Synthesis of Glycidylethylhexylphthalate and Its Effects on Poly(vinyl chloride) Films as a Novel Plasticizer

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ABSTRACT: To improve the processability and prevent the thermal degradation of poly(vinyl chloride) (PVC), various plasticizers and heat stabilizers have to be compounded. Phthalic plasticizers and metal soap stabilizers are usually used with epoxides as costabilizers. Epoxidized soybean oil (ESO), is one of the most commonly used epoxides because of its typical combined roles as a plasticizer and heat stabilizer in PVC compounds. ESO, however, sometimes causes surface contamination of PVC compounds because saturated fatty acids such as stearic and palmitic acids in soybean oil easily bleed onto the surface. In addition, some ingredients in ESO with hydroxide groups and unreacted double bonds during epoxidization also tend to increase the bleeding of ESO. This is due to their low compatibility with PVC resins. In this study, a novel plasticizer of PVC resins, glycidylethylhexylphthalate (GEHP), was synthesized, and its performance was evaluated. GEHP was designed to act as a plasticizer like normal phthalic plasticizers and to act as a heat stabilizer like ESO. Through the addition of epoxy groups in phthalic compounds, the resistance to bleeding was improved, and the plasticizing and heat-stabilizing effects on the PVC compounds were preserved. Soft PVC films were prepared with GEHP. The mechanical properties, thermal stability, and bleeding properties of the films were investigated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1347–1356, 2005

Key words: poly(vinyl chloride) (PVC); stabilization; films

INTRODUCTION

Poly(vinyl chloride) (PVC) has been widely used in various applications, from rubbery parts to hard products, because it has excellent processability, durability, and contamination resistance. Unlike other plastics, with the addition of plasticizers, the processability of PVC can be markedly improved, and then it can be processed in the forms of sheets or films for flooring, packaging, and construction applications. PVC, however, can be easily decomposed by heat, light, and oxygen during processing and servicing. This can cause discoloration and a deterioration of the physical properties.[1–5] When polymers containing chlorine, such as PVC, decompose, hydrochloride (HCl) is generated, and it catalyzes and accelerates the decomposition reactions of the polymers.[6–8]

To improve the processability and prevent the thermal degradation of PVC, various plasticizers and heat stabilizers have to be compounded. Phthalic plasticizers and metal soap stabilizers are usually used with

epoxides as costabilizers. As epoxides perform as plasticizers and heat stabilizers in PVC, they have been classified as epoxy plasticizers.[9,10] Because of epoxide groups, which consist of cyclic ethers with three-membered rings, epoxy plasticizers are very compatible with PVC and other plasticizers. Also, they have a good heat-stabilizing effect on PVC.

Epoxidized soybean oil (ESO) is one of the most commonly used epoxy plasticizers.[11–13] ESO, however, sometimes causes the surface contamination of PVC products because saturated fatty acids such as stearic and palmitic acids in soybean oil easily bleed onto the surface of PVC compounds. Some ingredients with unreacted double bonds and hydroxide groups, formed during the epoxidization of soybean oil, tend to increase the bleeding of ESO because of their low compatibility with PVC resins. In addition, chlorohydrin compounds from the reaction of ESO and HCl cause the same problem.[14]

In this study, a novel plasticizer for PVC resins, glycidylethylhexylphthalate (GEHP), was synthesized through the substitution of one of the ethyl hexyl groups in diethylhexylphthalate (DEHP) with a glycidyl group. GEHP was designed to improve the bleeding resistance, while acting as a plasticizer such as normal phthalic plasticizers and a heat stabilizer such

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TABLE I
Recipes for PVC Films

Ingredient	Film A	Film B	Film C	Film D	Film E
PVC	100	100	100	100	100
Stabilizer	2	2	2	2	2
DEHP	50	45	45	—	—
GEHP	—	—	5	—	50
ESO	—	5	—	50	—

as ESO. We expected the addition of epoxy groups in the phthalic compounds to improve the resistance to bleeding and the plasticizing and heat stabilizing effects on the PVC compounds to be preserved.

Soft PVC films were prepared with GEHP, DEHP, and ESO. The mechanical properties, thermal stability, and bleeding resistances of these films were investigated.

EXPERIMENTAL

Materials

Phthalic anhydride (PA) and 2-ethylhexanol (2-EH) were provided by Aekyung Petrochemical Co. (Ulsan, Korea) and Sunoco (Philadelphia, PA). Technical grades were used without further purification, and their purity levels were 99.8 and 99%, respectively. Epichlorohydrin (ECH) and other solvents, such as toluene, n-hexane, and ethyl acetate, were reagent-grade and were used after distillation.

Benzyltrimethylammonium and NaOH were used as a catalyst and as a counteractive, respectively, after being dried in a vacuum oven at 80°C.

The degree of polymerization of PVC (P-1000, Hanhwa Co.) was 1000. Diethylhexylphthalate (DEHP; 99.8%; Aekyung Petrochemical Co., Ulsan, Korea), ESO, and a Ba–Zn stabilizer (Songwon Co., Ulsan, Korea) were used as received.

Synthesis of GEHP

PA (1 mol), 2-EH (1 mol), and toluene (2 mol) were placed in a 500-mL, four-necked, round-bottom flask equipped with a mechanical stirrer, a condenser, and a thermometer. As the solution was stirred under nitrogen at 100°C for 30 min, monoethylhexylphthalate (MEHP) was obtained.[15–18]

After the addition of 3 mol of ECH and 0.2 g of benzyltrimethylammonium to the MEHP solution, the solution was refluxed at 110°C for 1.5 h. Through gas chromatography (GC, HP series II, USA) equipped with a flame ionization detector and a nonpolar column (HP-5), this solution was determined to contain 65% GEHP and 20% chlorohydrin ethylhexylphthalate (CHEHP).[19–22] At 30°C, 0.24 mol of NaOH was put into the GEHP/CHEHP mixture, and the mixture was stirred for 5 h. During this reaction, NaCl was crystallized and CHEHP was converted into GEHP. It was confirmed with GC that the final product was 80% of the GEHP mixture. After water washing for the removal of NaCl and NaOH, the products were distilled
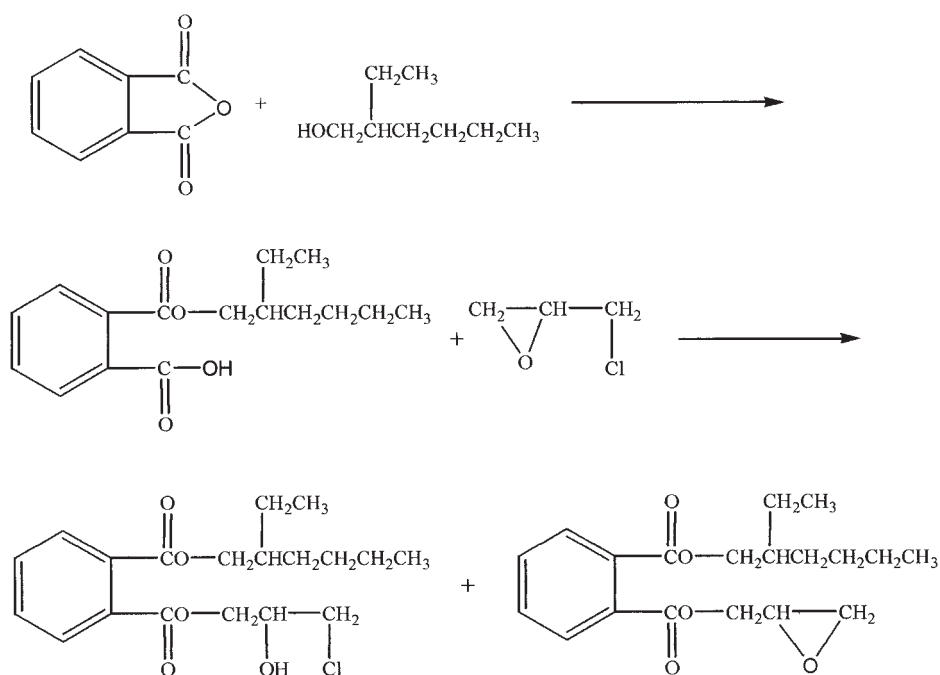
Scheme 1 Esterification of PA and 2-EH and reaction of MEHP and ECH.
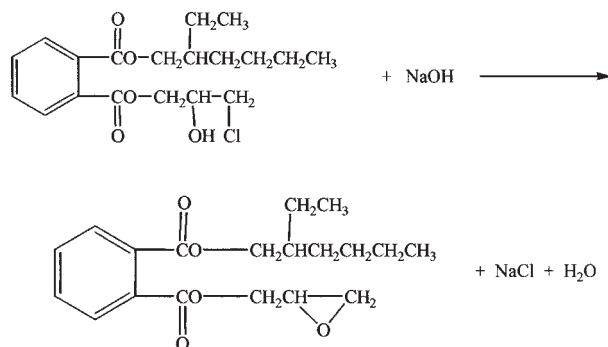
Scheme 2 Conversion of CHEHP into GEHP.

at 100°C *in vacuo*. For further purification of the GEHP mixture, the mixture was dissolved in hexane and ethyl acetate (5:1) and then passed through a silica-filled column. GEHP was acquired by the removal of the solvents, and the purity of GEHP was 99.1%.

Preparation of the soft PVC films

In 100 phr PVC, various plasticizers and a Ba–Zn stabilizer (2 phr) were mixed at 160°C for 5 min with a two-roll mill (Toyoseiki 287, Tokyo, Japan). The recipes for the PVC films are presented in Table I. The PVC films were prepared with a hand press (Carver 2697, Wabash, IN) at 175°C for 3 min.

Analysis

IR and NMR

The synthesis of GEHP was confirmed with a Fourier transform infrared (FTIR) spectrometer (Nicolet 730, Madison, WI) and with ^{1}H-NMR and ^{13}C-NMR (DRX 500, Brucker, Rheinstetten, Germany). Chloroform and CDCl$_3$ were used as the solvents. For the IR spectrum, a solution of GEHP was coated onto a KBR disk and then dried.

Acid value

About 1 g of a sample was dissolved in ethanol, and 1% phenolphthalein was added. This solution was titrated with a 0.1N KOH ethanol solution. The acid value was calculated according to ASTM D 1045.

TABLE II
Compositions of the GEHP Mixtures

GEHP (%)	CHEHP (%)	2-EH (%)	PA (%)	Others (%)
80.1	11.3	4.2	0.2	4.2

TABLE III
Properties of GEHP

Specific gravity (20/20°C)[a]	0.991
Color[a]	20
Acid value (mg of KOH/g of sample)	0.11
Epoxy content (g equiv of epoxy groups/ 100 g of sample)	4.73
Iodine value (cg of iodine absorbed by 1 g of sample)	0

[a] ASTM D 1045.

Epoxy content

To a 50-mL mixture of chloroform and chlorobenzene, 1–1.5 g of a sample and a Claton yellow/ethanol solution were added, and a 0.2N HBr acetic acid solution was used for titration. The HBr solution was added until the violet solution became bluish green. The epoxy content was calculated according to ASTM D 1652.[23,24]

Iodine value

To a sample (5 ± 1 g) in a 500-mL flask, 10 mL of a CCl$_4$ solution was added to dissolve the sample. After the addition of 10 mL of a Witz solution, the solution was agitated until it was clear and was placed in a dark room at 15°C for 30 min. The Witz solution was made of 7.9 g of ICl$_3$ and I$_2$ dissolved in a solution of 99% acetic acid, and the total volume of the solution was adjusted to 1 L.

With 0.1N Na$_2$S$_2$O$_3$, the sample solution was titrated until it became yellowish. After the addition of 1 mL of a starch solution, it was continuously titrated until it became clear. The blank test was performed with 10 mL of CCl$_4$ and 10 mL of a Witz solution. The epoxy content was calculated according to ASTM D 460.

Discoloration

The PVC films were aged in a convection oven (Toyoseiki, Tokyo, Japan) at 180°C. The degree of discoloration of the PVC films was investigated every 20 min until the films became dark. The UV absorbance on a 0.01 wt % tetrahydrofuran (THF) solution of the discolored samples at 500 nm was measured with a UV spectrometer (PerkinElmer Lambda 2, Boston, MA).[25–27]

Generation of HCl

About 5 g of chopped PVC films (4 mm × 4 mm × 2 mm) was placed in a branched tube, which was put into an oil bath at 175°C; heated nitrogen gas flowed through the tube at a rate of 100 mL/min. The N$_2$ gas, carrying the generated HCl, passed through 100 mL of
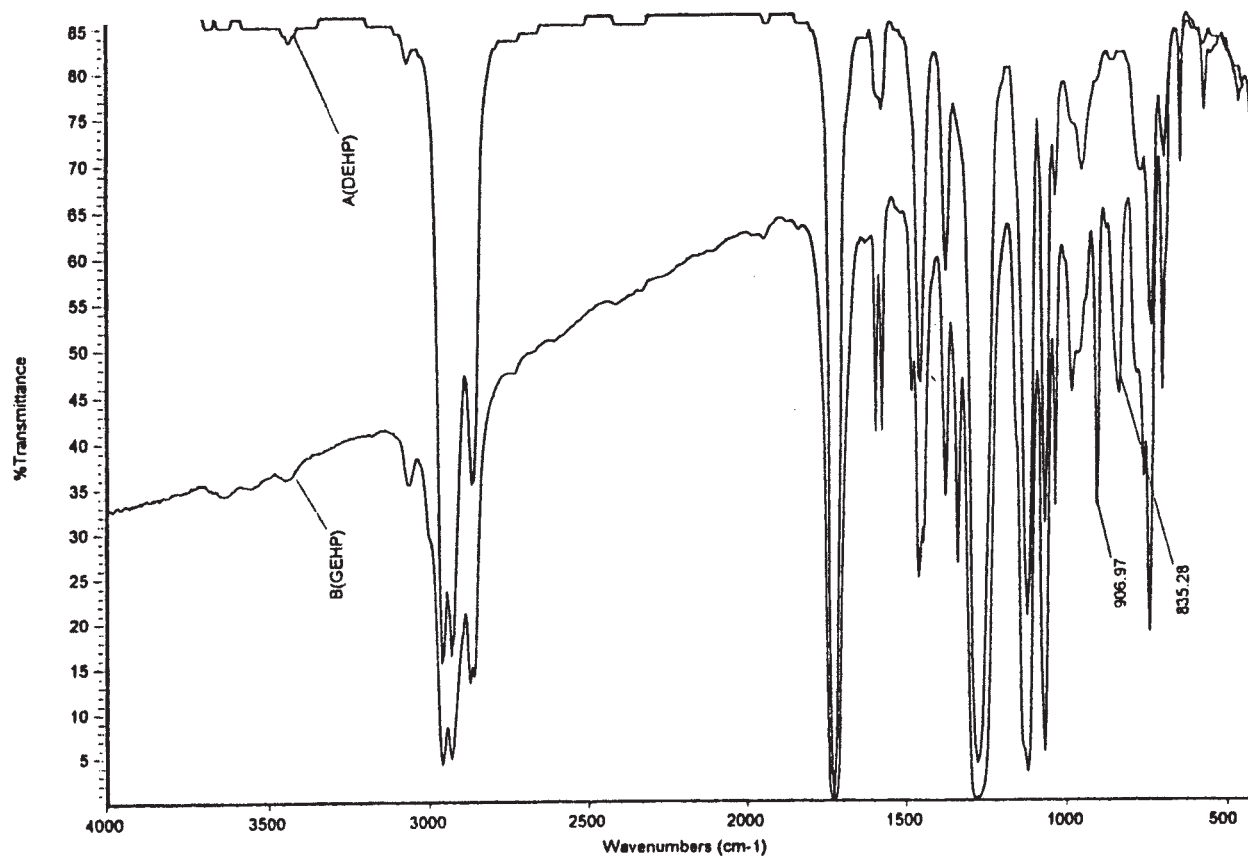
Figure 1 FTIR spectra of (A) DEHP and (B) GEHP.

distilled water and HCl dissolved in the water. The variation of the conductivity of the distilled water was measured at 25°C. The conductivity and concentration of the HCl solution were calibrated with standard HCl solutions.[25–27]

Properties of the PVC films

Mechanical properties and cold flexible temperatures

The tensile strengths at break, the moduli at 100% elongation, and the elongations at the break of the PVC films before and after heat aging were measured with an universal testing machine (Instron 1011, Canton, MA) at a crosshead speed of 200 mm/min with dumbbell-type specimens. With the exception of the highest and lowest values from the data of the seven specimens, the average results were reported. Heat aging was performed at 100°C for 48 h in a convection oven.

The hardness was investigated with a Toyoseiki model S Shore A hardness tester, and the sample thickness was more than 12 mm.

The cold flexible temperatures were measured according to JIS K 6745 with a Toyoseiki Clash–Berg tester with a modulus of 3.17×10^3 kg/cm^2.

Volatility

The PVC films (25 mm × 25 mm × 1 mm) were placed in a convection oven at 120°C for 120 h and cooled to room temperature in a desiccator for 1 h. The weight changes were measured before and after the heating.

Extraction

The extraction resistance to gasoline and water was measured. The samples (30 mm × 30 mm × 1 mm) were soaked in gasoline and water at 30°C for 24 h. After being rinsed with flowing water, the samples were dried at 50°C for 4 h in a convection oven. The weight losses before and after the dipping were measured.

Bleeding

The films (60 mm × 90 mm × 1 mm) were sandwiched between clean filter papers. These samples were placed in a convection oven at 120°C for 10 days. It was observed whether the filter papers were contaminated or not. The weights of the films were measured after the washing of the surfaces of the films with CCl$_4$
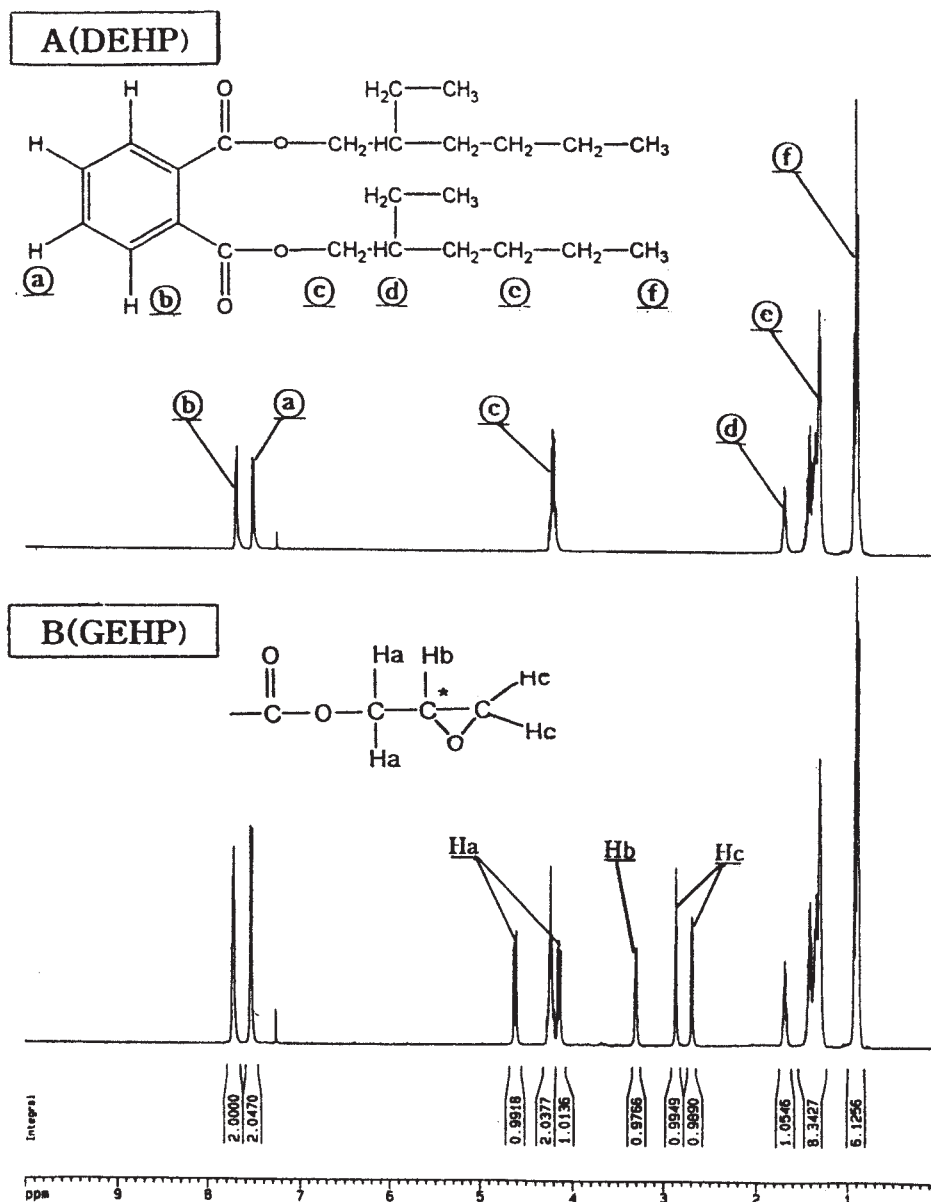
Figure 2 ^{1}H-NMR spectra of (A) DEHP and (B) GEHP.

and drying at room temperature. The weight changes (%) before and after the washing were calculated.

RESULTS AND DISCUSSION

Synthesis of GEHP

The synthesis of GEHP is depicted in Schemes 1 and 2. Monoethylhexylphthalate (MEHP) was produced through the heating of PA/2-EH mixtures. As the measured acid value of MEHP agreed with the theoretical acid value of 201.8 mg of KOH/g, we could confirm the synthesis of MEHP.

GEHP was synthesized through the reaction of MEHP and ECH, and the degree of reaction of MEHP was 100% according to the GC data. From this reaction, a mixture with 65% GEHP and 20% CHEHP was obtained. After the addition of NaOH, some CHEHP was converted into GEHP, as shown in Scheme 2, and the compositions of the final products are shown in Table II.

As this GEHP mixture passed through a silica-filled column, 99% of the GEHP was received. The properties of the purified GEHP, such as the epoxy content, iodine value, and acid value, are presented in Table
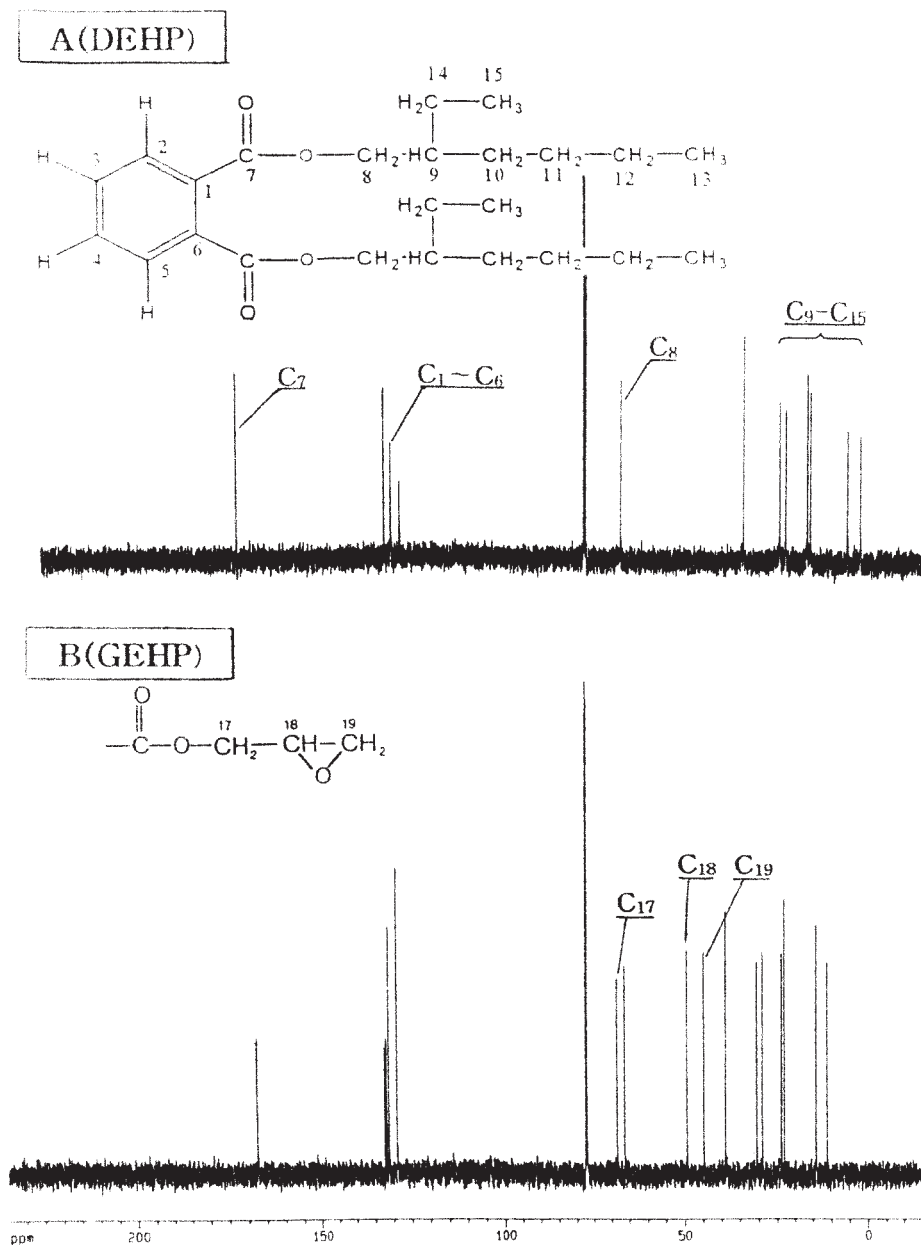
Figure 3 ^{13}C-NMR spectra of (A) DEHP and (B) GEHP.

III. From these results, we could confirm that equivalent epoxy groups were introduced and that no double bonds existed in GEHP.

The chemical structures of DEHP and GEHP were analyzed with FTIR, ^{1}H-NMR, and ^{13}C-NMR, as shown in Figures 1–3.

The IR spectra of DEHP and GEHP are shown in Figure 1. The characteristic peaks of the CO stretching (1724 cm^{-1}) and substituted benzene ring (1600 cm^{-1}) were observed for both DEHP and GEHP. On the basis of the 835- and 906-cm^{-1} peaks for the stretching of the epoxy group, the introduction of the glycidyl group was confirmed.

In Figure 2, 4.16 and 4.61 ppm peaks of =CH$_2$, a 3.30 ppm peak of —CHO, and 2.69 and 2.86 ppm peaks of —CH$_2$O can be observed for GEHP.

As shown in Figure 3, 167 ppm peaks of —COOCH$_2$— were observed for DEHP and GEHP. However, 44.8, 49.3, and 68.3 ppm peaks from the glycidyl groups were only found for GEHP.
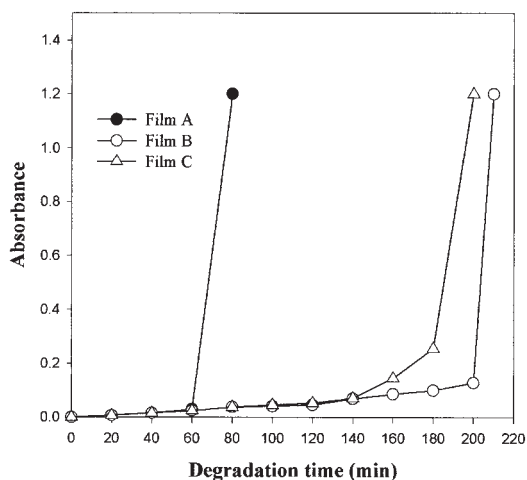
Properties of the PVC films

Heat resistance

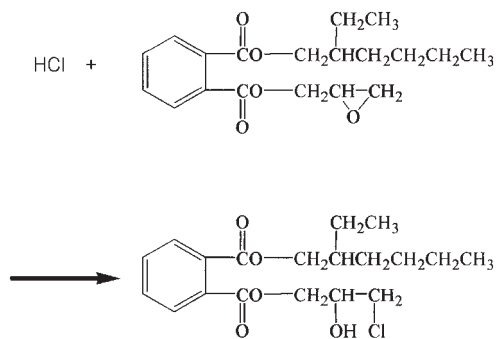Photographs of PVC films with respect to the oven aging time are shown in Figure 4, and the UV absor-
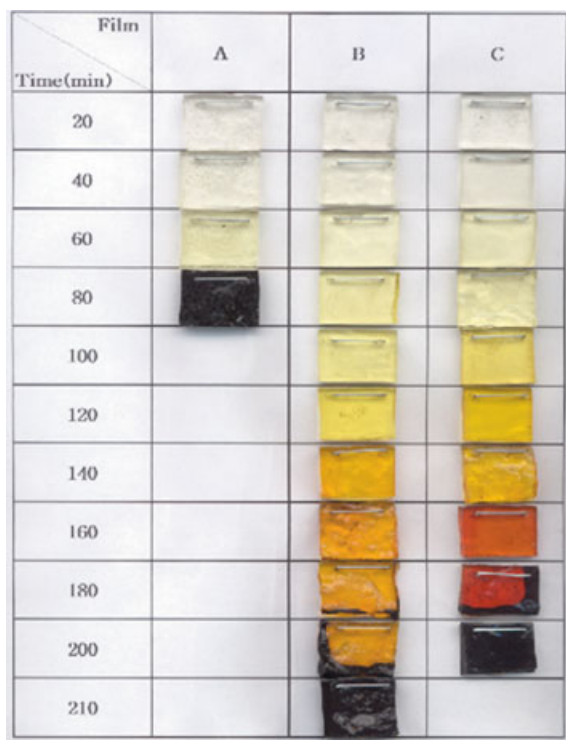
Figure 4 Discoloration of PVC films aged at 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 3 Reaction of HCl and GEHP.

The ability of GEHP to stabilize PVC was proven with the FTIR spectrum of extracts from aged film C (Fig. 6). The characteristic peaks of —OH stretching (3500 cm^{-1}) were found for the extracts but not for GEHP. This agrees with Scheme 3.

The dehydrochlorination rates of the PVC resin and films are shown in Figure 7. For the PVC resin without heat stabilizers or plasticizers, the generation of HCl started immediately after the heating and continuously increased during the test.

For film A, which contained DEHP and the Ba–Zn heat stabilizer, there was no generation of HCl by 60 min. After this point, however, film A rapidly generated HCl like a PVC resin. It was inferred that the Ba–Zn stabilizer suppressed the initial generation of HCl, but as the amount of the stabilizer decreased, dehydrochlorination started, and it was accelerated by barium and zinc chlorides that were produced during the stabilization.

For films B and C, the generation of HCl was not detected during the test time. This was the typical synergy effect between the Ba–Zn stabilizers and epoxy-containing plasticizers. These results corresponded to the results of Figures 4 and 5. It can be concluded that GEHP as a novel plasticizer provides heat resistance to PVC compounds, just like ESO.

bance of THF solutions of the aged samples is presented in Figure 5. The heat resistance of films B and C, compounded with ESO and GEHP instead of DEHP, was superior to that of film A, which had only DEHP. This was due to the epoxy groups in ESO and GEHP, which were able to react with HCl, generated from PVC, as shown in Scheme 3.

Figure 5 UV absorbance of PVC films as a function of the aging time.

Mechanical properties

The mechanical properties of the PVC films before and after heat aging are presented in Table IV. As for the modulus and elongation at break of films A, D, and E, the plasticizing effect of GEHP was higher than that for DEHP and ESO. This was due to the low molecular weight of GEHP (334 g/mol), in comparison with those of DEHP (390 g/mol) and ESO (1000 g/mol). ESO showed the lowest variation of physical properties after heat aging. The differences in the mechanical properties before and after aging between GEHP and DEHP, however, were marginal, except that the variation of the modulus for GEHP was a little smaller
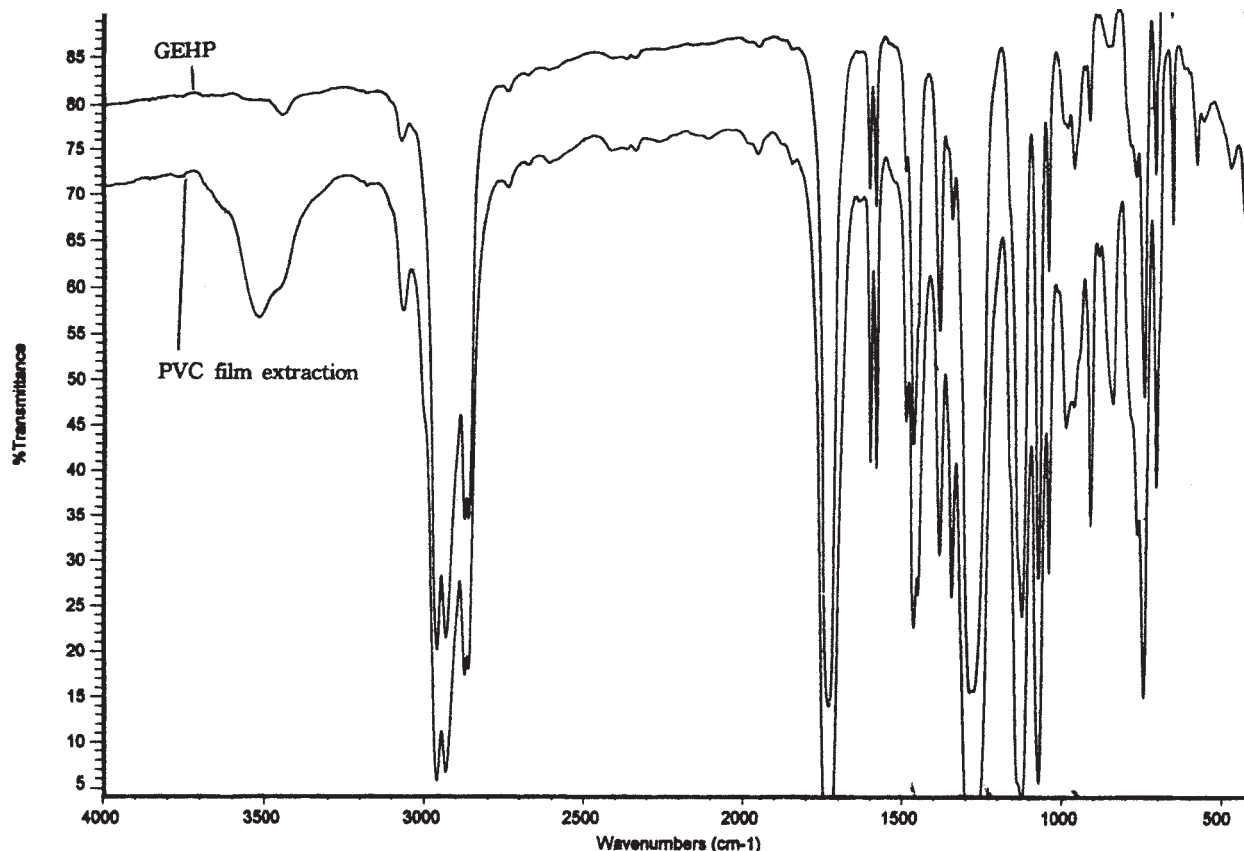
Figure 6 FTIR spectra of GEHP and extracts from aged PVC films.

than that of DEHP. Substituting 5 phr DEHP for the same amount of ESO (film B) and GEHP (film C) did not make much of a difference on the physical properties of PVC.

Cold flexible temperature

The flexibility of PVC at low temperatures was affected by the polarity, the molecular weight, and the

Figure 7 Dehydrochlorination rate of PVC films at 175°C.

number and structure of alkyl groups of plasticizers. As the molecular weight and polarity increased, the flexibility decreased because of strong intermolecular interactions and difficulties for molecular movement. When the plasticizers had the same molecular weight, the methylene chains became straighter and more flexible at low temperatures.

As shown in Table V, the cold flexible temperatures of the PVC films plasticized with DEHP and GEHP were better than those of the films plasticized with ESO. This was inferred from the low molecular weight and the low concentration of the polar groups of DEHP and GEHP in comparison with those of ESO. We expected the combined use of DEHP and GEHP or ESO to reduce the cold flexibility of PVC, but with small amounts of GEHP and ESO, the variations were not significant.

Volatility, extraction, and bleeding resistance

The weight losses of the PVC films by volatilization and extraction in water and gasoline are shown in Table VI. The volatility, extraction, and bleeding of the plasticizers from the resin were strongly dependent on the vapor pressure, molecular weight, solubility, compatibility, and chemical structure of the plasticizers.
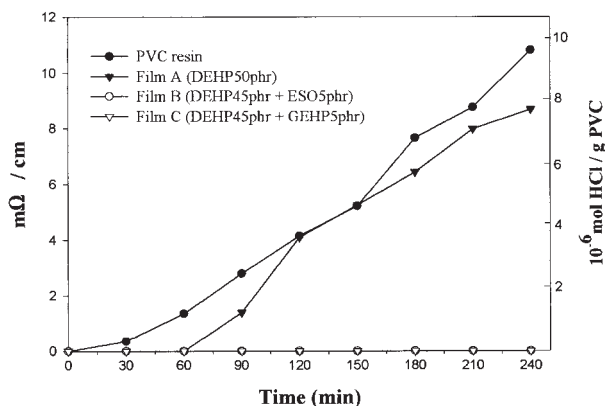
TABLE IV
Mechanical Properties of the PVC Films Before and After Heat Aging

Sample	Hardness	Before aging			After aging		
		Modulus at 100% elongation (kgf/mm^2)	Tensile strength at break (kgf/mm^2)	Elongation at break (%)	Modulus at 100% elongation (kgf/mm^2)	Tensile strength at break (kgf/mm^2)	Elongation at break (%)
Film A	89	101	205	330	117	190	303
Film B	90	103	208	327	117	192	302
Film C	89	98	203	336	111	188	310
Film D	91	120	218	308	124	214	304
Film E	88	94	201	344	106	187	320

ESO, which had a high molecular weight and polar epoxide groups, showed the lowest weight loss by gasoline and water extraction. The resistance of extraction by gasoline for GEHP was better than that of DEHP, but the water resistance was the opposite. This was attributed to the polar groups of GEHP. The molecular weights of GEHP and DEHP were similar, so the more polar GEHP had higher resistance to gasoline extraction and lower resistance to water than DEHP. As reported by Lawrence and Mcintyre,[28] the loss contents by water extraction decreased with the number of nonpolar alkyl carbons.

The volatilization loss also increased in the following order: ESO, GEHP, and DEHP. As ESO had the highest vapor pressure, the weight loss of film D was the lowest. It was concluded that the volatilization loss was largely affected by the molecular weight of the plasticizers, and GEHP had stronger interactions with PVC than DEHP because of the polar functional groups of the two ester groups and an epoxide group.

With the substitution of a small amount of GEHP into DEHP, the weight loss by gasoline extraction and the volatilization of plasticized PVC could be improved.

The results of the bleeding test for the PVC films are presented in Table VII. Film D, plasticized with ESO, had the highest bleeding loss. The chlorohydrin compounds from the reaction of HCl and epoxides in ESO reduced the compatibility of ESO with PVC. The bled ESO accumulated on the film surface and made the surface sticky, and this caused it to become contaminated with dirt and other particles.

GEHP exhibited similar bleeding resistance to DEHP, and there was no accumulation on the surface, as was the case for ESO.

CONCLUSIONS

A novel plasticizer for PVC, GEHP, was synthesized, and its performance was evaluated. In GEHP, a glycidyl group with epoxy oxygen and an ethyl hexyl group were linked to PA through an ester linkage. GEHP combined the merits of a typical PVC plasticizer, DEHP, and a heat stabilizer, ESO. This plasticizer was compounded in a PVC resin, and the mechanical properties, cold flexible temperatures, and extraction resistance of the PVC films were investigated.

GEHP improved the heat resistance of the PVC films because the epoxy groups could react with HCl, which was generated during the thermal decomposition of PVC, like ESO in the PVC compounds. From the results of the bleeding test, it was concluded that the compatibility of GEHP was higher than that of ESO and similar to that of DEHP. The plasticizing effect of GEHP was higher than that of DEHP and ESO because of the low molecular weight of GEHP and its higher compatibility with PVC. GEHP also showed better low-temperature flexibility than ESO and similar low-temperature flexibility to DEHP.

TABLE V
Cold Flexible Temperatures of the PVC Films

Sample	Temperature (°C)
Film A	−24.1
Film B	−22.3
Film C	−23.5
Film D	−14.0
Film E	−23.0

TABLE VI
Weight Losses of the PVC Films After Extraction and Volatilization Testing

Sample	Weight loss by extraction (%)		Weight loss by volatilization (%)
	Gasoline	Water	
Film A	7.1	0.09	18.1
Film B	7.1	0.10	15.8
Film C	5.9	0.18	16.4
Film D	4.8	0.06	0.2
Film E	5.4	0.34	12.4

TABLE VII
Bleeding Test Results

Sample	Contamination of paper[a]	Weight loss (%)
Film A	○	0.51
Film B	△	0.55
Film C	○	0.50
Film D	×	3.62
Film E	○	0.61

○ = no detection; △ = slight detection; × = detection.

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