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BRIEF COMMUNICATION

The wettability effect of branched polyglycerols used as performance additives for water-based printing inks

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Abstract The aim of this work was to study the influence of primary and secondary hydroxyl groups in the branched polyglycerol on the selected properties of water-based printing ink and copies printed with water-based flexographic printing inks. The branched polyglycerols were synthesized through anionic ring-opening polymerization using trimethylolpropane as a starting material. Obtained polyglycerol exhibited an irregular structure containing primary and secondary or predominantly primary hydroxyl groups in the macromolecule. The analysis (FTIR, ^{1}H NMR, ^{13}C NMR) confirmed the structure of polyglycerols. Obtained polyglycerols were then used as a performance additive in a water-based flexographic printing ink. The contact angles of the printing inks on the printing base were measured. The impact of a small amount of branched polyglycerol on the printing ink color was examined by studying the optical density of a full-tone area, the color values (CIELAB), the total color difference ΔE^{*}_{ab}, and gloss of the dried ink film. In general, the addition of branched polyglycerol containing only primary hydroxyl groups improved the wettability of the plastic film and gloss of printing ink with an acceptable total color difference ΔE^{*}_{ab} in contrast to branched polyglycerol with primary and secondary hydroxyl groups.

Keywords Polyglycerol, Flexographic water-based inks, Performance additives, Wettability

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Introduction

Hyperbranched polymers (HBPs) and dendrimers are a new class of polymers. Dendrimers are characterized by a highly branched structure of great regularity and a compact shape, with a large number of polar end groups and symmetry in structure.[1] Hyperbranched polymers are globular and highly branched macromolecules with a large number of functional groups. In contrast, HBPs exhibit polydispersity and irregularity in terms of branching and structure.[1]

Dendrimers and hyperbranched polymers have found a number of applications in the printing industry. HBPs polymers may be used in the printing industry as performance additives for offset or flexographic printing inks in order to improve print quality and print performance, for instant gloss of the print, adhesion of the dried ink film to the printing substrate, and abrasion resistance of print.[2–4] Dendrimers and hyperbranched polymers characterized by regular structure have found application in printing inks, wherein a dye or pigment is incorporated in the dendrimer molecule of the printing ink dedicated for ink-jet printing technology.[5–7] Furthermore, commercially available dendrimers PAMAM® (Dendritech, USA) are used in ink-jet inks dedicated for printing on various nonabsorbent and nonporous surfaces (glass, metal, plastic bases) characterized by improved water and moisture and deteriorated abrasion resistance.[8,9] In addition, hyperbranched polycarbonates can be used as pigment dispersants in offset and flexographic printing inks, dyeing fibers paints, or wall and façade paints.[10]

Last but not least, hyperbranched polyesters were used in order to modify the properties of flexographic solvent-based printing inks. The addition of hyperbranched polyesters from Boltorn™ family improved the color properties of the overprinted sample and its abrasion resistance.[11,12]

Flexographic printing technology requires low and rapid viscosity inks. The viscosity should be lower than 0.05–0.5 Pa·s.[13] However, this technology is suitable for printing on paper materials, as well as nonporous and nonabsorbent substrates used in packaging industry. There are three types of flexographic inks used for these applications: water-based, solvent-based, and UV curable. Nowadays, due to ecological reasons, attention in the printing industry is focused on production of water-based printing inks in order to minimize the evaporation of organic solvents into the environment. Printing with water-based inks on nonabsorbent substrates, for instance, plastic films, is linked with some problems. The adhesion of the water-based ink film to the plastic film is worse than solvent-based ink because of a low proper wetting of these surfaces. Moreover, the wet rub resistance of overprinted plastic films with water-based inks is usually poor. It is well known that the surface tension of flexographic printing ink has to be lower than the surface free energy of the plastic film to allow proper wetting and adhesion between the layers of the ink film and the plastic film. In order to decrease the surface tension of water-based inks, organic co-solvents or surfactants are added into water-based inks.

In our work, we propose addition of branched oligo- and polyglycerols into water-based printing inks instead of surfactants or volatile co-solvents. Polyglycerols are environmentally friendly, biodegradable, biocompatible, and nontoxic. Furthermore, oligoglycerols (2–10 units) are approved as food and pharma additives by the FDA[14]; therefore, hyperbranched polyglycerols have already found application in drug delivery systems.[15,16] Traditionally, oligo- and polyglycerols are used in different industries, i.e., food, pharmaceutical, cosmetic, soap, toothpastes, fuel, or paint.[17,18] Hyperbranched polyglycerol has already found applications as surfactants in liquids for treating lithographic printing plates[19] or as an organic solvent in a water-based ink-jet printing ink in order to prevent paper deformation.[20,21] Polyglycerols are much more stable against acidic or basic hydrolysis in contrast to polyesters.[21] Furthermore, the advantage of polyglycerols is their remarkable solubility in water due to the functional hydroxyl end groups.

The aim of this work is to present a wettability effect of branched polyglycerols containing predominantly primary hydroxyl groups or primary and secondary hydroxyl end groups and the possibility of their applications on the printing ink and print properties. The structures of obtained polyglycerols are presented in Fig. 1. The influence of polyglycerol on several printing ink properties (rheology, contact angle) and print quality parameters (optical density, color values, and gloss) was estimated.

Materials and methods

Materials

All of the reagents for polyglycerol synthesis were purchased from Sigma-Aldrich (Poznań, Poland) and were used as received, without further purification.

As an original printing ink, water-based printing ink (FlexiWet), color black, supplied by Chespa (Poland) was used. This ink was characterized with a kinematic viscosity of 19 s. This printing ink is recommended for printing on plastic films. For printing, oriented polypropylene (BOPP), polyethylene (PE),[22] and polyethylene terephthalate[23] films were used. The plastic films were activated by a corona treatment, and they were transparent and had a thickness of 20 µm for BOPP, 50 µm for PE, and 12 µm for PET.

Characterization of polyglycerol

The chemical structure of obtained polyglycerols was characterized on a Bio-Rad FTS 165 FTIR spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded at room temperature, using tetramethylsilane as an internal standard and deuterated solvent (DMSO-d_6), on a Varian VXR 400 MHz spectrometer; the spectra were analyzed using MestReNova v.6,2,0-7238 (Mestrelab Research S.L) software.

Synthesis of polyglycerol

Synthesis of PG-1

Potassium (0.97 g, 0.025 mol) was placed together with trimethylolpropane (10.0 g, 0.075 mol) in a 500-mL round flask equipped with a magnetic stirrer and a thermometer. Then the mixture was heated at elevated temperature (65°C) at inert gas atmosphere for 15 min. Next, a mixture of ethoxyethyl glycidyl ether, EEGE (131.56 g, 0.9 mol), dissolved in THF was added at a rate of 1.5 mL h^{-1} to the mixture using a dosing pump at elevated temperature (95°C). Simultaneously, the THF was removed from the reaction mixture. Upon the completion of adding the EEGE, methanol (150 g) and 15% hydrochloric acid (150 g) were added to the reaction mixture. The reaction mixture was stirred for 24 h at 50°C. Next, the reaction mixture was neutralized by adding solid potassium carbonate, and the solvent was removed under reduced pressure (0.5 mmHg). The obtained product was a dark yellow, viscous liquid.

Yield 123.1 g (87%), ^{1}H NMR (DMSO-d_6, 500 MHz); δ (ppm) = 4.75–4.50 (m, 15H, O$\underline{H}$), 3.67–3.14 (m, 64H, C$\underline{H}_2$O, C$\underline{H}$O and C$\underline{H}_2$O$_{TMP}$), 1.33–1.19 (m, 2H, C$\underline{H}_2$O$_{TMP}$), 0.83–0.71 (m, 3H, C$\underline{H}_{3TMP}$); ^{13}C

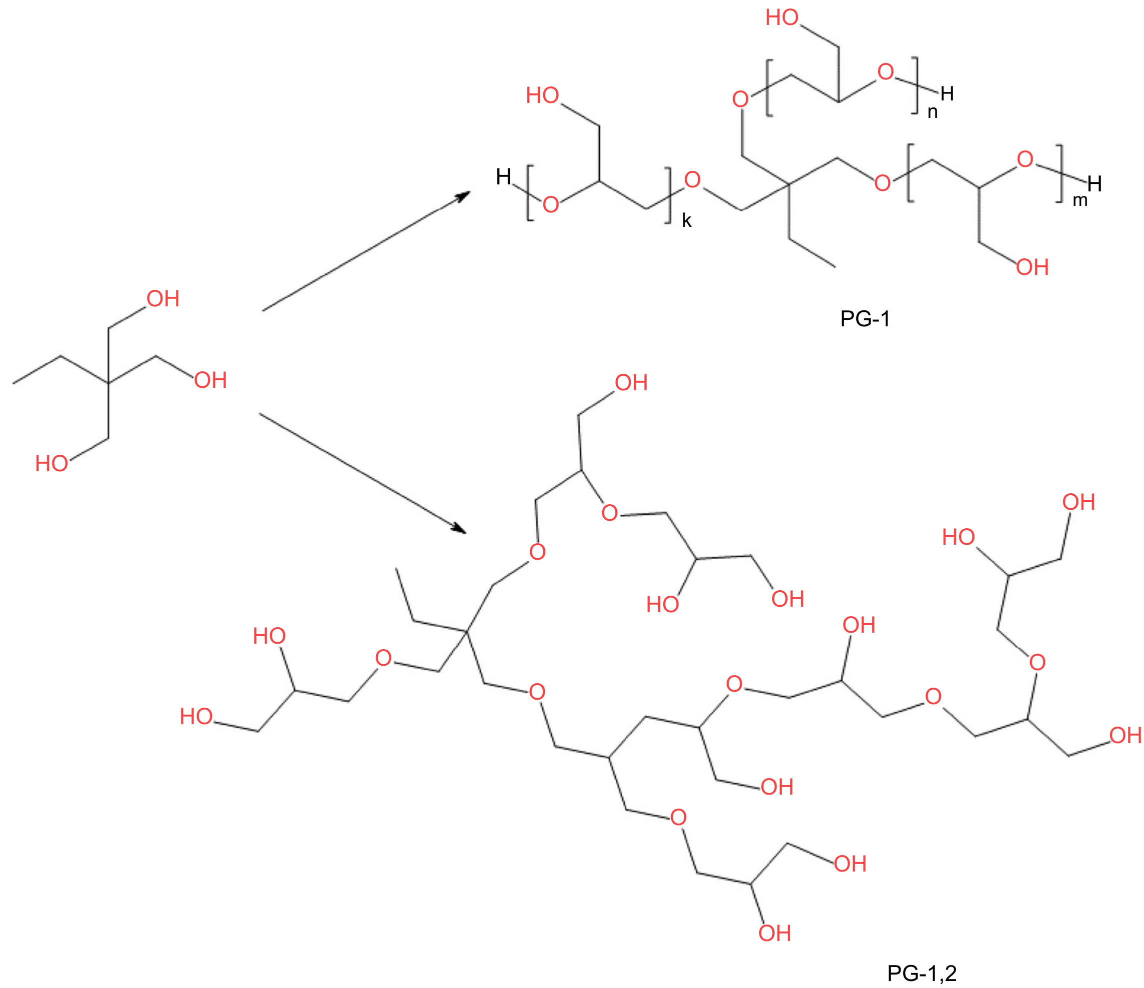

Fig. 1: Structures of obtained polyglycerols

NMR (DMSO-d_6, 125 MHz); δ (ppm) = 80.0, 70.4$_{TMP}$, 69.4, 60,9, 64.6, 60.1, 42.8$_{TMP}$, 22.6$_{TMP}$; FTIR (KBr): ν (cm^{-1}) = 803, 839, 1040, 1105, 1202, 1457, 2281, 2934, 3292.

Synthesis of PG-1,2

Potassium (0.97 g, 0.025 mol) was placed together with trimethylolpropane (10.0 g, 0.075 mol) in a 500-mL round flask equipped with a magnetic stirrer and a thermometer. Then the mixture was heated at elevated temperature (65°C) at inert gas atmosphere for 15 min. Next, a mixture of glycidol (66.67 g, 0.9 mol) dissolved in THF was added at a rate of 1.5 mL h^{-1} to the mixture using a dosing pump at elevated temperature (95°C). Next, after 33 h of adding the mixture of glycidol with ether, the obtained product was dissolved in water and neutralized by 10% hydrochloric acid. The solvent was removed under reduced pressure (0.5 mmHg). The obtained product was a light yellow, viscous liquid.

Yield 126.8 g (89%), ^{1}H NMR (DMSO-d_6, 500 MHz); δ (ppm) = 4.78–4.49 (m, 13H, O$\underline{H}$), 3.65–3.11 (m, 61H, C$\underline{H}_2$O, C$\underline{H}$O and C$\underline{H}_2$O$_{TMP}$), 1.34–1.1 (m, 2H, C$\underline{H}_2$O$_{TMP}$), 0.84–0.70 (m, 3H, C$\underline{H}_{3TMP}$); ^{13}C NMR (DMSO-d_6, 125 MHz); δ (ppm) = 80.0–79.0$_{CH2O}$, 71.8–70.4$_{TMP}$, 69.5–69.1$_{CHOH}$, 60.7–61.1$_{CH2OH}$, 42.8$_{TMP}$, 22.6$_{TMP}$; FTIR (KBr): ν (cm^{-1}) = 804, 839, 1041, 1101, 1200, 1457, 2280, 2931, 3300.

Preparation and characterization of inks

The modified ink was prepared by drop-wise addition of a calculated weight of polyglycerol to pure FlexiWet ink, while continuously stirring. The mass fraction of LPG was 0.01, because the best print quality was obtained after addition of 0.01 of the hyperbranched polyglycerols.[11,12] Then the ink was stirred for 30 min using a mechanical stirrer. The rheological characteristics of the printing inks (the original process printing ink and the ink with added hyperbranched polyglycerol) were specified by the flow time in a flow cup (volume 100 mL, outlet diameter 4 mm), according to an ISO standard.[24] The measurements were taken at 23°C; the relative error in the measurements was less than 3%, and the kinematic viscosity was 19 ± 0.5 s for the printing inks. Contact angle and surface tension measurements of the investigated inks were taken using a DSA 30E drop shape analysis system (Krüss, Germany). Smooth and horizontal sessile drops of the liquids were deposited on a solid surface plastic film (BOPP, PE, PET) using needles of 0.5 mm diameter. The contact angle was measured on static drops. The drop shape analysis was done 15 s after the drop deposition with Tangent method 1. The surface tension of investigated inks was determined by pendant drop method using needles of 2 mm diameter. Environmental conditions were stable, with temperature 23 ± 1°C. The reported contact angle and surface tension values are the mean of five samples.

Printing and characterization of prints

Laboratory printing was carried out with a Flexiproof instrument (TMI Machines, UK). The printing speed was 60 m·min^{-1}, and the printing engagement was 38, 31, and 26 for PET, BOPP, and PE plastic films, respectively. The printing plate, made of a photopolymer prepared by the digital laser photochemical method, had dimensions of 260 × 90 mm and a thickness of 1.7 mm. The pressure between the anilox engraved roller (6 cm^3·m^{-2} volume, resolution or line ruling of 160 lines per cm^{-1}) and the plate cylinder was 98. All factors were kept constant during the printing process (printing speed, anilox roller, and printing pressure). Printing was performed under controlled environmental conditions of 23°C and 50% relative humidity (RH).

The optical densities of full-tone area, 75% tone fields, L^*, a^*, b^* measurements, and gloss of prints were precisely described in previous works.[11,12] The optical densities of the full-tone area and specific ink color components L^*, a^*, b^* were determined using a SpectroEye spectrophotometer (GretagMacbeth, Switzerland). Measurements of the optical density of the full-tone area were taken at the following settings: D50 illuminant using a 2° observer, 0°/45° measuring geometry, with a polarization filter, white standard: proofing paper. The measurements of L^*, a^*, b^* were taken using these settings with absolute as a white standard according to ISO standard.[25] The reported results are the average of the measurements from a minimum of six areas on two different prints.

The gloss (in the gloss units, GU) of the prints was measured at 20°, 60°, and 85° geometry conditions with the use of a Picogloss (BYK-Gardner, Germany). Data collection was performed at six different positions of the samples in both directions: cross and machine direction according to ISO standard, and the reported values are the average of these measurements.

Results and discussion

Polymer synthesis and characterization

In this work two branched polyglycerols were synthesized in order to assess the wettability and hydroxyl group effect. Obtained polymers were synthesized through a ring-opening polymerization using TMP as a starting material (see Fig. 1). Branched polyglycerols were characterized by irregular branched structure and predominately with primary hydroxyl functional groups (PG-1) or with secondary and primary hydroxyl groups (PG-1,2). Our previous work shows that branched glycerols have a positive effect on the wettability, the adhesion, and wet or dry rub resistance.[18,26,27]

Ink properties

Before printing, the selected properties of the printing ink were estimated: the wettability of the printing base by the ink (by measuring the contact angle of printing ink on the various plastic films) and surface tension (pendant drop method).

The printability of polymer bases depends on wettability of the bases by the printing ink. Furthermore, the wettability of the base by the inks influences the adhesion between the base and the dried ink layer, the print quality, and mechanical properties of prints.

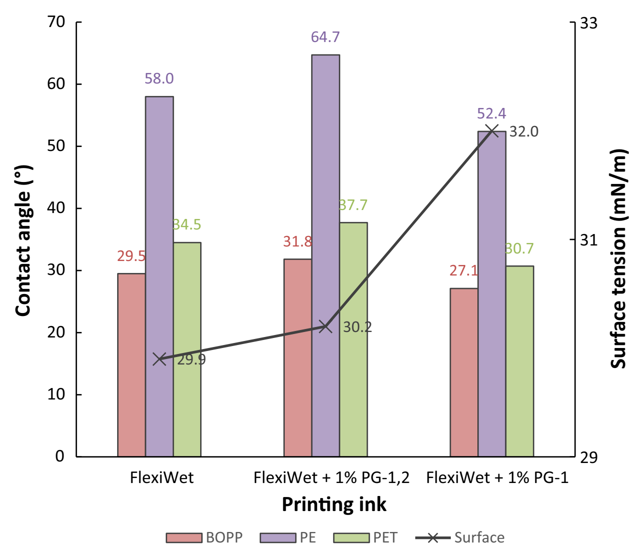

Fig. 2: Properties of investigated printing inks: contact angle and surface tension measured at $t = 23°C$ for the original flexographic printing ink and after the addition of polyglycerols

Better wettability (so smaller values of contact angles) should indicate better adhesion of the ink layer to the base. The wettability may be estimated as a direct measurement of the static contact angle of the ink on the base. The contact angle together with surface tension of the ink without and with the addition of investigated polyglycerols is shown in Fig. 2. The addition of PG-1 decreases the contact angle of the ink; therefore, an improvement of the wettability is observed. The addition of PG-1 decreases the contact angle from 29.5° to 27.1.4°, from 58.0° to 52.4°, and from 34.5° to 30.7°, for the BOPP, PE, and PET plastic film, respectively. In general, the addition of PG-1 decreases the contact angle about 9–12%.[28] On the other hand, the addition of PG-1,2 increases the contact angle of the ink. The higher contact angles are observed for the PE plastic film, and the lower contact angles for the BOPP plastic film.

The surface tension of the ink slightly increases with an increasing mass fraction of polyglycerols. The highest value of surface tension was observed for the printing ink containing PG-1 (32.0 mN·m^{-1}), which is higher than surface tension of solvent-based inks we previously observed.[11,12] Hence, the values of surface tension are higher than the surface free energy of typical plastic films, i.e., the surface free energy of untreated PE and BOPP is lower than 30 mJ·m^{-2}, as reported in the literature.[29] The printing process requires that the surface tension of the printing ink is lower than the surface free energy of the plastic film.

Print quality

The print quality was determined as the properties of the print, i.e., the optical density of the full-tone area, the optical density of 75% tone fields, the color values (L^*, a^*, b^*), and gloss.

Before print quality measurements are taken, the adhesion of the dried ink film should be quantified by simple adhesion test (tape test).[30,31] Adhesion of the original ink to BOPP and PE base was generally much better than adhesion on a PET film. The adhesion of the dried ink film modified with obtained polyglycerol was noticeably better. However, the values of contact angles on the plastic films indicate that the better adhesion to the BOPP or PET than to PE film is expected. Probably, the interaction between the dried ink film and the top layer of PET film is quite poor. The indirect method of assessing adhesion may be the measurements of abrasion resistance. The dry and wet abrasion resistance of overprinted PE, BOPP, and PET base by printing ink containing PG-1,2 is visibly worse than prints overprinted with original printing ink or printing ink with the addition of PG-1.[28]

The values of optical density of full-tone area, optical density of 75% tone fields, relative printing contrast, and gloss are listed in Fig. 3. The optical density assesses the thickness of the dried ink layer. Higher values of optical density refer to thicker dried

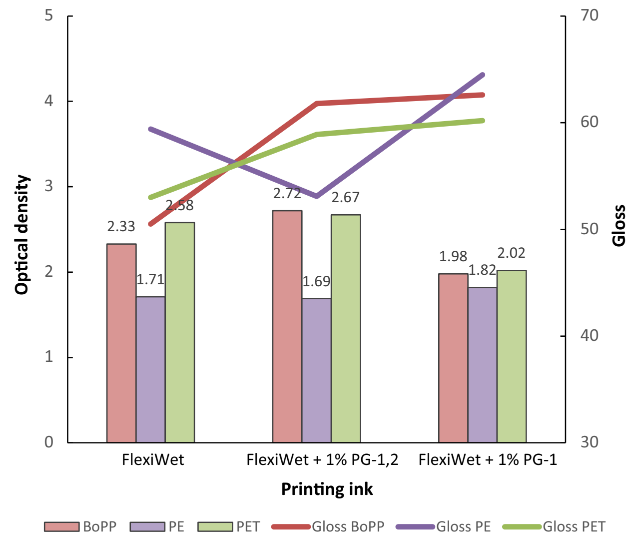

Fig. 3: Optical densities of full-tone area and gloss of ink layers printed with the investigated printing inks

ink layers. It is well known that the thickness of the dried ink layer depends on the wettability of the base by the ink during the printing process. Better wettability is connected with a thinner dried ink layer and lower optical density, assuming constant division of the ink in the inking unit during the printing process, not influenced by the used additive. The optical density of full-tone area decreases with the addition of the PG-1. On the other hand, values of optical density of prints overprinted with the ink with the addition of PG-1,2 are higher than for originally printing ink or ink with the addition of PG-1. However, it should be mentioned that all optical density values are high. The flow curves of printing inks were presented by us previously[28]; the presence of polyglycerols had a noticeable effect on the flow curve.[28] This effect is strongly related to contact angle of the printing ink on the printing base. It might be connected with the greater capacity of primary hydroxyl groups in the macromolecule for hydrogen bonding. The incorporation of secondary hydroxyl groups into the branched molecule of polyglycerol unfavorably affects the wettability effect of the printing ink, and the contact angle is higher together with optical density of full-tone area and gloss.

Gloss is one of the most important parameters in printing and packaging technology, because gloss affects the print quality by providing a better overall look and greater depth to colors.[32] Gloss is a property of a material that is responsible for light reflection from a surface. The methods for measuring gloss depend on the kind of base that is used. The original FlexiWet printing ink is a middle–high gloss, so the gloss values were in the range 30–70 gloss units (GU). Hence, a measuring geometry with an angle of 60° was used according to the ISO standard.[33] In general, the addition of polyglycerols to the FlexiWet printing ink increases the gloss of the prints. This effect is stronger

Table 1: L^*, a^*, b^* values and total color difference ΔE^*_{ab} of ink layers printed with the investigated printing inks

Printing ink	L^*	a^*	b^*	ΔE^*_{ab}
BOPP				
FlexiWet	2.58	0.77	0.87	
FlexiWet + 1% PG-1,2	1.44	− 0.03	− 0.46	1.9
FlexiWet + 1% PG-1	5.97	2.04	3.26	4.3
PE				
FlexiWet	9.70	0.33	0.50	
FlexiWet + 1% PG-1,2	19.36	− 0.19	− 0.29	9.7
FlexiWet + 1% PG-1	5.04	1.56	2.38	5.2
PET				
FlexiWet	2.01	0.32	0.27	
FlexiWet + 1% PG-1,2	1.62	− 0.04	− 0.19	0.7
FlexiWet + 1% PG-1	6.87	2.11	3.63	6.2

for the PG-1 than for PG-1,2. The differences are in the range of 12.1 GU for BOPP prints, 5.1 GU for PE prints, and 7.2 for PET prints for the printing ink containing PG-1. The gloss of the prints is also related to better wettability of the printing ink and smoothing process of the printing ink while drying.

The color values (L^*, a^*, b^*) together total color differences are presented in Table 1. The total color differences (ΔE^*_{ab}) were calculated from equation[24]:

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

where ΔL^*, Δa^*, and Δb^* are the differences between the value of the ink with the addition of polyglycerols and the original ink. The L^* value is a measure of the lightness of an object and is quantified on a scale where $L^* = 0$ for a perfect black diffuser and $L^* = 100$ for a perfect reflecting diffuser. For BOPP and PET printing bases, the values of L^* decrease with the addition of PG-1,2 and increase with the addition of PG-1. This effect is strongly connected with optical density and the thickness of the dried printing ink. The thinner layer of printing ink is related to the ‘‘lighter color’’ of the ink. Therefore, low values of total color difference (ΔE^*_{ab}) are observed for the printing ink with the addition of PG-1,2; the values are lower than 2, demonstrating that differences occurred but it cannot be observed with the human naked eye. Furthermore, higher values of ΔE^*_{ab} are observed for the printing ink with the addition of PG-1, due to the thinner printing ink layer. The overprinted PE base was characterized by very poor print quality, and the values of color values (L^*, a^*, b^*) and total color differences are quite high.

Conclusions

In this work, we have demonstrated the wettability effect of branched polyglycerols and the impact of primary and secondary hydroxyl groups on wettability. Obtained polyglycerols PG-1,2 and PG-1 exhibited irregular structure containing primary and secondary hydroxyl groups or predominantly primary hydroxyl groups in the macromolecule, respectively. Polyglycerols were synthesized by ring-opening polymerization using trimethylolpropane as a starting material.

The impact of the polyglycerols on the wettability, surface tension, optical density, and color parameters (L^*, a^*, b^*) is reported in this paper. The addition of branched polyglycerols strongly affects the wettability of the base by printing ink. Furthermore, the wettability of the ink on the film influences the print quality. We have proven that polyglycerols containing predominately primary hydroxyl groups in the macromolecule have improved the print quality of the prints.

Our results help to understand phenomena which occur during printing, support the use of branched polyglycerols as performance additives for water-based printing inks, and may open up new possibilities for applications of these environmentally friendly polymers.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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