Synthesis and Properties of Isosorbide-based Eco-friendly Plasticizers for Poly(vinyl chloride)

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Abstract

In this study, eco-friendly and effective plasticizers, based on isosorbide, were synthesized and characterized. The esterification of isosorbide was conducted using different alkyl chain lengths of various fatty acids. The optimal esterification degree of isosorbide was obtained with a fatty acid of short alkyl chain length, after reaction with $\text{Ti}(\text{OBu})_4$ catalyst, at 220°C , after 6 h. An esterified isosorbide, with long alkyl chain length, was epoxidized to further enhance its plasticizing properties and enable low-cost production. The high epoxidation degree (91%) indicated efficient epoxidation by formic acid and hydrogen peroxide. Finally, the mechanical, thermal, and plasticizing properties of the prepared isosorbide-based plasticizers were compared to a commercial plasticizer. The plasticizers prepared in this study, particularly isosorbide di epoxidized oleate, could be used as eco-friendly and effective plasticizers for practical PVC applications.

1. Introduction

Poly(vinyl chloride) (PVC) is a popular thermoplastic for various applications, such as cable insulation, pipes, construction, packaging, window profiles, and automobile interior materials, because of its low-cost production, easy fabrication, high chemical stability, and good mechanical properties [1–3]. However, applications of PVC products are limited, owing to the rigidity and brittleness imparted by dipoles in the C-Cl structure of PVC, hindering chain mobility [4]. Therefore, to process flexible PVC products, such as, cable insulation, and automobile interior materials, plasticizers are required as additive materials to reduce the melt viscosity, and glass transition temperature (T_g) during PVC processing [5, 6].

Various phthalate-based plasticizers, such as dioctyl phthalate (DOP) [7, 8], di-(2-ethylhexyl) phthalate (DEHP) [9], n-butyl phthalate (BBP) [10, 11], and di-isononyl phthalate (DINP) [12], are preponderant because of their excellent plasticizing effects, low cost, good compatibility, low volatility, and high water resistance. However, these phthalate-based plasticizers have several disadvantages, such as fatal toxicity, migration, and material degradation [13]. To overcome these drawbacks, petroleum-based plasticizers, using trimellitate, adipate, and terephthalate, have been investigated [14–16]. However, petroleum-based plasticizers are expensive and contribute to the greenhouse effect and environmental pollution because of petroleum mining and lead to depletion of fossil fuel resources [17]. Therefore, the development of new plasticizers, with non-toxicity, high resin-compatibility, low cost, and efficient plasticizing ability, is vital.

Compared to phthalate-based plasticizers, bio-based plasticizers exhibit reduction in chain interactions, and easy formation of free volumes in the PVC, owing to interactions of the epoxy group and alkyl chains, with the polar segment of the PVC, forming a flexible PVC structure [18, 19]. Bio-based plasticizers, developed using bioresources, including vegetable oils [20, 21], epoxidized oils [22, 23], fatty acid esters [24], esterified oils [25], cardanol [26–28], and isosorbide esters [29, 30], have been reported. Among the various bioresources, isosorbide, an isomer of 1,4:3,6-dianhydrohexitol, is commercially produced by the dehydration of glucose-derived sorbitol. Isosorbide diesters are biodegradable, sustainable, and thermally

stable heterocyclic diols, which are easily esterified by reacting isosorbides with fatty acids [31]. Isosorbide diester plasticizers exhibit good compatibility with PVC because of their chemical structure, which is similar to that of phthalate-based plasticizers. Moreover, their properties can be controlled by varying the alkyl chain length using different fatty acids [32, 33].

To the best of our knowledge, this is the first study to introduce isosorbide di epoxidized oleate as a green plasticizer for PVC processing. Here, isosorbide was esterified with a series of fatty acids, and the isosorbide diester plasticizer with short alkyl chain length showed high compatibility with PVC. However, fatty acids with short alkyl chain length are not suitable for industrial applications because of high material costs. Therefore, the isosorbide diester with long alkyl chain length was epoxidized to enhance its plasticizing properties. The resulting isosorbide di epoxidized oleate, as a plasticizer for PVC sheets, was characterized by analyzing its plasticizing, chemical, mechanical, and thermal properties. As confirmed by precise analytical results, the isosorbide di epoxidized oleate plasticizer exhibits potential as a promising alternative for practical PVC applications.

2. Experimental

2.1. Materials

Isosorbide, octanoic acid (C8, ≥98%), decanoic acid (C10, ≥98%), lauric acid (C12, ≥98%), palmitic acid (C16, ≥99%), stearic acid (C18:0, ≥98.5%), oleic acid (C18:1, ≥99%), formic acid (95-97%), titanium (IV) butoxide (≥97.0%), and sodium hydroxide (≥98%) were purchased from Sigma-Aldrich. Myristic acid (C14, >99.0%), hydrogen peroxide (30% in water), and toluene (>99.5%) were purchased from Tokyo Chemical Industry Co., Ltd., and PVC resin (P-1000) was donated by the Hanwha Chemical Corporation (Table 1). The Ca-Zn organic liquid complex (CZ-400) thermal stabilizer was supplied by the Songwon Industry Corporation.

Table 1
Basic properties of PVC resin (P-1000)

Properties	Typical value	Methods
Degree of polymerization	1000 ± 50	JIS K 6720-2
Apparent density	0.55 ± 0.04 g/cm ³	ASTM D1895
Volatility	<0.3%	ASTM D3030
Sieve pass	100%	HSC method (42 mesh, 350 μm)

2.2. Synthesis of isosorbide dioctanoate

Isosorbide (122 g, 0.8 mol) and toluene (100 mL) were stirred at room temperature in a 1 L 4-necked flask, equipped with a Dean-Stark column, under N₂. Subsequently, octanoic acid (277.25 g, 1.92 mol) and titanium (IV) butoxide (1 g, 0.3 mol%) were added and kept at 130°C for 5 h. After toluene removal, the

reaction was maintained at 220°C, for 10 h, and on reaction completion, the mixture was stirred under vacuum (10 hPa) at 220°C until the pH was <3, followed by natural cooling to 70°C, under ambient conditions. The mixture was neutralized with a saturated NaOH aqueous solution until pH=0, and then, it was extracted using a separatory funnel. Isosorbide dioctanoate (ISODO) (261 g, 0.70 mol) was obtained at 120°C, under 10 hPa, after the removal of residual solvent and moisture (Fig. 1(a)).

2.3. Synthesis of isosorbide di epoxidized oleate

Isosorbide dioleate (ISODOL, 270 g, 0.35 mol), formic acid (9.21 g, 0.18 mol), and toluene (60 mL) were stirred in a 1 L 4-neck flask, with a Dean-Stark column. Hydrogen peroxide (48.14 g, 1.42 mol) was slowly added using a drawing funnel, at 35°C, for 2 h, and then, the reaction mixture was kept at 60°C for 10 h. Subsequently, the mixture was purified using a separatory funnel, and deionized water (300 mL). Isosorbide di epoxidized oleate (ISODEOL, 259.44 g, 0.32 mol) was obtained after the removal of residual solvent and moisture at 120°C under 10 hPa (Fig. 1(b)).

2.4. PVC sheet processing

The PVC resin, plasticizer (50–60 phr), and stabilizer (2.5 phr) were mixed at 90°C, using a Henschel mixer (5 L, Jooshin Industrial Co.), and the mixture was compounded at 170°C for 5 min in a test mixing roll (TOYOSEIKI 287, rotation ratio: 14:19.6 rpm). The PVC sheet was fabricated using a hot-press machine (Carver, Auto Series Presses) at 175°C for 3 min under 5 ton pressure and then cooled in water (20°C). The dimensions of the mold were 200 mm × 200 mm × 1 mm. In a comparative study, PVC sheets were prepared with commercial plasticizers (DEHP and DOP) using the same method.

2.5. Characterization

Fourier-transform infrared spectroscopy (FT-IR, Nicolet 5700, Thermo) was used to analyze changes in the isosorbide structure. Solubility parameters (δ) of the plasticizers were calculated according to Small's cohesive energies [34], and epoxy values of the synthesized plasticizers were calculated according to ASTM D1652-04. The PVC specimens were prepared as type IV dumbbell-type, according to ASTM D638. The tensile stress, elongation, and 100% modulus were measured using a universal test machine (UTM, INSTRON 3369), according to ASTM D882. The hardness was measured using a Shore A-type hardness meter (e-Asker), according to ASTM D2240. Thermogravimetric analysis (TGA, TG209 F3, NETZSCH) was performed in the range of 30–700°C at a heating rate of 10°C/min under N₂ atmosphere.

3. Results And Discussion

The esterification of isosorbide was conducted using various catalysts for synthesizing bio-based plasticizers. The conversion yields of a water-soluble acid catalyst (H₂SO₄), and organic catalysts (TsOH, and Ti(OBu)₄) were analyzed to optimize the esterification of isosorbide with octanoic acid. The conversion results are summarized in Table 2. The conversions of isosorbide with H₂SO₄ and TsOH catalysts were 32% and 63%, respectively, indicating inefficient conversion of the -OH moieties at the *syn*-position due to steric hindrance of the isosorbide. The highest conversion (87%) was obtained with 1

mol/L $\text{Ti}(\text{OBu})_4$ catalyst after reaction at 220°C for 6 h, indicating improved conversion efficiency of the -OH group at the *syn*-position. Therefore, $\text{Ti}(\text{OBu})_4$ was used as an organic catalyst. To elucidate the influence of the alkyl chain length, a series of isosorbide diesters were synthesized, using fatty acids having different numbers of carbons (C8–C18), such as, octanoic acid (ISODO), decanoic acid (ISODD), lauric acid (ISODL), myristic acid (ISODM), palmitic acid (ISODP), stearic acid (ISODS), and oleic acid (ISODOL).

Table 2
Conversions yields of isosorbide esterification with oleic acid, using different catalysts, chemical equivalents, and temperatures

Batch No.	Catalyst	Chemical equivalent (mol/L)	Temperature ($^\circ\text{C}$)	Conversion (%)
1	H_2SO_4	1	150	30
2	H_2SO_4	1.5	150	32
3	H_2SO_4	1	220	30
4	TsOH	1	150	55
5	TsOH	1.5	150	62
6	TsOH	1	220	63
7	$\text{Ti}(\text{OBu})_4$	1	150	60
8	$\text{Ti}(\text{OBu})_4$	1.5	150	62
9	$\text{Ti}(\text{OBu})_4$	1	220	87

Changes in the chemical structure of isosorbide before and after esterification were analyzed using FT-IR spectroscopy (Fig. 2(a)). The broad peak at 3392 cm^{-1} (attributed to the -OH group of fatty acids (C8, C10, and C18)) disappeared, indicating efficient conversion of the -OH group, during esterification. The peak intensity of the -OH group for isosorbide (at 1421 cm^{-1}) decreased, indicating esterification of the -OH groups located at the anti- and syn-positions in the isosorbide with the acid group of octanoic acid [35]. Thus, isosorbide efficiently reacted with the fatty acids, and remained in the system. The peak intensities at 2925 and 2856 cm^{-1} for ISODO were stronger than those of isosorbide, confirming the formation of CH_2 and CH_3 , respectively, in ISODO [33]. The intensity of the characteristic peak assigned to $\text{C}=\text{O}$ at 1737 cm^{-1} increased significantly after esterification. Furthermore, the characteristic peaks at 1159 and 1097 cm^{-1} exhibited enhancement after esterification, owing to $\text{C}-\text{O}-\text{C}$ group formation [36]. FT-IR spectra were analyzed to study changes in the chemical structure before and after epoxidation. As shown in Fig. 2(b), ISODOL exhibited characteristic peaks at 3009 and 1600 cm^{-1} , for $\text{C}=\text{C}$ and $\text{C}-\text{H}$ groups, respectively. After epoxidation (ISODEOL), the peak intensity at 3009 cm^{-1} (for the $\text{C}=\text{C}$ group)

decreased, while the characteristic peak of the epoxy group appeared at 820 cm^{-1} , indicating synthesis of the epoxidized plasticizer [37, 38].

The epoxidation of ISODOL was investigated as a function of reaction time to obtain the highest yield, and the calculated results are shown in Fig. 3. The epoxy value and conversion increased with increasing reaction time, with the highest values of 3.9% and 91%, respectively, obtained after 12 h reaction time, indicating effective transformation of the ISODOL double bonds into the epoxy group [39]. Thus, ISODEOL was epoxidized from ISODOL, using formic acid and hydrogen peroxide, in agreement with the FTIR results (Fig. 2(b)). The ISODEOL plasticizer could improve PVC compatibility due to its high degree of conversion [40].

Compatibility is an important parameter for evaluating the processability and mechanical properties of PVC. Therefore, compatibilities of the synthesized plasticizers were evaluated and compared with those of a commercial DEHP plasticizer. To conduct the measurement in the form of a sheet, PVC was mixed with a plasticizer (50 phr) and stabilizer (2.5 phr) at 90°C using a Henschel mixer. Compatibility between PVC and the plasticizer was evaluated in terms of the solubility parameter (δ) (Table 3). The δ value of PVC was 9.7, and the δ values of isosorbide-based plasticizers decreased with increasing alkyl chain length (C8–C18, originally from fatty acids). ISODO and ISODD exhibited similar solubility parameters ($\delta = 8.7$) compared to the commercial DEHP plasticizer ($\delta = 8.9$). The absorption times of the plasticizers increased with increasing alkyl chain length. A short absorption time indicates good miscibility and wettability. The plasticizers with $>\text{C}12$ were not absorbed because of high molecular weight. Thus, plasticizers with short alkyl chain length ($<\text{C}10$) exhibit enhanced compatibility with PVC. The ISODOL plasticizer was not absorbed into PVC before epoxidation, while the ISODEOL plasticizer was absorbed into the PVC resin within 6 min 16 s after epoxidation. Additionally, the δ value increased from 8.4 to 8.7 after epoxidation, moving closer to the δ value (8.9) of DEHP. Thus, the PVC compatibility of ISODOL was improved by epoxidation [41]. To evaluate processability, PVC compounds were prepared with different plasticizers, using a two-roll mill, at 170°C . As shown in Table 3, the PVC resins with DEHP, ISODO, and ISODD plasticizers melted, whereas the resins with ISODL, ISODM, ISODP, and ISODS plasticizers did not melt. Thus, processability of the PVC compounds depended strongly on the alkyl chain length of the plasticizers, in agreement with results of the compatibility assessment. Considering the compatibility and processability of PVC, the synthesized ISODEOL, with the functionalized epoxy group, is a suitable plasticizer for PVC. It is a non-toxic, bio-based, and low-cost material, with efficient plasticizing ability.

Table 3
Compatibilities and processabilities of PVC with different plasticizers

Plasticizer	Solubility parameter (δ)	Absorption time	Melting condition	Molding condition
PVC only	9.7	-	-	-
DEHP	8.9	6 min 12 s	melted	molded
ISODO (C8)	8.7	6 min 30 s	melted	molded
ISODD (C10)	8.7	8 min 40 s	melted	molded
ISODL (C12)	8.5	up to 15 min	-	-
ISODM (C14)	8.3	up to 15 min	-	-
ISODP (C16)	8.0	up to 15 min	-	-
ISODS (C18)	7.5	up to 15 min	-	-
ISODOL	8.4	up to 15 min	-	-
ISODEOL	8.7	6 min 16 s	melted	molded

Using this bio-based plasticizer, the final PVC product could be employed in real applications. To assess the mechanical properties of plasticized PVC sheets with different plasticizers, the tensile stress, elongation at break, 100% modulus, and hardness were measured. As shown in Table 4, the tensile stress and 100% modulus of the PVC sheets increased with increasing alkyl chain length of the plasticizer, while the elongation at break decreased. This could be attributed to the relatively high molecular weight of the plasticizer, which increased with increasing alkyl chain length, whereas relatively small molecules could form the free volume in PVC. Compared to DEHP, ISODO exhibited higher tensile stress and 100% modulus, which could be attributed to formation of different degrees of free volume in the PVC, owing to the structural characteristics of ISODO (linear C8 alkyl chain) and DEHP (branched alkyl ester). Hardness of the PVC sheets increased with increase in alkyl chain length of the plasticizer and decreased slightly with increase in plasticizer content. Mechanical properties of PVC are attributed to free volume formation due to the alkyl chain length, and amount of plasticizer. Thus, ISODEOL was confirmed to be the most efficient plasticizer for PVC sheets, compared to other bio-based novel plasticizers in this study.

Table 4
Mechanical properties of PVC sheets with different plasticizers

PVC sheet	Tensile stress (kgf/mm ²)	Elongation-at-break (%)	100% modulus (kgf/mm ²)	Hardness
DEHP 50	1.96	338	1.01	84.6
ISODO 50	2.03	321	1.04	85.3
ISODO 55	1.92	346	0.98	84.2
ISODD 50	2.12	309	1.09	86.2
ISODD 55	1.98	336	1.01	84.7
ISODEOL 50	2.18	298	1.24	87.3
ISODEOL 60	1.98	331	1.03	84.8

PVC products formed using a plasticizer should be thermally stable. TGA thermograms were used to elucidate the thermal degradation behaviors of PVC sheets with different plasticizers (Fig. 4). The initial thermal degradation in the 190–350°C range was due to the dehydrochlorination of PVC [42]. The second region at 350–430°C was due to the formation of an aromatic structure, by polyene cyclization [29]. Finally, at temperatures above 430°C, the polyene structure was thermally degraded [43]. Table 5 summarizes the characteristic temperature points for TGA thermograms of PVC: the initial degradation temperature (T_i), weight loss temperatures of 10% (T_{10}) and 50% (T_{50}), and the residue at 700°C (% R_{700}). The T_i values of DOP, ISODO, ISODD, and ISODEOL were 190, 200, 210, and 236.8°C, respectively. The values of T_i , T_{10} , T_{50} , and R_{700} for ISODEOL were higher than those of DOP, ISODO, and ISODD. Notably, the R_{700} value of ISODEOL significantly increased to 11.37%, which was significantly higher than those of the others. Thus, higher thermal stability of the epoxy groups within ISODEOL enhanced the thermal stability of PVC.

Table 5
Thermal properties of PVC sheets with different plasticizers

Plasticizer	T_i (°C)	T_{10} (°C)	T_{50} (°C)	R_{700} (%)
ISODEOL	236.8	277.3	347.0	11.37
ISODD	210.0	268.0	311.5	8.11
ISODO	200	261.7	304.4	8.36
DOP	190	250.7	293.2	1.85

4. Conclusions

In this study, eco-friendly and efficient plasticizers were synthesized for the practical application of PVC sheets by the esterification and epoxidation of isosorbide. The plasticizing properties of isosorbide diesters were strongly dependent on the isosorbide alkyl chain length, indicating the suitability of isosorbide diesters with short alkyl chain lengths as plasticizers for PVC. Subsequently, considering their low industrial cost, isosorbide diesters with long alkyl chain lengths were epoxidized. The epoxidized isosorbide diesters, particularly ISODEOL, showed better plasticizing, mechanical, and thermal properties than commercial plasticizers. Thus, the epoxidized isosorbide diester plasticizers synthesized in this study could be potential alternatives for commercial plasticizers in future green industries.

Declarations

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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Author Contributions

Conceptualization: B.-M.L., J.J.H., and T.S.H.; Methodology and investigation: B.-M.L., J.J.H., and T.S.H.; Writing-original draft preparation: B.-M.L.; Writing-review and editing, and supervision: T.S.H. All authors have read and agreed to the published version of the manuscript.

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Figures

Figure 1

Synthesis of (a) isosorbide diester (ISODOL) and (b) isosorbide diepoxidized oleate (ISODEOL)

Figure 2

FT-IR spectra of (a) isosorbide and isosorbide dioctanate (ISODO) and (b) isosorbide dioleate (ISODOL) and isosorbide diepoxied oleate (ISODEOL)

Figure 3

Epoxy values and conversions for the ISODEOL as a function of the reaction time

Figure 4

TGA thermograms of PVC sheets with different plasticizers