Valorization of Waste Polyethylene Terephthalate as a Functional Binder for Ballpoint Pen Ink: A Circular Economy Approach

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Abstract

The global accumulation of polyethylene terephthalate (PET) waste poses a serious environmental challenge, and the stationery industry remains dependent on virgin petrochemical binders for ballpoint pen inks. This study presents a sustainable upcycling approach that converts waste PET into a functional ink binder. PET bottles were chemically depolymerized via glycolysis with glycerol using zinc acetate as a catalyst. The reaction conditions were systematically optimized, yielding the following optimal parameters: a PET-to-glycerol mass ratio of 1:1.1, 0.6 wt% catalyst, 230 °C, and 4 hours of reaction time. The resulting oligomeric resin (number-average molecular weight, Mn ≈ 1,800 g/mol) was confirmed by FT-IR, GPC, and HPLC. The depolymerization product was formulated into a black ballpoint pen ink with nigrosine dye as the colorant and phenol as the solvent. The optimal formulation (binder:phenol:nigrosine = 7:2:1, plus 0.8 wt% Span-80) exhibited excellent performance: appropriate viscosity, a drying time of ≤19 seconds, reliable temperature resistance from –20 to 40 °C, strong UV resistance of ≥72 hours, and extended storage stability of ≥340 days. All properties met or exceeded industry standards. This work demonstrates a practical, cost-effective, and sustainable route for upcycling PET waste into a high-value stationery product, reducing plastic pollution while replacing petrochemical binders.

Keywords: Waste PET Recycling, Glycolysis, Ballpoint Pen Ink, Circular Economy, Sustainable Materials, Oligomeric Resin

1. INTRODUCTION

The exponential growth in the production and consumption of plastics has led to a global environmental crisis, with polyethylene terephthalate (PET) being one of the most significant contributors due to its widespread use in packaging, particularly single-use beverage bottles [1-3]. The recalcitrance of PET to natural depolymerization, coupled with inefficient waste management systems, has resulted in severe ecological pollution, threatening marine life and terrestrial ecosystems [4, 5]. This pressing challenge has catalyzed intensive research into sustainable waste management strategies, moving beyond landfilling and incineration towards advanced recycling and upcycling methods that align with the principles of a circular economy [6, 7]. Conventional mechanical recycling, which involves physical reprocessing of PET waste, often leads to a decline in material properties—a process known as downcycling—limiting its application to lower-value products [8]. In contrast, chemical recycling, particularly depolymerization, offers a promising pathway for "closed-loop" recycling by breaking down PET into its monomers or oligomers, which can be repurified and repolymerized into virgin-quality materials [9]. Among various chemical methods, glycolysis has emerged as a particularly attractive technique due to its operational simplicity, moderate reaction conditions, and the high utility of its products, primarily bis(2-hydroxyethyl) terephthalate (BHET) and its oligomers [10, 11]. These glycolyzed products have been successfully valorized as precursors for a range of value-added materials, including unsaturated polyester resins (UPRs) [9], polyurethane (PU) foams and coatings [12-14], and alkyd resins [15], demonstrating the versatility of this recycling approach.

Parallel to the challenge of plastic waste, the manufacturing of everyday consumer goods, such as writing inks, continues to rely on virgin petrochemical feedstocks. Ballpoint pen ink is a complex colloidal system whose performance is critically dependent on its resin binder, which governs properties like viscosity, adhesion, drying characteristics, and stability [16, 17]. Conventional binders include glyptal resins, phenol-formaldehyde resins, and various acrylic polymers [18]. The synthesis of these resins is often energy-intensive and contributes to the overall cost and environmental footprint of the ink. Therefore, identifying sustainable, low-cost, and high-performance alternative binders is a pertinent industrial goal.

While previous literature has explored the use of recycled PET for solvents like ethylene glycol [19], and while its glycolysis products have been extensively used in resins for coatings and foams, a critical gap remains. To the best of our knowledge, the direct application of the oligomeric product from PET glycolysis as the primary film-forming binder in ballpoint pen ink has not been systematically investigated or reported. Unlike conventional binders, the hydroxyl-terminated oligoester derived from PET-glycerol glycolysis offers enhanced compatibility with polar solvents and dyes, while the retained aromatic backbone provides improved film hardness and thermal stability. This represents a significant opportunity for innovation, merging the urgent need for plastic waste valorization with the demand for greener chemical products.

This study, therefore, aims to bridge this gap by developing a comprehensive process for converting waste PET into a functional binder for ballpoint pen ink. We present a systematic investigation encompassing: (1) the optimization of the glycolysis reaction of waste PET with glycerol to produce a suitable oligomeric binder; (2) the formulation of a high-performance ballpoint pen ink using this binder, a colorant, a solvent, and performance-enhancing additives; and (3) a thorough evaluation of the final ink's properties against standard industrial benchmarks. This work not only provides a practical solution for PET waste management but also introduces a sustainable and economically advantageous feedstock for the stationery industry, embodying the principle of "upcycling" by transforming waste into higher-value functionality.

2. MATERIALS AND METHODS

2.1. Materials

The chemical reagents used in this study were purchased from commercial suppliers in China. Waste PET bottles were collected, cleaned, and cut into approximately 1 cm² flakes. Glycerol (industrial grade, >95%), which was employed as the glycolyzing agent, and zinc acetate (reagent grade, 98%), which was used as the catalyst, were obtained from Wuhan Pust Chemical Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd., respectively.

For the formulation of the ink, nigrosine (alcohol-soluble) was used as the dye and was sourced from Shanghai Aladdin Biochemical Technology Co., Ltd. Phenol (≥99.5%) was selected as the solvent and was also procured from Shanghai Aladdin Biochemical Technology Co., Ltd. Sorbitan monooleate (Span-80, 99%) was utilized as the surfactant and was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Depolymerization of Waste PET

The glycolysis of waste PET was carried out in a 500 mL three-neck flask equipped with a condenser, mechanical stirrer, and thermometer. Previously washed and dried PET pieces were placed in the flask along with glycerol. The mixture was heated to 100°C with continuous stirring at 200 rpm to ensure uniform mixing and water removal. Zinc acetate catalyst was then added to the reaction mixture. The temperature was subsequently raised to above 200°C, and the reaction was carried out with stirring to complete the depolymerization process. After the reaction was complete, the product mixture was cooled to 60°C and extracted with warm water (50-60°C) using a separatory funnel. This washing process was repeated three times to effectively remove unreacted glycerol and the zinc acetate catalyst. After separating the oligomer-rich organic layer, it was dehydrated under reduced pressure at 80°C for 2 hours.

2.3. Ink Formulation and Preparation

Nigrosine was dissolved in phenol while stirring at 500 rpm for 1 hour at 60°C to form a uniform dye-solvent mixture. PET depolymerization products were added to the dye-solvent mixture, and the temperature was raised to 80°C. The mixture was stirred for 3 hours to ensure complete dissolution. The surfactant was added to the uniform mixture. After continuing stirring at 80°C for 1 hour, it was cooled to room temperature and left for 8 hours. The mixture was filtered through a 200-mesh sieve to remove undissolved impurities, yielding the final ballpoint pen ink.

2.4. Methods for analyzing depolymerization products

The depolymerization rate of PET was quantitatively determined using a gravimetric method to assess the conversion of solid PET into soluble oligomers and monomers. Upon completion of the glycolysis reaction, the mixture was first cooled to 70°C to maintain fluidity for sampling. A precise amount of the reaction product (approximately 0.5 g) was then extracted and dissolved in 50 mL of toluene at 70°C for 30 minutes with continuous stirring. During this dissolution step, all depolymerization products, including oligomers, were completely dissolved in the toluene, while any unreacted PET remained as insoluble solid particles. The solution containing the insoluble residue was subsequently subjected to vacuum filtration using a pre-weighed glass fiber filter. The retained solid was thoroughly washed with warm toluene to remove any adsorbed decomposition products, followed by methanol washing to eliminate residual glycerol. The filter containing the unreacted PET was then dried in an oven at 80°C until constant weight was achieved. The depolymerization rate was calculated based on the mass difference between the initial PET and the recovered unreacted PET.

The chemical structure of the PET depolymerization product was characterized using a Fourier transform infrared (FT-IR) spectrometer. The FT-IR spectra were recorded on a Bruker Tensor 27 (Germany) spectrometer in the wavenumber range of 4000–500 cm^{-1}. The analysis was performed using the KBr pellet method.

The molecular weight of the PET depolymerization product was measured using a PL-GPC120 gel permeation chromatography analyzer (Polymer Laboratories, UK). Separation was performed on a polystyrene-divinylbenzene (PS-DVB) copolymer column using toluene as the mobile phase at a flow rate of 1.0 mL/min. The column temperature was maintained at 40°C, and a refractive index (RI) detector was used for detection.

The composition of the effluent collected during the depolymerization reaction was analyzed using a Smartline high-performance liquid chromatograph (Knauer, Berlin, Germany) equipped with an RI detector. Chromatographic separation was achieved on a sulfonated polystyrene-divinylbenzene copolymer column suitable for ion-exclusion chromatography. The mobile phase was 0.01 M H_2SO_4 solution at a flow rate of 0.4 mL/min. The column temperature was maintained at 40°C. The injection volume was 20 μL.

2.5. Ink performance evaluation

The formulated ink was evaluated against standard performance metrics:

Viscosity: Measured using an efflux viscometer (TQC VF2049) at 25 °C, with the time for the ink to flow through the viscometer orifice recorded. When measured with the efflux viscometer at 25°C, the viscosity should be between 80 s and 1390 s. A value below 80 s may cause writing discomfort and impair the performance of the oil-based ink system, while a value exceeding 1390 s may reduce drying efficiency. The optimal range is 150–300 s.

pH: A mixture of ink (5 g) and a 1:1 ethanol-glycerol solution (45 mL) was prepared. The pH was measured using a calibrated pH meter at 20 °C. The pH value should be maintained between 6 and 8.

Density: Measured using a density meter at 20 °C. The density should be between 1.15 and 1.4 g/cm^3. Stability is significantly reduced if this value is exceeded.

Drying Time: Two parallel lines (10 cm) were drawn on office paper. A 500 g weight (bottom diameter 50 mm) was placed on the paper, and the time until no ink transfer occurred when the paper was separated was recorded. The drying time should be ≤30 seconds.

Ink Discharge Rate: The initial mass of the ballpoint pen refill was measured. After drawing 400 lines (25 cm each) on office paper, the final mass was measured. The ink discharge rate was calculated as [(initial mass – final mass)/initial mass] × 100%. The ink discharge should not exceed 40%.

Temperature Resistance: Refills were stored horizontally in a freezer (-20 ± 1 °C) and an oven (40 ± 2 °C) for 24 h. The ink discharge was evaluated by writing at a speed of 20~25 mm/s, with a 60 g weight attached to the refill. After storage for 24 hours at -20°C and 40°C, the ink must be able to start writing lines immediately or within a line length of 10 cm, with no leakage observed when the pen is held upside down.

UV Resistance: Ink samples (4 cm × 5 cm) were placed 10 cm away from a 30 W UV lamp (wavelength 253 nm). The time until a significant color difference ($\Delta E > 3$) was recorded using a colorimeter. The UV resistance should be ≥50 hours.

Storage Stability: Refills were stored outdoors at ambient temperature. The ink performance was tested every 20 days, and the storage period until performance deterioration (e.g., viscosity > 1390 s, drying time > 30 s) was recorded. A shelf life of ≥6 months is required [20, 21].

Rheological Properties: The steady-shear and viscoelastic properties of the ink were measured using a rotational rheometer (TA Instruments DHR-3) with a cone-plate geometry (diameter: 40 mm, cone angle: 1°). Steady-shear flow curves were obtained by measuring the viscosity (η) as a function of shear rate ($\dot{\gamma}$) in the range of 0.1 to 100 s^{-1} at 25 °C. Amplitude sweeps were performed at a constant frequency of 1 Hz to determine the linear viscoelastic region (LVR). Frequency sweeps were conducted from 0.1 to 100 rad/s at a strain within the LVR to record the storage modulus (G') and loss modulus (G''). Measurements were performed in triplicate [22].

Colorimetric Properties: The color strength and shade of the ink were evaluated using a spectrophotometer (X-Rite 518) with a D65 illuminant and 10° standard observer. The ink was uniformly applied on standard office paper using a bar coater (applicator thickness: 50 μm). The Color Strength (K/S value) was calculated using the Kubelka-Munk equation [23].

$$K/S = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (1)$$

where R_∞ is the reflectance of the sample at the wavelength of maximum absorption (λmax). The CIE L*a*b* color space coordinates were measured to determine the color coordinates: L* (lightness), a* (red-green axis), and b* (yellow-blue axis). The color difference (ΔE) of the ink was calculated using the following equation [24, 25]：

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

3. RESULTS AND DISCUSSION

3.1. Optimization of PET Glycolysis Conditions

3.1.1. Effect of Catalyst Type and Reaction Time

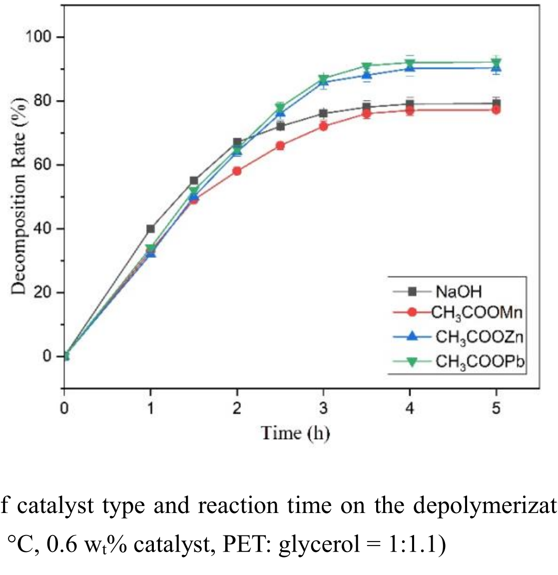


FIGURE 1. Effect of catalyst type and reaction time on the depolymerization rate of waste PET (Reaction conditions: 230 °C, 0.6 w_t% catalyst, PET: glycerol = 1:1.1)

The glycolysis of waste PET was systematically investigated using sodium hydroxide, lead acetate, manganese acetate, and zinc acetate as catalysts. After four hours, depolymerization efficiencies were 92% (lead acetate), 89.2% (zinc acetate), 79% (sodium hydroxide), and 77% (manganese acetate) (**Figure** 1). Although lead acetate showed the highest activity, its severe toxicity precludes practical use. Sodium hydroxide caused corrosion and generated wastewater. Through comprehensive evaluation, zinc acetate was determined to represent the optimal compromise, achieving 89.2% depolymerization with moderate toxicity and reasonable cost.

Based on the kinetic data, a reaction time of 4 hours was selected. Extending the reaction to 5 hours yielded negligible improvement (89.2% → 89.3%), making longer reaction times economically unjustified.

3.1.2. Effect of Catalyst Dosage

As shown in **Figure** 2, increasing zinc acetate from 0.1 wt% to 0.5 wt% raised the depolymerization rate from 49% to 86.5%. Beyond 0.6 wt%, the rate plateaued at 89.2%, indicating kinetic saturation. Therefore, 0.6 wt% was selected as the optimal catalyst dosage; higher loadings provided no additional benefit.

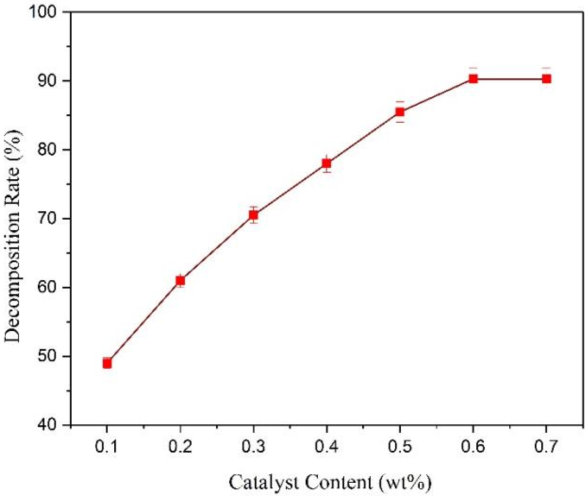


FIGURE 2. Effect of catalyst dosage on the depolymerization rate of waste PET (Reaction conditions: 230 °C, 4 h, PET : glycerol = 1:1.1)

3.1.3. Effect of Reaction Temperature

Figure 3 shows that increasing the temperature from 180°C to 210°C increased the depolymerization yield from 50% to 85.6%. Above 210°C, the increase slowed, reaching 89.2% at 230°C with no further improvement at 240°C. Accordingly, 230°C was selected as the optimal reaction temperature.

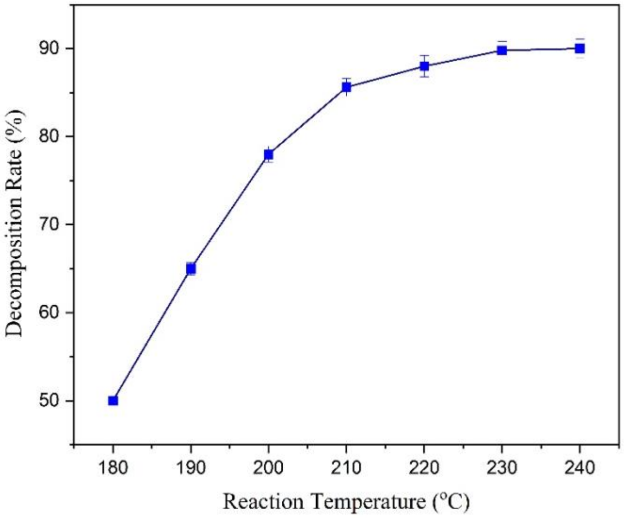


FIGURE3. Effect of reaction temperature on the depolymerization rate of waste PET (Reaction conditions: 0.6 wt% zinc acetate, 4 h, PET:glycerol = 1:1.1)

3.1.4. Effect of Glycerol Amount

As shown in **Figure** 4, increasing the glycerol-to-PET (G:P) mass ratio from 0.5 to 1.1 raised the depolymerization rate from 50.4% to 89.2%. Further increasing the ratio to 1.3 resulted in only a marginal increase (89.2% → 89.25%). Thus, a G:P ratio of 1.1 was selected as optimal.

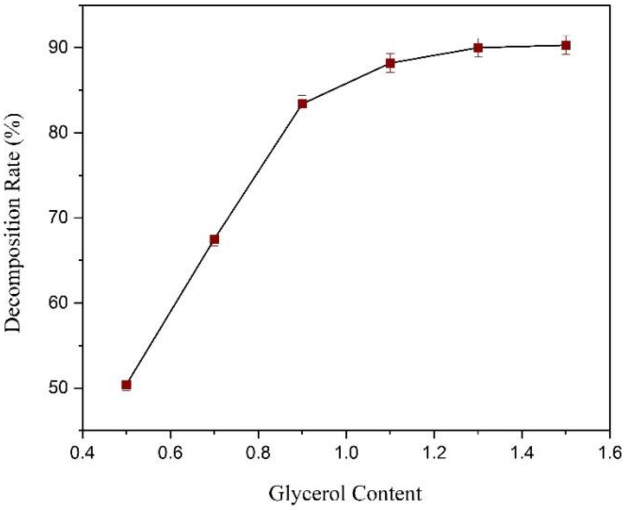


FIGURE 4. Effect of glycerol content on the depolymerization rate of waste PET (Reaction conditions: 0.6 wt% zinc acetate, 230°C, 4 h)

3.2. Characteristics of depolymerization products

The FT-IR spectrum (**Figure** 5a) shows characteristic absorptions of hydroxyl-terminated oligoesters: a broad O-H stretch at ~3380 cm⁻¹, a carbonyl (C=O) stretch at 1715 cm⁻¹, and C-O stretches in the 1300–1000 cm⁻¹ region. These features confirm the preservation of ester linkages and the presence of hydroxyl end groups, which are essential for the binder's compatibility with polar solvents and dyes.

GPC analysis (**Figure** 5b) revealed a number-average molecular weight (Mn) of 1,823 g/mol, a weight-average molecular weight (Mw) of 4,450 g/mol, and a polydispersity index (PDI) of 2.44. The average degree of polymerization was approximately 6–7, and the moderate polydispersity is typical for this type of oligomeric mixture, supporting its suitability as an ink binder.

HPLC analysis of the effluent (**Figure** 5c) identified two major peaks corresponding to water (retention time: 1.321 min) and ethylene glycol (retention time: 6.534 min). Ethylene glycol is an inevitable byproduct of decomposition, and water likely arises from oligomer recombination and glycerol decomposition at high temperatures. These byproducts are consistent with the expected transesterification and dehydration reactions.

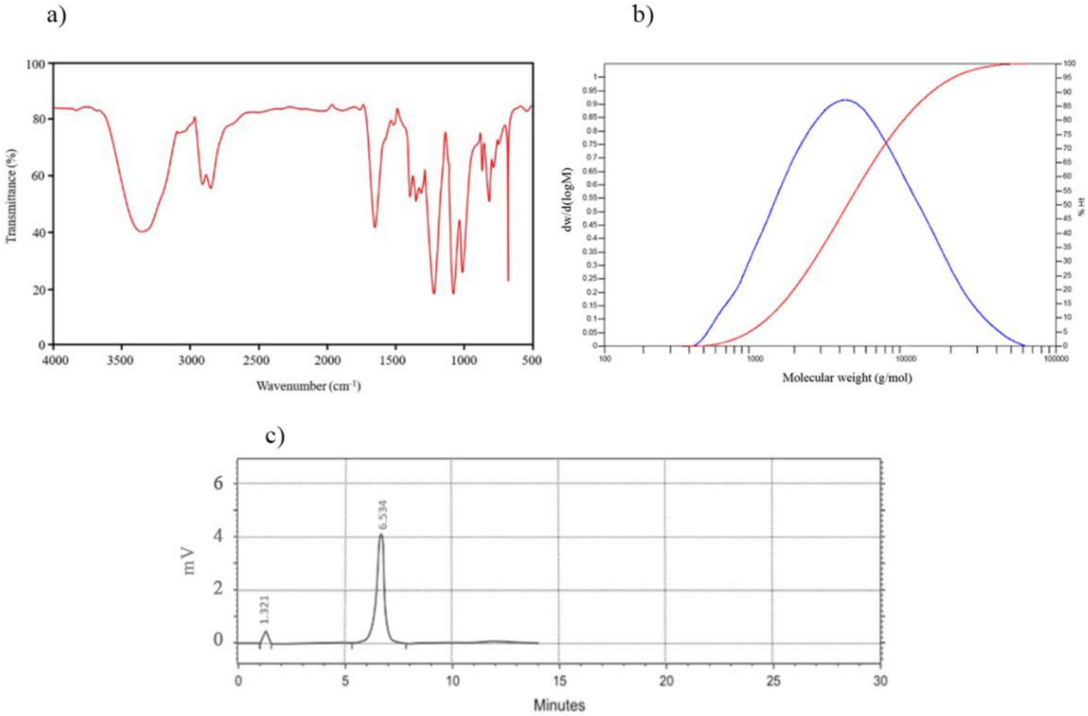


FIGURE5. Characteristics of the depolymerization products
(a): FT-IR, (b): GPC, (c): HPLC of the effluent

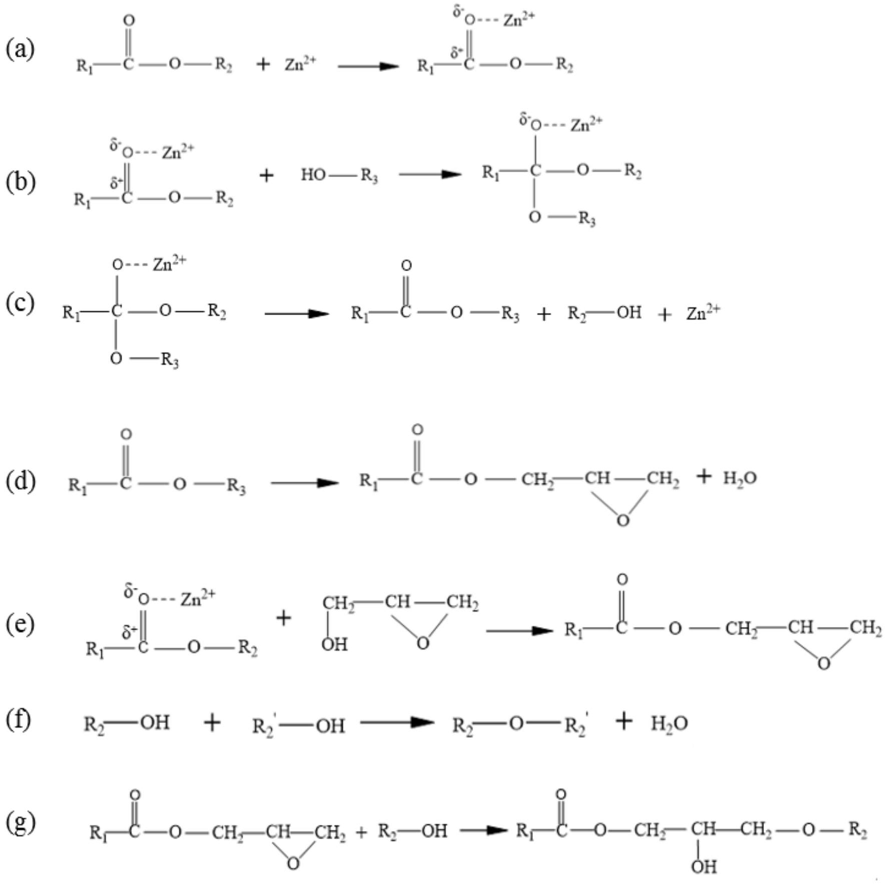
3.3. Mechanism of PET Glycolysis

Through analysis of the degradation product characteristics and a literature review, a plausible reaction pathway for PET glycolysis is proposed. The glycolysis of PET catalyzed by zinc acetate proceeds through a transesterification mechanism, which can be divided into three steps.

Step 1: Activation of the carbonyl group by a catalyst. Zinc acetate ($Zn(OAc)_2$) acts as a Lewis acid catalyst [26, 27]. The zinc ion (Zn^{2+}) coordinates with the carbonyl oxygen in the ester bonds of the PET backbone, increasing the partial positive charge on the carbonyl carbon (**Scheme** 1a) and facilitating nucleophilic attack [28].

Step 2: Nucleophilic attack, chain scission, and catalyst regeneration. The primary hydroxyl group of glycerol attacks the activated carbonyl carbon, forming an unstable tetrahedral intermediate (**Scheme** 1b). This intermediate breaks down, cleaving the PET chain and simultaneously yielding glycerol-PET oligomers and hydroxyl-terminated PET oligomers (including ethylene glycol, EG) while regenerating the catalyst (**Scheme** 1c). This catalytic cycle repeats, leading to complete PET degradation.

Step 3: Dehydration reaction. This side reaction is activated at high temperature. An intramolecular dehydration reaction proceeds at the glycerol terminal portion of the glycerol-PET oligomer (**Scheme** 1d), producing water [30]. An alternative pathway involving attack of free glycidol (derived from glycerol dehydration) on PET has also been proposed (**Scheme** 1e) [31]. Additionally, at high temperatures, ether bonds (-C-O-C-) form through condensation reactions (**Scheme** 1f), observed as a peak around 1120 cm^{-1} in FT-IR spectra [30]. Epoxy-terminated oligomers can react with hydroxyl groups of other oligomers (**Scheme** 1g), contributing to molecular weight increase and branched structures [32].



R_1: PET chain containing terephthalate

R_2, R_2': Hydroxyethyl terminal chain

R_3-OH: Glycerol

SCHEME1. Reaction pathway of PET glycolysis.

3.4. Optimization of Ink Formulation

3.4.1. Effect of Binder (PET Depolymerization Product) Content

Table 1 summarizes the effect of binder content (50–80 wt%) on ink properties. As binder content increased, viscosity and density increased, while drying time and ink discharge rate decreased. Optimal temperature resistance was achieved at 65–70 wt% binder. Based on the overall assessment, 70 wt% binder was selected as optimal, providing a balanced combination of viscosity (210 s), drying time (19 s), and stability.

TABLE1. Effect of binder content on ink performance (Nigrosine: Phenol=1: 2, 25 °C).

Binder Content (wt%)	Viscosity (s)	pH	Density (g/cm³)	Drying Time (s)	Ink Discharge Rate (%)	Temperature Resistance (24 h)		UV Resistance (h)	Storage Stability (days)
						-20±1,℃	40±2,℃		
50	59	6.0	1.21	32	43	Δ	⊗	59	220
55	79	6.1	1.25	27	40.5	Δ	⊗	63	260
60	103	6.1	1.29	24	37.6	Δ	⊗	68	280
65	169	6.1	1.33	21	35.3	O	Δ	72	300
70	210	6.2	1.35	19	34.6	O	O	72	340
75	289	6.4	1.40	17	31.5	Δ	Δ	71.5	360
80	362	6.4	1.42	15	30.2	⊗	⊗	71	360

Note: ○: Excellent; Δ: Good; ⊗: Poor. All values are means of three independent measurements. The relative standard deviation (RSD) was <6% for all quantitative measurements except pH (absolute SD < 0.05) and storage stability (RSD < 8%).

3.4.2. Effect of Colorant (Nigrosine) Content

Table 2 shows the influence of nigrosine content (5–20 wt%). Viscosity, density, and UV resistance increased with nigrosine content up to 10–13 wt%, beyond which UV resistance deteriorated. Temperature resistance was optimal at 8–10 wt% nigrosine. Storage stability decreased at higher pigment loads due to sedimentation. Color depth (ΔE) peaked at 10 wt% nigrosine. Therefore, 10 wt% nigrosine was selected as optimal.

TABLE 2. Effect of nigrosine content on ink performance (Binder: Phenol=7: 2, 25 °C).

Nigrosine Content	Viscosity (s)	pH	Density	Drying Time (s)	Ink Discharge	Temperature Resistance (24 h)	UV Resistance	Storage Stability	Color Difference

(wt%)			(g/cm³)		Rate (%)	-20±1,°C	40±2,°C	(h)	(days)	(ΔE)
5	162	6.4	1.30	25	37.2	Δ	⊗	59	360	0.5
8	182	6.3	1.33	22	35.5	O	Δ	63	350	0.8
10	210	6.2	1.35	19	34.6	O	O	72	340	1.2
13	227	6.2	1.36	16	34.2	Δ	O	70	330	1.0
15	252	6.1	1.36	15	33.8	Δ	Δ	65	300	0.8
18	271	6.1	1.37	15	33.1	⊗	Δ	60	280	0.7
20	283	6.0	1.37	15	32.8	⊗	⊗	58	260	0.6

Note: ○: Excellent; Δ: Good; ⊗: Poor. All values are means of three independent measurements. The relative standard deviation (RSD) was <6% for all quantitative measurements except pH (absolute SD < 0.05) and storage stability (RSD < 8%). Color difference (ΔE) measurements had an uncertainty of ±0.1.

3.4.3. Effect of Solvent (Phenol) Content

Table 3 presents the effect of phenol content (15–25 wt%). Lower phenol content increased viscosity and decreased drying time and ink discharge rate. Temperature and UV resistance were optimal at 20 wt% phenol. Storage stability decreased at lower phenol content, likely due to resin aggregation. Consequently, 20 wt% phenol was selected as optimal.

TABLE 3. Effect of phenol content on ink performance (Binder: 70 wt%, Nigrosine: 10 wt%, Additives: 5 wt%, 25 °C).

Phenol Content (wt%)	Viscosity (s)	pH	Density (g/cm³)	Drying Time (s)	Ink Discharge Rate (%)	Temperature Resistance (24 h)		UV Resistance (h)	Storage Stability (days)
						-20±1, °C	40±2, °C		
25	181	6.5	1.30	21	37.2	Δ	⊗	60	360
23	192	6.4	1.33	20	36.5	O	Δ	64	350
20	210	6.2	1.35	19	34.6	O	O	72	340
18	259	6.0	1.43	14	34.2	Δ	O	70	320
15	302	5.8	1.47	12	33.8	⊗	Δ	64	310

Note: ○: Excellent; Δ: Good; ⊗: Poor. All values are means of three independent measurements. The relative standard deviation (RSD) was <6% for all quantitative measurements except pH (absolute SD < 0.05) and storage stability (RSD < 8%).

3.4.4. Effect of Surfactant (Span-80):

Table 4 summarizes the effect of Span-80 concentration (0–1.5 wt%). Adding Span-80 reduced viscosity, slightly increased drying time, and improved temperature resistance (particularly at –20°C) and storage stability, with optimal performance at 0.5–0.8 wt%. The ink discharge rate remained largely unchanged, and color difference (ΔE, see **Table** 2) was not affected.. Thus, 0.8 wt% Span-80 was selected as optimal.

TABLE 4. Effect of surfactant content on ink performance (Binder:Phenol:Nigrosine = 7:2:1,

25 °C).

Surfactant Content (wt%)	Viscosity (s)	Ink Discharge Rate (%)	Temperature Resistance (-20±1°C)	Storage Stability (days)	Drying Time (s)
0.0	210	34.6	Δ	340	19
0.2	200	34.8	Δ	350	19
0.5	190	34.5	O	360	20
0.8	185	34.2	O	370	21
1.2	184	33.8	Δ	365	22
1.5	183	33.5	⊗	360	23

Note: ○: Excellent; Δ: Good; ⊗: Poor. All values are means of three independent measurements. The relative standard deviation (RSD) was <6% for all quantitative measurements except storage stability (RSD < 8%).

3.5. Rheological and Colorimetric Analysis of the Optimized Ink

3.5.1. Rheological Behavior

Figure 6a shows pronounced shear-thinning behavior: viscosity decreased significantly with increasing shear rate. In Figure 6b, G″ was consistently higher than G′ across the measured frequency range, indicating dominant liquid-like behavior with a weak gel network. This structure, imparted by the oligomeric PET-glycerol products, explains the ink's anti-settling properties and shear-induced liquefaction.

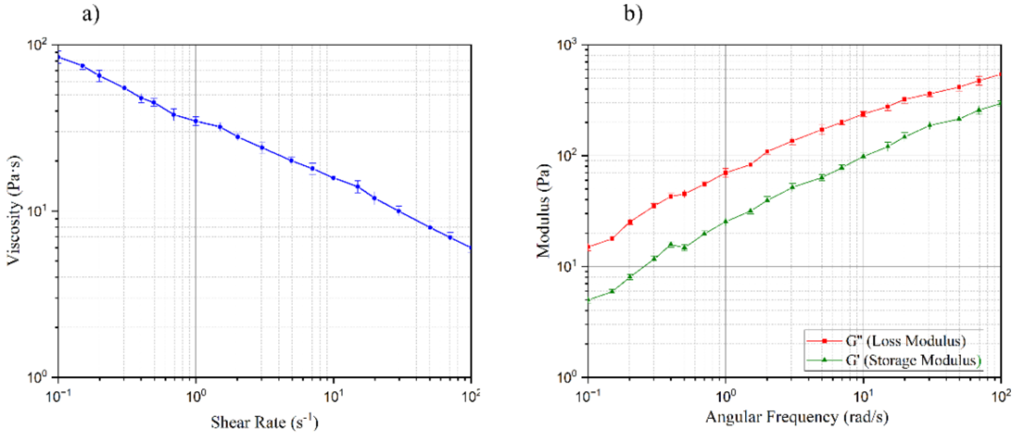


FIGURE 6. Rheological behavior of the optimized ballpoint pen ink
(a): Steady-shear flow curve (b): Dynamic frequency sweep

3.5.2. Colorimetric Properties

Table 5 compares the optimized ink with a commercial reference. The K/S value (28.5 vs. 29.1) and ΔE (0.6) indicate that the waste PET-based ink achieves a commercially acceptable black color.

TABLE 5. Colorimetric data of the optimized ink compared to a commercial reference.

Sample	K/S (at λ_{max})	L*	a*	b*	ΔE
Optimized Ink	28.5	25.3	-0.2	0.5	-
Commercial Ink	29.1	24.8	0.1	0.3	-
Color Difference	0.6	0.5	0.3	0.2	0.61

3.6. Overall Ink Performance

Table 6 shows that all indicators met or exceeded industrial standards for ballpoint pen ink, demonstrating its potential for practical application.

TABLE 6. Comprehensive performance of the optimized ballpoint pen ink

Performance Indicator	Test Result	Industrial Standard
Viscosity (25 °C)	110-150 s	80–1390 s
pH	7.0-7.5	6–8
Density (20 °C)	1.15–1.25 g/cm³	1.15–1.40 g/cm³
Drying Time (20 °C)	≤19 s	≤30 s
Ink Discharge Rate (100 m)	≤40%	≤45%
Temperature Resistance (-20 ± 1 °C, 24 h)	No leakage	No leakage
Temperature Resistance (40 ± 2 °C, 24 h)	No leakage	No leakage
UV Resistance (253 nm)	≥70 h	≥50 h
Storage Stability (Ambient)	≥300d	≥340d

Note: Standards referenced: ISO 12756:2016 and ISO 27668-1:2017.

4. CONCLUSIONS

This study demonstrates that waste PET depolymerization products can serve as a functional binder for ballpoint pen ink. The key findings are as follows:

1. **Optimal PET Glycolysis Conditions**: Waste PET was depolymerized with glycerol using 0.6 wt% zinc acetate at 230 °C for 4 h with a PET:glycerol mass ratio of 1:1.1. The oligomeric product (Mn ≈ 1,800 g/mol) consisted primarily of hydroxyl-terminated oligoesters, as confirmed by FT-IR, GPC, and HPLC.
2. **Optimal Ink Formulation:** The ink formulated with PET-derived binder, phenol, and nigrosine at a 7:2:1 mass ratio plus 0.8 wt% Span-80 exhibited appropriate viscosity, drying time (≤19 s), temperature resistance (–20 to 40 °C), UV resistance (≥72 h), and storage stability (≥340 days), meeting industry standards.
3. **Environmental and Economic Benefits:** This approach offers a cost-effective alternative to conventional binders by utilizing waste PET, reducing plastic pollution while providing a sustainable feedstock for ink production.

Future research will focus on improving the water resistance of the ink and expanding the application of waste PET depolymerization products to other types of inks (e.g., gel pens, markers). Ongoing work in our group is directed toward water-based ink formulations using the same PET-derived binders, which would eliminate the need for hazardous organic solvents such as phenol.

CRediT Author Statement

Ri Myong Kim: Project administration, Conceptualization. **Jun Hyok Oh**: Writing – original draft, Project administration. **Il Song Ryang**: Conceptualization, Writing – original draft. **Jong Nam Kim**: Supervision. **Yong Il Kim**: Formal analysis. **Guk Chan Kim**: Methodology, Formal analysis. **Kuang Min Ho**: Data curation. **Kum Hyok Ju:** Characteristic Analysis, Mechanism Interpretation. **Ryong Chol Son:** Writing – original draft, Data curation.

Acknowledgments

The authors would like to thank the Hamhung Ballpoint Pen Factory for providing experimental facilities and technical support.

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