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Properties of UV-curable screen printing inks containing oligolactide acrylates

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Abstract

This study was aimed at investigating the properties of UV-curable screen printing inks prepared from oligolactide acrylates. Those resultant inks were applied on substrates and cured by UV radiation. Then, properties of the cured ink films were evaluated and compared with a commercial acrylate ink. The degradation temperature of ink film was found at around 436°C. In addition, thus obtained films were glossy and transparent without yellowness. The weathering resistance of ink films tested by a Xenon test chamber for 500 h showed that ink films exhibited acceptable outdoor durability. Discoloration due to the degradation of lactide chain was observed, albeit color differences (ΔE) were satisfactorily less than 1. When compared to a commercial polyester acrylate ink, the prepared inks exhibited comparable properties. As a result, these prepared inks are commercially possible for substituting non biodegradable commercial inks particularly outdoor applications.

1. Introduction

UV-curable screen printing ink is widely used for decorating polymer substrates [1]. Compared with the widely used, conventional solvent-based inks, the UV-curable inks have several advantages including fast curing at room temperature, low curing energy consumption, no VOCs, and low total production cost [2]. The general formulations usually contain acrylate oligomers, acrylate monomers, photoinitiators, and additives.

The acrylate oligomers, which impart the basic properties of the cured ink film, are mostly viscous liquid having a viscosity ranging from 1,000 to 1,000,000 mPa·s at 25°C with a molecular weight ranging from approximately 500 to 20,000 g·mol^{-1} [3]. The backbone of the acrylate oligomers may have an epoxy, ester, urethane, or acrylic repeating unit, but the functionality of end group is of acrylate groups.

Acrylate monomers are employed in the ink formulation as diluents to reduce viscosities of the ink to suitable printing viscosities. The acrylate monomers used in UV-curable printing inks are commonly light-colored liquids having molecular weight from approximately 150 to 500 g·mol^{-1} with viscosities from 5 to 200 mPa·s at 25°C. Examples of acrylate monomers are polyglycol acrylates such as 1,6-hexaediol diacrylate (HDDA) and polyether acrylates. Mixtures of oligomers and monomers are typically used to optimize the physical properties of the cured ink film [4].

Photoinitiators are molecules when absorbing UV generate the free radical reactive species which are able to react with acrylate groups of oligomers and monomers. The free radicals continue the reaction which leads to the crosslinking of the components in the ink formulation, transforming the ink from liquid to solid. Examples of photoinitiators are α-hydroxyketone, phenylglyoxylate (Irgacure 754), α-aminoketone, and acylphosphine oxides [5]. The reactivity of UV-curable ink depends on the type and the amount photoinitiators in the formulation.

Additives are used in tiny amounts to fine tune properties of the inks. For example, levelling agents give a smooth surface, defoamers prevent the formation of air bubbles in the dried film or during the printing, and rheology modifiers increase viscosity and thixotropic behavior of the inks [6]. The polyether-modified polydimethylsiloxane (BYK-333) not only acts as a levelling agent and a defoamer, but also as a slipping agent in the ink formulation.

The formulation of any printing inks has to take into account the method of printing, the substrate, and the end-use requirements. The fundamental requirements of a UV-curable ink are fast cure, good adhesion, good intercoat adhesion, high opacity, product resistance (such as detergent), water resistance, and moderate flexibility [7]. The

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requirement that has been recently increasing is the demand for the inks which are consisted of environmentally friendly ingredients.

Oligolactide acrylates has been studied as oligomers for UV-curable coating because its backbone was made from lactide repeating unit which is a made from a renewable resources [8,9]. The physical properties of oligolactide acrylates in UV-curable screen printing inks have been covered in the previous studied [10,11]. In Thailand, 60% of UV-curable screen printing market is for printing polymer for packaging [12]. Apart from decorating polymer packaging, UV-curable screen printing inks are also used for printing outdoor advertisement, signages, and banners which require inks with additional properties.

Therefore, the propose of this research was to investigate the thermal stability, optical properties, and weathering resistance of UV-curable screen printing inks prepared from oligolactide acrylates. Properties of three UV-curable screen printing inks prepared from three kinds of oligolactide acrylates (BDAN-900, HDAN-900, and DDAN-900) were analyzed and compared with an ink prepared from a commercial polyester acrylate oligomer, EB524.

2. Materials and experimental procedures

2.1 Materials

UV-curable screen printing inks were formulated from three oligolactide acrylates as a main ingredient. The molecular weights of the oligolactide acrylates are around 900 g·mol^{-1}. Another ink was formulated from EB524, a polyester diacrylate, as a commercial standard. The details of the oligolactide acrylates and ink preparation were described in detail in a previous article [11]. The chemical structres for the olicolactide acrylates were shown in Figure 1, while the formulations of all inks are shown in Table 1.

2.2 Chemical analysis of EB524

The functional groups and structure of EB524 were analyzed by Fourier transform infrared spectroscopy (FTIR) on a Spectrum 100 Fourier transform infrared spectrometer with Universal ATR (PerkinElmer, USA) at the wavenumber range of 4000-650 cm^{-1} with resolution of 1 cm^{-1} and with 4 scans. The chemical structure of EB524 was determined by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) on a Fourier 300 NMR spectrometer (Bruker, USA) at 300 MHz using $CDCl_3$ as a solvent at room temperature.

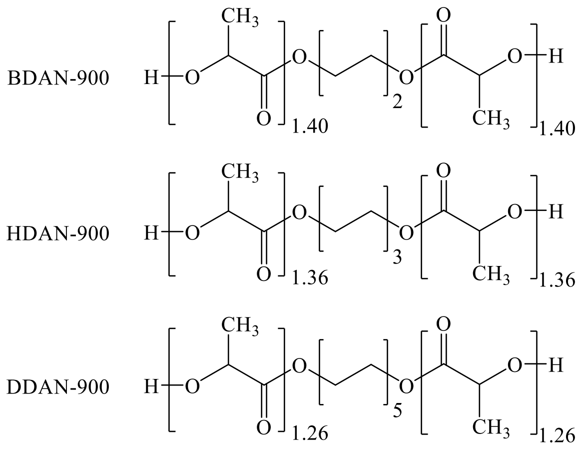

Figure 1. Chemical structure of BDAN-900, HDAN-900, and DDAN-900 [11].

Table 1. Screen printing ink formulations [11].

Material	Formulation			
	BD	HD	DD	EB
BDAN-900	60			
HDAN-900		60		
DDAN-900			60	
EB524				60
HDDA[a]	34	34	34	34
Irgacure 754[b]	5	5	5	5
BYK-333[c]	1	1	1	1

[a] 1,6-hexanediol diacrylate
[b] 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
[c] polyether-modified polydimethylsiloxane

2.3 Film preparation

For TGA analysis, the ink film samples were prepared by coating the inks on a glass plate with a four-sided film applicator (Sheen Instruments, UK). The wet film thickness was 90 µm. The inks were cured with the UVB at intensities of 200 mJ·cm^{-2} by a UV curing unit having a 3 kW medium-pressure mercury lamp, and the UV intensity was measured by UV Power Puck II (EIT Instruments, USA). The cured ink films were cut into size and removed from the glass plate.

For the other tests, the ink films were prepared by printing the inks on white FasCal 400 vinyl stickers (Avery Dennison, USA) through a stencil with 140 lines·cm^{-1} polyester screen printing mesh using a 80 shore A, U-shaped polyurethane squeegee blade. Wet film thickness was approximately 15 µm. The inks were cured with the UVB intensities of 200 mJ·cm^{-2}.

2.4 Testing and characterizations

The thermal stability of the cured ink films was investigated by thermogravimetric analysis (TGA) using a 209 F3 Tarsus thermogravimetric analyzer (NETZSCH, Germany). Each scan was carried out from 35°C to 700°C at a heating rate of $20°C·min^{-1}$ under nitrogen gas flow through the sample cell at 110 $ml·min^{-1}$.

The gloss of cured ink films was determined at an angle of 60° according to ASTM D523 using a Micro-Gloss 60° digital gloss meter (BYK-Gardner, Germany). After the sample was tested for gloss at five different positions, the average value was reported as the final value.

The yellowness index of cured ink films was measured in accordance with the ASTM E313 using a UltraScan VIS spectrophotometer (HunterLab, USA). The measurement was made at 10° observer under D65 illuminant. CIE Tristimulus values (X, Y, X) from the measurement were used to calculate the yellowness index using the following equation:

$$\text{Yellowness Index} = \frac{100\,x\,(1.3013X - 1.1498Z)}{Y} \quad (1)$$

where X, Y and Z are the CIE Tristimulus values.

The transparency of the cured ink films was examined by using a UltraScan VIS spectrophotometer (HunterLab, USA). The percentage transmittance (%T) of the cured ink films over a wavelength range of 360–780 nm was measured at 10° observer under D65 illuminant.

Weathering resistance of the cured ink films was tested according to ASTM G155 in a Q-Sun XE-1 Xenon test chamber (Q-lab, USA). The test cycle used was Cycle 1 (Daylight, irradiance 0.35 $W·m^{2}$, wavelength 340 nm, 102 min light at 63°C black panel temperature and 18 min light and water spray) for 500 h. FTIR spectroscopy was performed to study the degradation of the films after the accelerated weathering test. Color measurements were performed with a UltraScan VIS spectrophotometer (Hunterlab, USA). Three coordinates (L*, a* and b*) were determined for each sample before and after the weathering test for 100, 200, 300, 400, and 500 h. The calculation of color difference (ΔE) was carried out using the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

where Δa* and Δb* represent the increase or decrease in levels of chromaticity and ΔL* represents the luminosity difference

The gloss of cured ink films after the accelerated weathering test was determined at an angle of 60°.

3. Results and discussion

3.1 Property of acrylate oligomers

The FTIR spectrum of EB524 shown in Figure 2 exhibit the C-H stretching peaks at 2945 and 2864 cm^{-1} and the C-H bending peaks at 1370 cm^{-1}. Three peaks appearing at 1599, 1580, and 1447 cm^{-1} are attributed to C-C stretching of benzene rings, while the peaks at 1189, 1118, 1067, and 1041 cm^{-1} are related to C-O-C stretching. The strong peak at 1717 cm^{-1} and the weak peak at 1257 cm^{-1} are assigned to the C=O and C-O stretching of ester groups, respectively. The peak of $-CH_3$ bending of methyl substituted aromatic rings is found at 740 and 705 cm^{-1}. The spectrum also shows the C=C stretching of acrylate groups was at wavenumbers of 1636 and 1619 cm^{-1}, while the peaks of $=CH_2$ bending, wagging, and twisting of acrylate groups are found at 1408, 974, and 811 cm^{-1}, respectively.

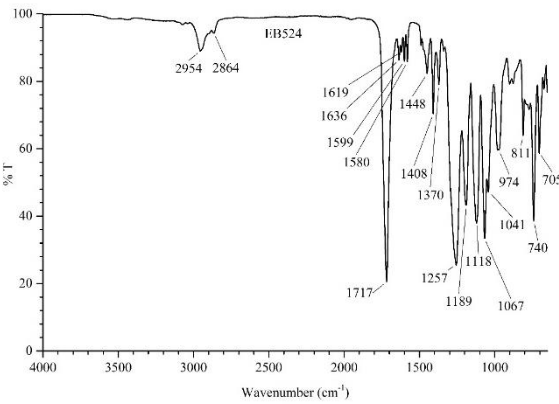

Figure 2. FTIR spectrum of EB524.

Figure 3 shows the ^{1}H-NMR spectrum of EB524. The peaks at 7.69 ppm and 7.49 ppm are contributed to methine protons of aromatic rings. The signals of the characteristic peaks of protons of the acrylate double bonds are detected at 6.39 ppm, 6.11 ppm, and 5.81 ppm. The peak at 4.48 ppm and 4.15 ppm are attributed to methylene protons next to ether oxygens and ester groups, respectively. The peaks at 1.71 ppm and 1.40 ppm are attributed to methylene protons, and the peak at 0.95 ppm is assigned to methyl protons.

FTIR and [1]H-NMR results show that EB524 is an acrylate oligomer with methyl substituted aromatic structures having the methylene repeating unit.

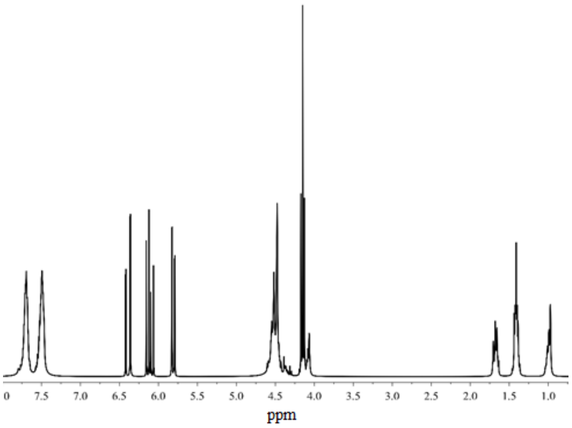

Figure 3. [1]H-NMR spectrum of EB524.

3.2 Thermal stability

Thermogravimetric analysis (TGA) is one of the techniques commonly used to evaluate the thermal stability and the decomposition of polymers at various temperatures. Figure 4 shows TGA thermograms of the cured ink films prepared from oligolactide acrylates and EB524 measured from 35°C to 700°C under nitrogen atmosphere. TGA results are summarized in Table 2. The initial weight loss which occurred at 120°C to 170°C probably corresponds to losses of volatile substances such as moisture and degradation products of unreacted photoinitiators as well as unreacted monomers [13]. The T_d of 5% weight loss which was approximately 271 and the Td of 50% weight loss which was approximately 420°C for all the inks containing oligolactide acrylates. The use of monomers with higher functionality will raise thermal stability of the resulting inks which are higher thermal stability [14]. The main T_d of all the inks takes place at approximately 430°C, corresponding to the degradation of acrylate oligomers occurring through decarboxylation, formation of monomers and alcohols [15]. In general, a thermoplastic polylactide polymer degrades completely leaving no residue [16]. The residual weights of the cured ink films at 700°C are probably brought about by the formation of the thermoset crosslink structure after UV curing. EB524 provided a cured ink film with slightly higher thermal stability which is probably due to its aromatic structure. From the TGA results, it can be concluded that the inks prepared from oligolactide acrylates can be used in the hot environment.

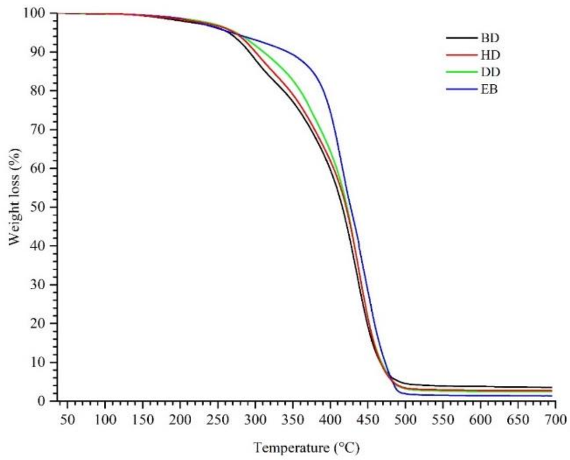

Figure 4. TGA thermograms of cured screen printing ink films.

3.3 Optical property

Gloss is an important property of printing inks because it contributes to aesthetic appearance. Gloss is a complex phenomenon which can be affected by many factors such as surface smoothness, rheological properties, leveling, the degree of cure, etc. The gloss values of the cured ink films were measured by a gloss meter at 60° as shown in Table 3. The results show that the cured ink films have gloss values of 79.1 to 80.2. This might be attributed to the smoothness of the films. The inks prepared from oligolactide acrylates have higher gloss than that prepared from methacrylate glycolyzed polylactides by other researchers [17].

Table 2. Thermal analysis results of cured screen printing ink films.

Formulation	Weight loss at 100°C (%)	5% Weight loss temperature (°C)	50% Weight loss temperature (°C)	Maximum weight loss temperature (°C)	Residue (%)
BD	0.21	264	416	435	3.59
HD	0.14	274	421	437	2.71
DD	0.16	275	422	436	2.45
EB	0.11	268	427	446	1.38

The yellowness index of the cured ink films was measured by a spectrophotometer. The lower the yellowness index, the less yellowish the ink is. The yellowness index is negligible (less than 1.00) in all the inks as shown in Table 3. This is probably because the oligolactide acrylates have a light color. The use of the 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 photoinitiator (Irgacure 754) in the formulations also contributes to the minimal yellowness. On the contrary, a photoinitiator such as thioxanthone derivatives will provide a yellowish cured ink film.

Optical transparency of the cured ink films was determined by light transmittance measured by a spectrophotometer over a wavelength range of 360–780 nm. As observed from Table 3, all the cured ink films show high transparency with approximately 79% of light transmittance, which may result from the amorphous structure of the oligolactide acrylates, allowing light to transmit through their molecules. As show in Figure 5, the cured ink films prepared from oligolactide acrylates have similar light transmittance profile with that prepared from EB524. These results show that the inks prepared from oligolactide acrylates have comparable optical properties to that prepared from EB524.

Table 3. Optical properties of cured screen printing ink films.

Formulation	Gloss	Yellowness index	Transparency (%)
BD	79.6	0.25	78.98
HD	80.2	0.14	78.80
DD	79.1	0.51	78.82
EB	99.6	1.00	78.89

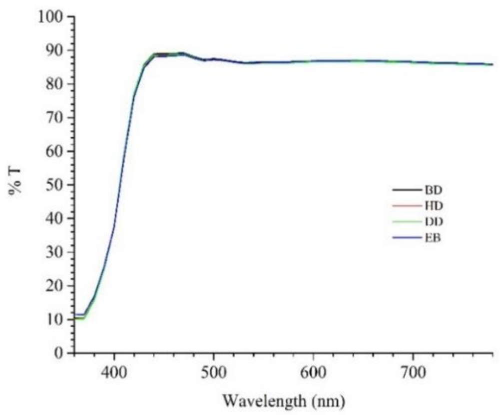

Figure 5. Transmittances of cured screen printing ink films.

3.4 Weathering resistance

Weathering resistance is an important property of printing inks as it determines the outdoor application of the inks. Crosslink polymers are normally more resistant to outdoor weathering than their linear counterparts are. This is because the restricted chain mobility reduces the extent of both propagation and initiation of the photodegradation process. The crosslinking overcomes the negative effects of the unreacted photoinitiators [18]. The cured ink films were tested in a Xenon test chamber for 500 h. The FTIR spectra shown in Figure 6 were collected from the cured films of the ink formulation BD before and after the accelerated weathering test in order to investigate the mechanism of degradation. After 500 h weathering test, a small shoulder was observed at 1842 cm^{-1} belonging to anhydride degradation products from photooxidation of the oligolactide chain [19]. The C=O stretching assigned to carbonyl groups of the oligolactide at 1755 cm^{-1} significantly decreases, indicating the degradation of the oligolactide chain. The C=O stretching assigned to carbonyl groups of acrylates at 1727 cm^{-1} is almost unchanged, suggesting that the crosslink network of HDDA was not yet degraded [20]. The small increase of the intensity of this peak may contribute to the formation of carboxylic and anhydride degradation products. The decrease of the intensities of characteristic peaks at 1183, 1131, 1087, and 1044 cm^{-1} belonging to C-O-C stretching of ester linkage confirms the degradation of the oligolactide chain. All of the other cured ink films also exhibited the same characteristic of FTIR spectra. Therefore, the degradation of the cured ink films prepared from oligolactide acrylates was the consequence of the degradation of lactide chain.

Color differences (ΔE) of the cure ink films as measured by a spectrophotometer are shown in Figure 7. When ΔE is greater than 1.0, the color difference can be noticed by human eyes [21]. It can be observed that ΔE increases with the increasing number of testing cycles from 100 to 500 h. The cured ink films prepared from oligolactide acrylates have ΔE lower than 1.0. This might be contributed by their aliphatic structure. As observed, the cured ink films become more weathering resistant (less ΔE) as the length of the spacer of oligolactide acrylates in the ink formulation increases. The ΔE of the inks is comparable with that prepared from EB524.

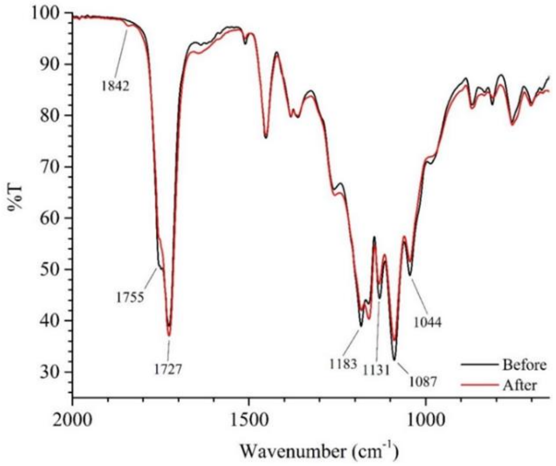

Figure 6. FTIR spectra of cured films of ink formulation BD before and after weathering test.

The weathering test causes a large number of different reactions to occur in the inks, for example chain scission and crosslinking. Some of these reactions may cause loss of materials from the surface of the inks which, in turn, will reduce surface smoothness and reduce gloss. It can be seen in Figure 8 that the gloss values of the cured ink films prepared from oligolactide acrylates and EB524 dropped by approximately 15 units after 500 h. The decrease of gloss is probably due to the decrease in surface smoothness of the cured ink films caused by photodegradation.

Weathering resistance can be improved by incorporating UV stabilizers, UV absorbers, or antioxidants into the ink formulations. These results show that oligolactide acrylates provide UV-curable inks which can withstand outdoor weathering.

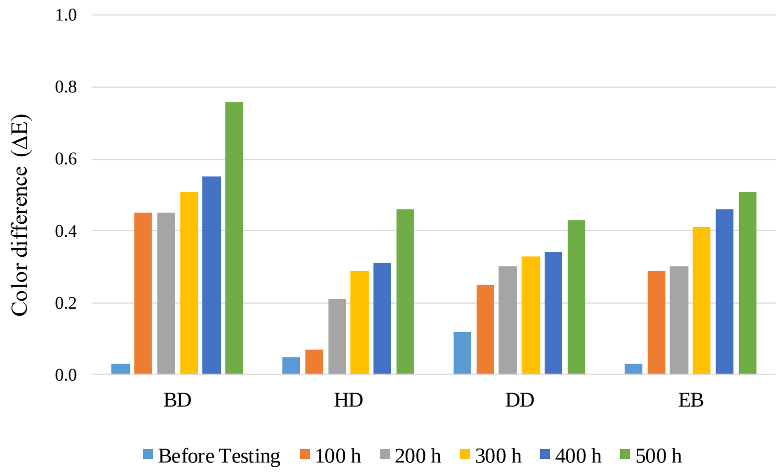

Figure 7. Color differences (ΔE) of cured screen printing ink films before and after weathering test.

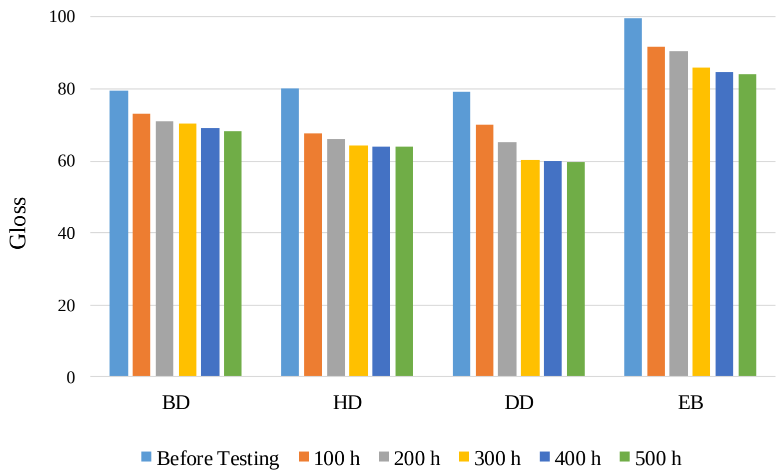

Figure 8. Gloss of cured screen printing ink films before and after weathering test.

4. Conclusions

The UV-curable screen printing ink prepared from oligolactide acrylates have thermal stability comparable with that prepared from EB524. Even though the gloss values are lower, the yellowness index and optical transparency of the cured ink films are in the same level of that prepared from EB524. As for weathering resistance, the inks have good weathering resistance with ΔE less than 1 after 500 h test. The results show that the UV-curable screen printing inks prepared from oligolactide acrylates have a potential to be used in outdoor application.

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