-As)

The functional groups and structures of the OL-OHs and the OL-As were analyzed using Fourier transform infrared spectroscopy (FTIR) on a Spectrum 100 spectrometer with Universal

ATR (PerkinElmer, Waltham, MA, USA). The chemical structures of the oligomers were characterized by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) on a Fourier 300 NMR spectrometer (Bruker, Billerica, MA, USA) at 300 MHz using CDCl_3 as a solvent. The number-average molecular weights of the OL-OHs were calculated from peak integrals of $^1\text{H-NMR}$ spectra. The thermal behavior of the oligomers was examined by differential scanning calorimetry (DSC) on DSC 204 F1 Phoenix (NETZSCH, Selb, Germany) at a heating rate and cooling rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen gas at a flow rate of $30\text{ mL}/\text{min}$. The sample was first heated from $-80\text{ }^\circ\text{C}$ to $180\text{ }^\circ\text{C}$ and then cooled to $-80\text{ }^\circ\text{C}$. After being kept isothermally at $-80\text{ }^\circ\text{C}$ for 5 min, the sample was reheated to $180\text{ }^\circ\text{C}$. Glass transition temperature (T_g) of the oligomers were determined from a second heating scan. Viscosities of the OL-As were measured by a cone and plate viscometer High Shear CAP-2000+ (Brookfield Engineering, Middleboro, MA, USA) at $25\text{ }^\circ\text{C}$ using a cone number 6 and viscometer speed was set in the range of 10–110 rpm.

2.5. Preparation of UV-Curable Screen Printing Inks

Clear UV-curable screen printing inks were prepared from the OL-As. Firstly, all OL-As were heated to $60\text{ }^\circ\text{C}$ and diluted with HDDA (30% *w/w*). The diluted OL-A (60% *w/w*) were mixed with HDDA (34% *w/w*), Irgacure 754 (5% *w/w*), and BYK-333 (1% *w/w*) by a high-speed mixer at a speed of 500 rpm for 15 min. Viscosities of the inks were measured at $25\text{ }^\circ\text{C}$ by CAP 2000+ viscometer using a cone number 1 at a speed of 50 rpm. The prepared inks were applied onto polylactide sheets through a 140 lines/cm polyester screen printing mesh with wet film thickness of 15 microns. The ink was cured at $25\text{ }^\circ\text{C}$ under a UV curing unit having a 3 kW, medium-pressure mercury lamp at a belt speed of 20 m/min. The integral UV intensity of UVB was $200\text{ mJ}/\text{cm}^2$ measured by UV Power Puck II (EIT Instrument, Sterling, VA, USA).

2.6. Characterization of UV-Curable Screen Printing Inks

The thermal property of the cured inks was examined by DSC. UV curing ability of the inks was investigated using FTIR by calculating the percentage conversion of the acrylate double bond using Equation (1) [19]:

$$\text{Double bond conversion (\%)} = \left[1 - \frac{\left[\frac{A(\text{C}=\text{C})}{A(\text{C}=\text{O})} \right]_i}{\left[\frac{A(\text{C}=\text{C})}{A(\text{C}=\text{O})} \right]_0} \right] \times 100 \quad (1)$$

where $A(\text{C}=\text{C})$ and $A(\text{C}=\text{O})$ represent integrated areas of acrylate double bond in the range of 1395 and 1424 cm^{-1} and carbonyl group in the range of 1661 to 1807 cm^{-1} , respectively, before UV curing (0) and after UV curing (i). The solvent resistance rub test according to ASTM D4752 [20] was used to evaluate the degree of cure of the inks by rubbing the cured ink film with methyl ethyl ketone (MEK) with a maximum of 200 double rubs. The printed samples were tested for adhesion by tape test according to ASTM D3359 [21], flexibility using a conical mandrel test apparatus (Sheen Instruments, Cambridge, UK), impact resistance using an impact tester (Sheen Instruments), and hardness by a pencil hardness tester (Sheen Instruments) according to ASTM D3363 [22]. Furthermore, water resistance was also determined based on ASTM D1647 [23]. The properties were then compared with a screen printing ink formulated from EB524, a commercial polyester diacrylate oligomer product. Additionally, a black screen printing ink was prepared from BDAN-900. The black ink was printed and cured by the same method as the clear one and the appearance of the ink print on a polylactide sheet was compared to that of a black printing ink made from EB524.

3. Results and Discussion

3.1. Synthesis of Oligolactide Diols (OL-OHs)

Oligolactide diols were synthesized from the ring opening reaction of L-lactide with three kinds of diol ring openers: BD, HD, and DD. The ring openers were selected from diols having short and

long alkyl chain length to investigate the effect of diol types on OL-OH properties. The proposed reaction scheme of the lactide oligomer synthesis together with the chemical structures of BD, HD, and DD, are given in Figure 1. The FTIR spectra of BDOH-900, HDOH-900, and DDOH-900 shown in Figure 2 exhibit the C–H stretching peaks at 3000, 2952, and 2891 cm^{-1} and the C–H bending peaks at 1387 and 1363 cm^{-1} , indicating the aliphatic structure of these OL-OHs. It can be seen that the intensities of the C–H stretching peaks increase as the methylene bridge (–CH₂–) in the ring openers increase. Two peaks appearing at 873 and 755 cm^{-1} are attributed to C–C stretching, while the peaks at 1185, 1131, 1089, and 1041 cm^{-1} are related to C–O–C stretching. The strong peak at 1751 cm^{-1} and the weak peak at 1276 cm^{-1} are assigned to the C=O and C–O stretching of ester groups, respectively. The broad peak at wavenumber around 3530 cm^{-1} reflects the presence of hydroxyl groups, whereas the –CH₃ bending peak can be seen at 1458 cm^{-1} [13,24]. Moreover, the absorption peak for –CO–O– ring of L-lactide at 934 cm^{-1} is not observed in all FTIR spectra, indicating that L-lactide monomer underwent ring-opening reaction with diol [25]. FTIR results suggest that the structures of the synthesized OL-OHs are aliphatic esters having hydroxyl groups.

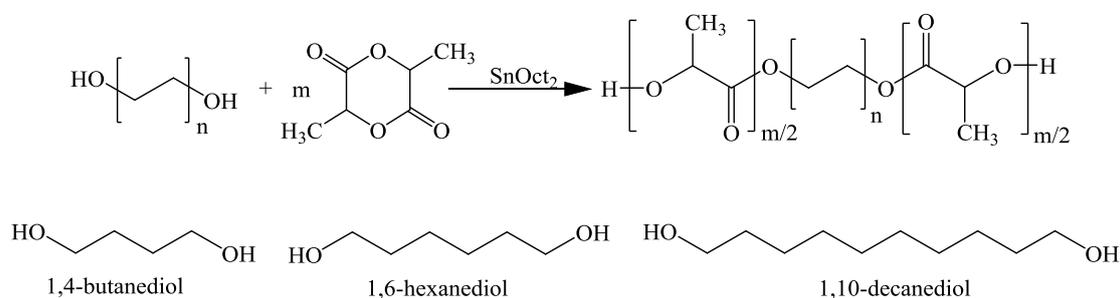


Figure 1. Ring opening reaction scheme of L-lactide with diol ring openers.

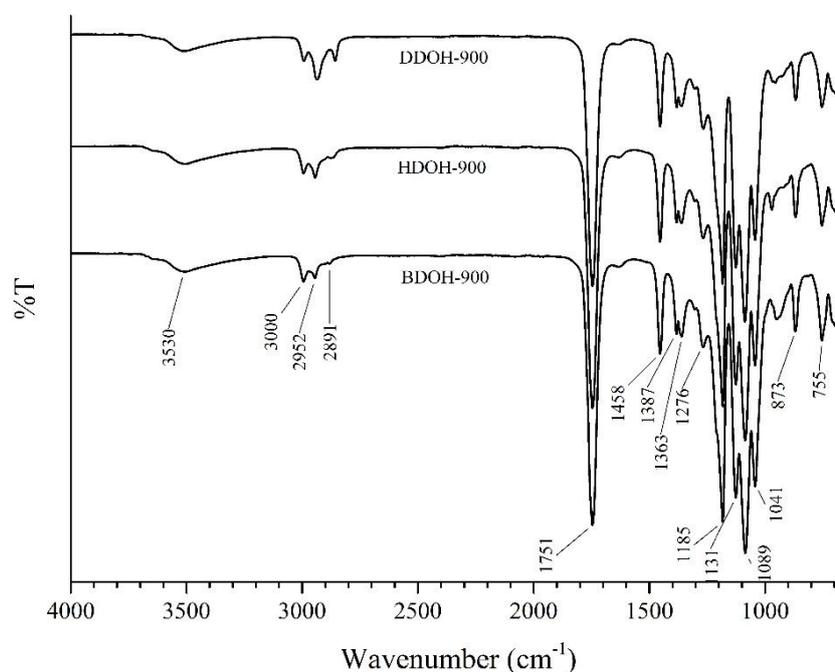


Figure 2. FTIR spectra of BDOH-900, HDOH-900, and DDOH-900.

Figure 3 shows the ¹H-NMR spectra of the synthesized OL-OHs with peak assignments. The strong peak at 5.18 ppm (a) and the weak peak at 4.32 ppm (a') are attributed to methine protons of the lactide unit in the repeating unit and at the chain end next to the terminal hydroxyl group,

respectively. The peaks at 1.56 ppm (b) and 1.38 ppm (b') are related to methyl protons of the lactide unit in the repeating unit and at the end next to the terminal hydroxyl group, respectively. The peaks at 4.12 ppm (c) and the peaks at 1.27 ppm, 1.34 ppm, and 1.69 ppm (d) are attributed to the outer and inner methylene protons of alkane diol ring openers, respectively. The peak at 2.88 ppm (e) is assigned to the protons of the terminal hydroxyl groups [13,26]. Similar to the FTIR result, the peak at 5.00 ppm belonging to methine protons of the lactide ring is not observed, indicating that L-lactide monomer completely underwent ring-opening reaction with the diol. FTIR and $^1\text{H-NMR}$ results are in good agreement with the structure of the OL-OH presented in Figure 1. Therefore, it can be concluded that the oligolactide diols were successfully synthesized.

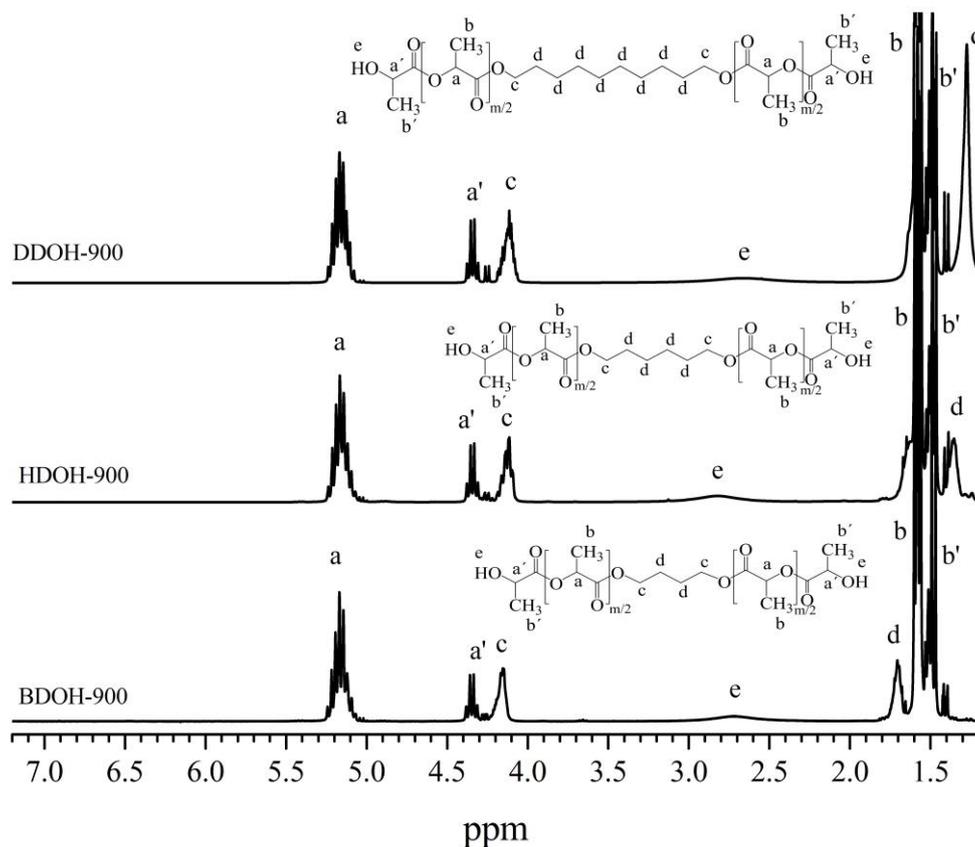


Figure 3. $^1\text{H-NMR}$ spectra of BDOH-900, HDOH-900, and DDOH-900.

3.2. Molecular Weights of Oligolactide Diols (OL-OHs)

From peak integrals of $^1\text{H-NMR}$ spectra, the number-average molecular weights (M_n) of the OL-OHs can be calculated through the degree of polymerization (DP) of the synthesized oligomers using Equations (2) and (3):

$$DP = (I_{5.18} + I_{4.32})/I_{4.32} \quad (2)$$

$$M_n = 144DP + MW_{diol} \quad (3)$$

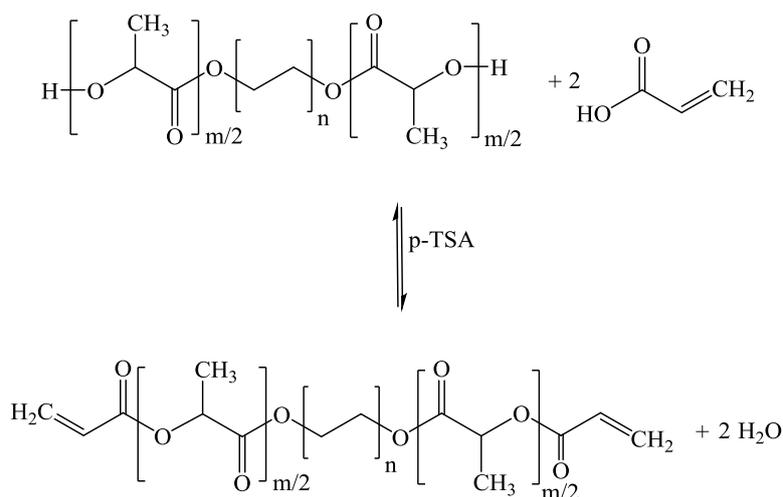
where $I_{5.18}$ and $I_{4.32}$ are the integral intensity of the peaks at 5.18 ppm (a) and 4.32 ppm (a'), respectively. 144 is the mass of the lactide repeating unit, and 2 is the mass of hydrogen atoms at the chain end. MW_{diol} is the mass of the ring openers. The DP and M_n values of the obtained OL-OHs are illustrated in Table 2. The molecular weights of OL-OHs range from 910 to 1487 g/mol which are close to the theoretical values. It can also be observed that M_n of OL-OH decreases when the amount of ring openers increases (Table 1). This observation is previously reported [14]. The results reveal that it is possible to tailor oligolactide diol of specific molecular weight.

Table 2. Molecular weights of synthesized oligolactide diols.

Sample	Theoretical		¹ H-NMR	
	DP	M _n (g/mol)	DP	M _n (g/mol)
BDOH-900	5.6	900	5.7	910
BDOH-1200	7.7	1200	7.3	1146
BDOH-1500	9.8	1500	8.7	1342
HDOH-900	5.4	900	5.8	958
HDOH-1200	7.5	1200	7.3	1176
HDOH-1500	9.6	1500	9.0	1413
DDOH-900	5.0	900	5.7	988
DDOH-1200	7.1	1200	7.5	1259
DDOH-1500	9.2	1500	9.1	1487

3.3. Synthesis of Oligolactide Acrylates (OL-As)

Oligolactide acrylates were synthesized by functionalizing oligolactide diols with acrylic acid (AA) using p-toluenesulfonic acid monohydrate as a catalyst. The reaction was carried out in the presence of a small amount of tert-butylhydroquinone acting as an inhibitor to prevent premature polymerization of AA during functionalization. The proposed reaction scheme of the functionalization of OL-OH with AA is shown in Figure 4. The FTIR spectrum of the OL-A (BDA-900), as displayed in Figure 5, shows the C=C stretching of acrylate groups at wavenumber of 1640 and 1626 cm⁻¹, while the peaks of =CH₂ bending, wagging, and twisting of acrylate groups are found at 1408, 988, and 810 cm⁻¹, respectively. Additionally, as compared with the FTIR spectrum of OL-OH (BDOH-900), the intensity of the peak at 3530 cm⁻¹ belonging to the hydroxyl groups decreases, indicating the reaction between the hydroxyl groups of the oligomer diol and the carboxyl groups of AA. The ¹H-NMR spectrum of the BDA-900 is shown in Figure 6. After functionalization, the signals of the characteristic peaks of protons of the acrylate double bond are detected at 6.42 ppm (g), 6.13 ppm (h), and 5.81 ppm (i). The peak intensity at 4.32 ppm representing methine protons of the lactide unit at the chain end next to the terminal hydroxyl group decreases, indicating the functionalization of oligolactide diol.

**Figure 4.** Acrylate functionalization scheme of an oligolactide diol with acrylic acid.

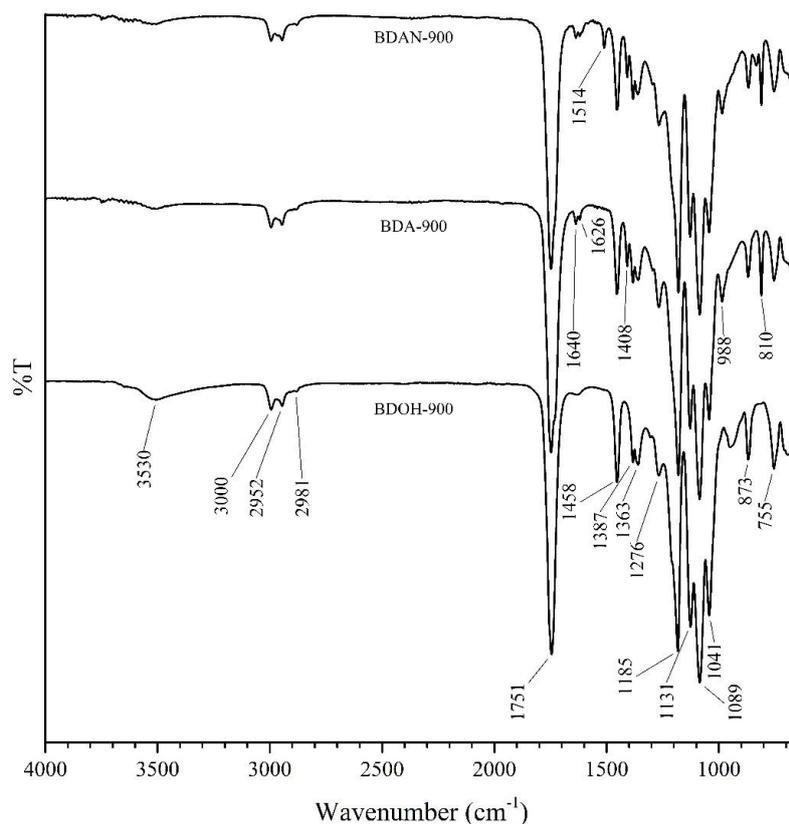


Figure 5. FTIR spectra of BDOH-900, BDA-900, and BDAN-900.

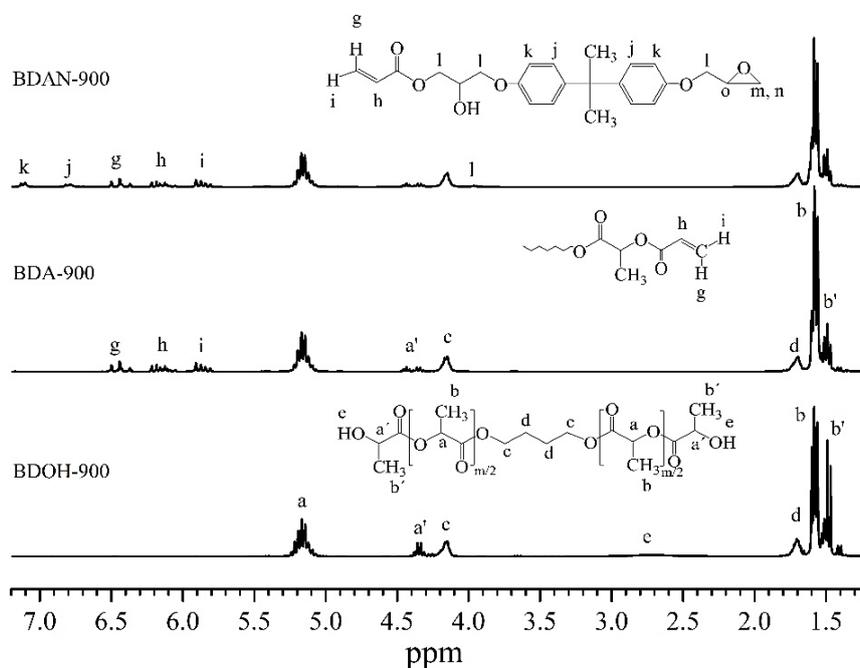


Figure 6. $^1\text{H-NMR}$ spectra of BDOH-900, BDA-900, and BDAN-900.

The degrees of functionalization calculated from the ratio of the integrated peak areas between 4.32 ppm and 5.81–6.42 ppm range from 49% to 69% for all samples as shown in Table 3. It can be observed that the degree of functionalization is higher when the molecular weight of OL-As is

lower and the alkyl chain length is longer. This is probably due to the lower viscosity of the reaction mixture. The fact that the degree of functionalization did not proceed to 100% might be because the functionalization is a reversible esterification reaction. Inefficient removal of the byproduct (water) may lead to the reversal of the reaction, resulting in incomplete functionalization. As previously reported, the functionalization with methacrylic anhydride provided a higher degree of functionalization (87% for BDA-1500) which is due to the irreversible transesterification reaction between hydroxyl and anhydride compounds [27].

Table 3. H-NMR integrals and degrees of functionalization of OL-As.

Sample	¹ H-NMR Integral				Degree of Functionalization (%)
	I _{6.42}	I _{6.13}	I _{5.81}	I _{4.32}	
BDA-900	1.00	0.93	0.99	0.57	63%
BDA-1200	1.00	0.94	1.01	0.83	54%
BDA-1500	1.00	0.97	1.02	1.04	49%
HAD-900	1.00	1.00	1.06	0.62	62%
HAD-1200	1.00	0.97	1.03	0.68	59%
HAD-1500	1.00	0.97	1.01	0.74	57%
DDA-900	1.00	0.96	1.02	0.46	69%
DDA-1200	1.00	0.97	1.02	0.59	63%
DDA-1500	1.00	0.91	0.98	0.75	56%

After vacuum distillation of the functionalized product to remove the azeotropic solvent and unreacted acrylic acid, it was found that some residual acrylic acid still remained in the product, as confirmed by acid value determination. The acid values of the obtained OL-As were around 10–15 mg KOH/g as shown in Table 4. In general, the acid value of the UV-curable acrylate oligomers should be lower than 5 mg KOH/g to avoid de-stabilization of the products during storage and skin irritation when handling [28]. Thus, the neutralization of the residual acrylic acid was performed by reacting with diglycidyl ether bisphenol A (DGEBA). From the FTIR spectrum of the neutralized oligolactide acrylate, BDAN-900, in Figure 5, the peak of C–C stretching of aromatic ring of bisphenol A is found at 1514 cm⁻¹, while the peaks of the C–O–C stretching and C–O stretching of oxirane ring at 831 and 915 cm⁻¹, respectively, are not observed. This indicates that the residual acrylic acid reacted with DGEBA via oxirane ring opening reaction as confirmed by a decrease in the acid value of OL-As after neutralization from 10–15 mg KOH/g to 3–5 mg KOH/g, as summarized in Table 4. As seen in Figure 6, the ¹H-NMR spectrum of BDAN-900 exhibits the peaks at 6.84 ppm (j) and 7.12 ppm (k) corresponding to the bisphenol A aromatic protons, while the weak peak at 3.69 ppm (l) belongs to the methylene protons of the glycidyl groups. Moreover, the peaks at 2.75 ppm (m), 2.89 ppm (n), and 3.33 ppm (o) relating to the protons of the oxirane ring disappear. ¹H-NMR result also indicates that DGEBA was completely reacted with the residual acrylic acid resulting in DGEBA acrylate which could be employed in the ink formulation without removal. The proposed neutralization reaction scheme is illustrated in Figure 7.

Table 4. Acid value and viscosity of oligolactide acrylates.

Sample	Acid Value (mg KOH/g)		Viscosity (mPa·s)
	Before Neutralization	After Neutralization	
BDAN-900	14.6	4.6	5300
BDAN-1200	12.3	4.1	13,000
BDAN-1500	15.1	3.1	23,000
HDAN-900	11.0	4.7	3700
HDAN-1200	13.0	3.9	12,300
HDAN-1500	14.6	4.5	18,300
DDAN-900	10.4	4.3	2900
DDAN-1200	10.5	5.1	8500
DDAN-1500	13.3	4.4	13,900

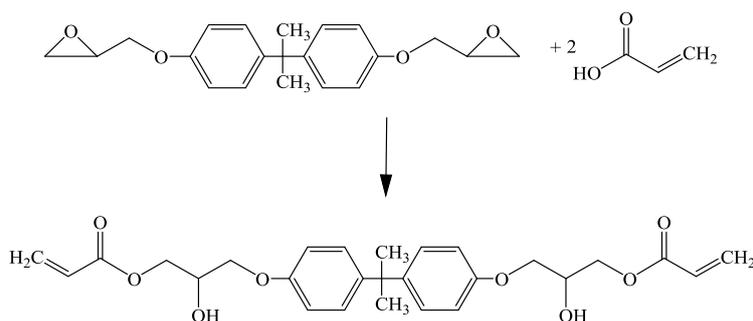


Figure 7. Neutralization reaction scheme of acrylic acid with diglycidyl ether bisphenol A [29].

3.4. Rheological Behavior of Oligolactide Acrylates

From experiments, the so obtained OL-As exhibit too high viscosity to be measured by a Brookfield viscometer. To reduce the viscosity, 30% (*w/w*) of hexanediol diacrylate (HDDA) as a diluent was added into OL-As. Viscosity values of the HDDA diluted OL-As measured at a shear rate of $1/166 \text{ s}^{-1}$ are summarized in Table 4. Results show that the viscosity values of OL-As ranging from 2900 to 23,000 mPa·s are recorded, suggesting that the as-prepared acrylate oligomers could be used for screen printing ink formulations.

As observed, the viscosity of OL-As was dependent on their molecular weight; the higher the molecular weight, the higher the viscosity. When considering the types of ring openers, the one having longer alkyl chain length was found to have lower viscosity. For example, HDAN-900 and BDAN-900 which have similar molecular weights of 958 g/mol and 910 g/mol, exhibited quite different viscosities of 3700 mPa·s and 5300 mPa·s, respectively. This might be due to the fact that the longer chain length exhibited less intermolecular hydrogen bonding interaction. Figure 8 represents the rheological behavior of the OL-As. It can be observed that all OL-As exhibit shear thinning behavior for which the viscosity decreases as the shear rate increases. This is probably because the hydrogen bonds between the oligomer chains are broken when the shear force is being applied, allowing the molecules to move more easily past one another. The higher the shear force, the more the hydrogen bonding is destroyed and the more easily the oligomer chains flow past each other, and so the lower the viscosity is. Moreover, it is observed that the yield stress of OL-As decreases with a decrease in the molecular weight but an increase in the chain length of ring opener. As seen from Figure 8, OL-As with the molecular weight of 1500 g/mol have the highest yield stress. This indirectly implies that greater force is required to allow the fluid to flow.

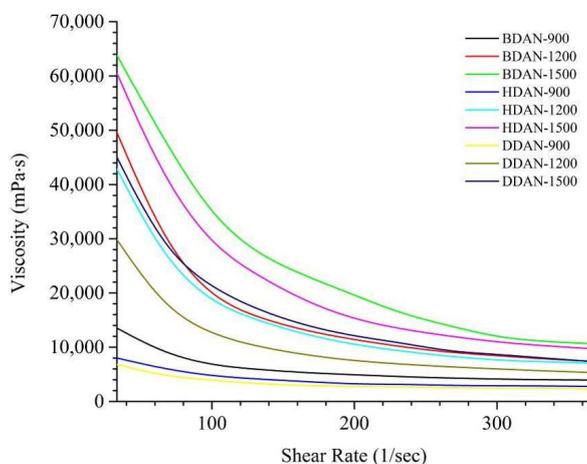


Figure 8. Viscosity value of OL-As at increasing shear rates.

3.5. Thermal Properties of Lactide Oligomers

DSC analysis was employed to study the thermal properties of OL-OHs and OL-As. The glass transition temperatures (T_g) of the synthesized oligomers are shown in Table 5. As observed, T_g of OL-OH is related to its molecular weight and the length of the ring opener's alkyl spacer; the higher the molecular weight, the higher the T_g . In the opposite direction, the longer alkyl spacer results in a decrease in T_g deriving from the effect of intermolecular hydrogen bonding interaction. When considering OL-As, T_g are lower than their corresponding OL-OHs. A decrease in T_g values of OL-As is probably due to the decrease in intermolecular hydrogen bonds when compared to the OL-OH counterpart, arising from the conversion of OL-OH hydroxyl groups to acrylate groups. As a result, chain mobility of OL-As increases due to the depletion of intermolecular hydrogen bonding interactions. As seen in Table 5, the T_g values of the OL-As range from -1.2 °C to -25.0 °C, which are similar to previous works [10,30]. After neutralization, T_g values of the OL-As increase which may be due to decreased mobility of the final product, caused by the presence of the neutralization product, DGEBA acrylate, which has aromatic rings in its structure (Figure 7). The DSC second heating thermograms of all the neutralized OL-As, as displayed in Figure 9, show only a T_g . No crystallization temperature and melting temperature are observed, suggesting that the oligomers are amorphous after heat treatment. Furthermore, no exothermic peak of any chemical reaction appeared during the first and second heating of the OL-As to 180 °C, indicating that the OL-As are stable at high temperature.

The T_g values of cured screen printing inks are also shown in Table 5. After UV curing, an increase in T_g is observed for all cases as a result of the formation of crosslinked film which restricts the chain mobility. In general, the higher the crosslink density, the higher the T_g . The crosslink density of the inks prepared from lower molecular weight OL-A is higher than those prepared from higher molecular weight OL-A because of the higher acrylate groups per unit weight. As a result, a higher increase in T_g could be observed. Considering the effects of the alkyl chain length on an increase in T_g , the cured ink prepared from OL-A with the longer chain length shows a higher increase in T_g . The increase in T_g of the cured inks after curing is also a consequence of the HDDA monomer, the crosslink film of which has T_g at around 60 °C [31]. The T_g results emphasize the physical properties such as moderate pencil hardness, high impact resistance, and high flexibility. This is probably due to the T_g values of cured inks which are close to the room temperature resulting in flexible cured films.

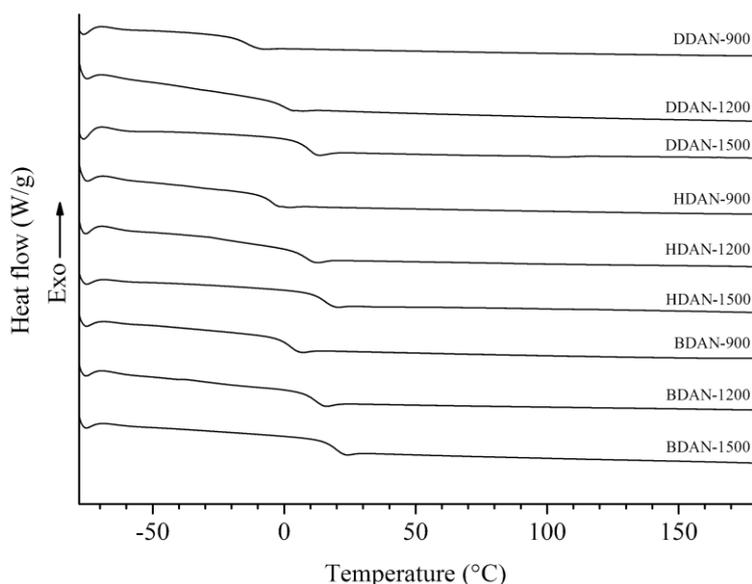


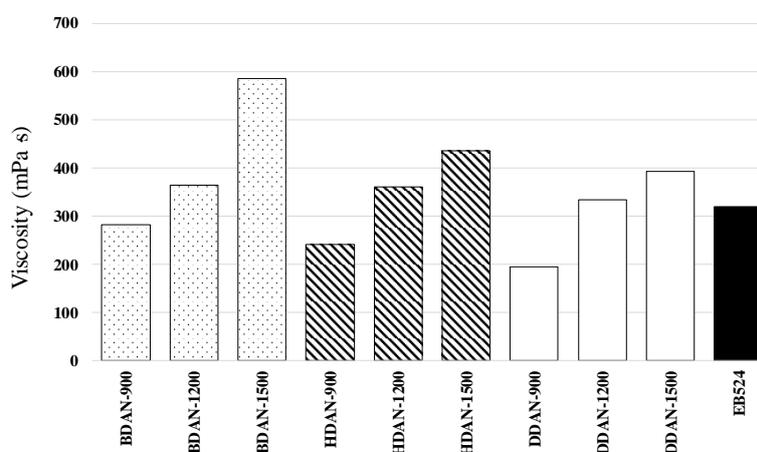
Figure 9. Differential scanning calorimetry (DSC) second heating thermograms of the neutralized OL-As.

Table 5. Glass transition temperatures of OL-OHs, OL-As, neutralized OL-As, and cured inks.

Original Oligolactide Diols	T_g (°C)			
	Diol	Acrylate	Neutralized Acrylate	Cured Ink
BDOH-900	1.0	−7.3	1.0	36.8
BDOH-1200	11.2	−2.1	10.3	30.3
BDOH-1500	17.1	−1.2	18.1	34.4
HDOH-900	−4.4	−12.8	−5.7	30.8
HDOH-1200	6.2	−1.9	6.6	35.3
HDOH-1500	11.4	−3.1	14.3	35.2
DDOH-900	−15.2	−25.0	−15.4	25.0
DDOH-1200	−0.8	−8.2	−0.9	33.2
DDOH-1500	8.5	−7.7	7.4	31.7

3.6. Properties of Screen Printing Inks

The clear UV-curable screen printing inks were prepared from OL-As and other ingredients. The viscosities of the wet inks were measured, and it was found that the viscosity of the ink was dependent on the viscosity of the OL-A. The higher the viscosity of the OL-A, the greater the viscosity of the ink, as shown in Figure 10. Similar to the OL-As, the rheological behavior of the obtained inks was dependent on the molecular weight of the OL-As. The inks also exhibited shear thinning behavior, and the high yield stress was observed for inks formulated from OL-As with the molecular weight of 1200 and 1500 g/mol. Therefore, OL-As with the molecular weights of 900 g/mol are preferable for ink formulations since they provide better flowing inks with lower viscosity.

**Figure 10.** Viscosity values of wet inks.

The inks were then printed on polylactide sheets and cured by UV radiation at 200 mJ/cm². The FTIR spectra of an uncured ink produced from BDAN-900 as well as the cured one are displayed in Figure 11. It can be observed that the intensities of the characteristic peaks of the acrylate groups at 1640, 1626, 1408, 988, and 810 cm^{−1} significantly decrease after UV exposure, indicating the curing of the ink. However, the acrylate peaks did not completely disappear, indicating the incomplete conversion of the acrylate double bonds. The conversion degree of the acrylate double bonds was then calculated using Equation (1). As shown in Table 6, the degree of acrylate double bond conversion after exposure to 200 mJ/cm² UV irradiation for all samples, including the ink prepared from a commercial polyester diacrylate oligomer (EB524), are more than 92% and high enough to lead to efficient photopolymerization. The fact that acrylate conversion did not reach 100% could be related to decreased mobility of acrylate groups when the ink was being cured and crosslinked. The curing of the inks was further confirmed by the solvent resistance rub test as will be presented later.

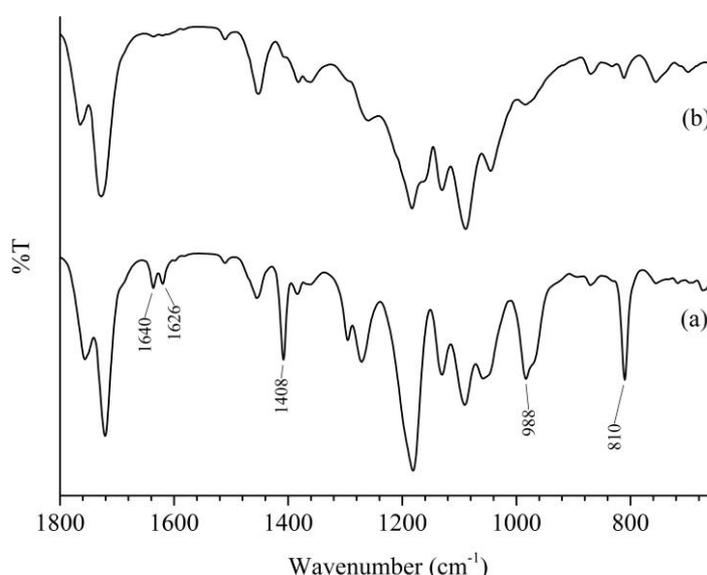


Figure 11. FTIR spectra of the screen printing ink made from BDAN-900 before (a) and after (b) UV curing.

Table 6. Double bond conversion (%) of oligolactide acrylate-based UV-curable inks.

Samples	Double Bond Conversion (%)
BDAN-900	95
BDAN-1200	95
BDAN-1500	96
HDAN-900	94
HDAN-1200	94
HDAN-1500	96
DCAN-900	94
DCAN-1200	94
DCAN-1500	92
EB524	93

Table 7 summarizes the properties of the UV cured films from OL-A based inks in comparison to that of ink prepared from EB524. The curing of the inks was evaluated by the solvent resistance rub test. The MEK double rub test results show that all inks were cured, thus forming crosslinked films. The cured ink films prepared from OL-As had no sign of blistering and softening after rubbing with MEK for 200 double rubs. As compared with the ink made from EB524, all ink films based on OL-As exhibit higher MEK rub resistance. This is probably due to the difference in the type and structure of the starting oligomers.

All the films had excellent adhesion on polylactide sheets, probably due to the presence of polar C=O and O–H groups in OL-As which can form hydrogen bonds with polylactide substrates. The flexibility measured by bending test, as well as the impact resistance of all the films were also excellent. This could be attributed to the long aliphatic chain structure of OL-As. For pencil hardness test, the ink films exhibited good hardness at a level of 3H due to high content of crosslinking. Moreover, the water resistances of the cured OL-A ink films were excellent in which no blistering, no swelling, and excellent adhesion were observed after being immersed in water for 24 h. These results show that the prepared inks have a potential use for printing biodegradable PLA containers where the water contact cannot be avoided. As compared with the properties of clear ink made from EB524, it is clearly seen that OL-A based ink films had similar properties, as shown in Table 7. In order to investigate the appearance of black ink print, BDAN-900 was selected to produce a black screen printing ink due

to its highest L-lactide content, while still having low viscosity. The black ink from EB524 was also prepared as a comparison. The formulation of the black ink was similar to that of the clear one except carbon black and triphenylphosphine oxide were added to provide color and to enhance through cure, respectively. The printed samples of the black inks are shown in Figure 12. It can be seen that black text printed from BDAN-900 based ink is clear and sharp and is similar to that of EB524. All results show that all the synthesized oligolactide acrylates can be used as starting materials for UV-curable screen printing inks.

Table 7. Properties of oligolactide acrylate-based UV-curable ink films.

Sample	MEK Double Rubs	Adhesion ^a	Flexibility (Ø/mm)	Impact Resistance (Inch-Pound)	Pencil Hardness	Water Resistance ^b
BDAN-900	200+	5B	3	160	3H	Excellent ^c
BDAN-1200	200+	5B	3	160	3H	Excellent ^c
BDAN-1500	200+	5B	3	160	3H	Excellent ^c
HDAN-900	200+	5B	3	160	3H	Excellent ^c
HDAN-1200	200+	5B	3	160	3H	Excellent ^c
HDAN-1500	200+	5B	3	160	3H	Excellent ^c
DDAN-900	200+	5B	3	160	3H	Excellent ^c
DDAN-1200	200+	5B	3	160	3H	Excellent ^c
DDAN-1500	200+	5B	3	160	3H	Excellent ^c
EB524	50	5B	3	160	2H	Excellent ^c

^a The maximum rate of adhesion is 5B and the minimum is 0B; ^b Time detected when films exhibited blistering after immersing in water; ^c No change after immersing for 24 h.

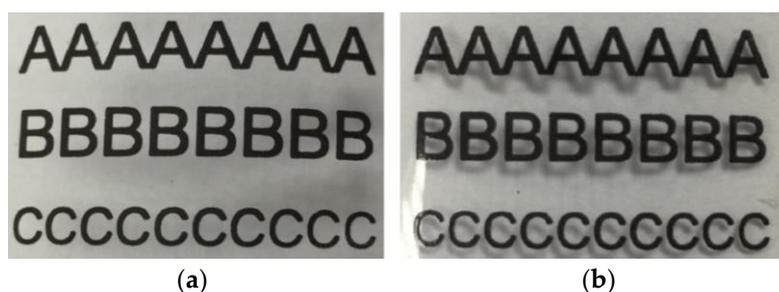


Figure 12. Printed samples of black UV-curable screen printing inks from HDAN-900 (a); EB524 (b).

4. Conclusions

UV-curable oligolactide acrylates having low viscosities were successfully prepared by functionalizing oligolactide diols with acrylic acid. Oligolactide diols were firstly synthesized by ring opening reaction of L-lactide with 1,4-butanediol, 1,6-hexanediol, and 1,10-decanediol. It was found that the viscosity of the oligolactide acrylates can be tailored by adjusting the amount or changing the type of the ring openers. An increase in the alkyl chain length of the ring openers resulted in oligomers with lower viscosity. Results show that this approach can be used to produce low viscosity, bio-based oligolactide acrylates for UV-curable screen printing inks. The inks formulated from oligomers with lower molecular weight exhibited better ink flow property. The OL-A based ink films exhibited properties that are comparable with that prepared from a commercial polyester diacrylate oligomer, suggesting that the synthesized oligolactide acrylates can be used as starting materials for UV-curable screen printing applications.

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