

Stabilization of Poly(vinyl Chloride). VIII. Synergisms between Epoxy Compounds and Metal Soaps.

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Synopsis

Effects of bisphenol A type epoxy compounds involving various average molecular weights on the zinc stearate/calcium stearate and the cadmium stearate/barium stearate synergetic soaps induced thermal stabilization of poly(vinyl chloride) (PVC) were investigated by colorimetry. The remarkable stabilization effects of epoxides could not be observed on the PVC films without synergetic soaps, while the stabilization of PVC was markedly enhanced by combined use of epoxides and synergetic soaps. The appearance of excessive coloration of cool color producing metal chloride-polyene complexes which were an origin of abrupt discoloration of stabilized PVC was retarded by using epoxides together with synergetic soaps. Moreover, as for PVC with or without synergetic soaps, the epoxy compounds did not inhibit the formation of longer polyene chains which were a chromophore for yellow orange of aged PVC. Further colorimetries and IR or X-ray photoelectron spectroscopies on the various PVC containing epoxy compounds and zinc chloride indicated that the epoxy groups caught the zinc chloride. The synergetic effect between epoxy compounds and synergetic metal soaps is ascribed to the action that the epoxides serve as an acceptor for the excessive cool color producing metal chloride produced from zinc stearate and cadmium stearate to retard the abrupt discoloration of stabilized PVC.

INTRODUCTION

The epoxy compounds are well known as a typical nonmetallic stabilizer for poly(vinyl chloride) (PVC).¹⁻⁸ Many workers had studied the stabilization mechanism of epoxides in the field concerning the dehydrochlorination of PVC. An acceptor for the liberated hydrogenchloride⁹⁻¹¹ and a retardant for the formation of the longer polyene chains, affected by the creation of an ether linkage with polymer backbone,¹¹⁻¹⁴ have been proposed as stabilization mechanisms involving epoxy compounds.

On the other hand, the marked effects on the inhibition of the thermal discoloration of PVC could not be observed by using epoxide without the synergetic metal soaps.

As was previously reported, the abrupt discoloration from the colorless to zinc chloride-polyene complex color (blue) or cadmium chloride-polyene complex color (bluish green), observed on the PVC films containing zinc stearate or cadmium stearate in the early heating stage, markedly inhibited the stabilization of PVC.^{15,16} This phenomenon in the PVC-zinc stearate system has been called "zinc burning." The epoxides retarded these abrupt discolorations of PVC compounds with the synergetic metal soaps.

The abrupt discoloration of PVC containing the synergetic metal soaps, such as zinc burning, is due to the marked formation rate, or coloration rate,

of zinc chloride–polyene complex and cadmium chloride–polyene complex, respectively.^{15,16} Therefore, the stabilization mechanism of epoxy compounds should be considered to be an acceptor for the excessive zinc chloride or cadmium chloride produced from the corresponding metal soap, because the excessive zinc chloride and cadmium chloride are a developer for the abrupt discolorations.

In the present work, the effects of adding epoxides to the stabilized PVC and mechanism of epoxides of stabilizing PVC are studied. The heat efficiencies of synergetic soaps were improved by the addition of the epoxides, owing to their actions as an acceptor for excessive cool color producing metal chlorides.

EXPERIMENTAL

Materials

PVC used in this work was Geon 103 EP. Commercially available di(2-ethylhexyl)phthalate (DOP), metal stearate, and the other materials were also used. Epoxy compound used in this work was 2,2-bis(4-hydroxyphenyl)propane diglycidyl esters (bisphenol A type) obtained from Tohto Kasei Co., which had average molecular weights of 380, 560, 1100, 1900, 2500, and 2600. They are abbreviated by prefixing EPX- such as EPX-380.

A mixture of 2 parts of zinc stearate and 1 part of calcium stearate [Zn/Ca(2/1)-st] and a mixture of 2 parts of cadmium stearate and 1 part of barium stearate [Cd/Ba(2/1)-st] were used as synergetic metal soap.

Preparation of PVC Film

PVC, DOP, metal stearate, and epoxy compound were milled on an open roll (4 × 8 in.) at 150°C for 5 min. Each PVC film contained 20 phr DOP and 3 phr synergetic metal soaps. The compound PVC film specimens (0.5 × 50 × 40 mm) were heated at 160 ± 2°C in Geer's oven. During compression of the roll film, the process time was minimized in order to avoid a heat history.

Colorimetry

PVC films were investigated by colorimetry at room temperature by using a Suga Shikenki Model AU-CH-1D differential colorimeter mounting a specimen holder window of 30 mm in diameter. Tristimulus values of each film were determined by averaging the values recorded from three different places on the film surface, using a white color standard plate ($Y = 84.5$, $X = 82.4$, and $Z = 93.7$) as a reflector.

Heat Treatment of PVC with Epoxy Compounds and Zinc Chloride

A mixture of dried zinc chloride, EPX-380, and PVC was milled on an open roll at 150°C for 5 min. The process time was maintained within 5 min, since the zinc burning was appeared more than 5 min.

One gram of resulting PVC compound was dissolved in 250 mL tetrahydrofuran at 40°C for 24 h and filtered by suction filtration. After the operation was repeated by three times, the gel part was dried under reduced pressure.

The dried gel was first subjected to combustion quantitatively to zinc chloride with few drops of hydrochloric acid. Then, the zinc chloride was titrated at pH 5 with EDTA-2Na aqueous solution by using Cu-PAN as an indicator.

X-Ray Photoelectron Spectroscopy (XPS)

XPS of powdered compound PVC, which were dried *in vacuo* in the presence of phosphorus pentoxide, was carried out under 10^{-5} Pa by using a Shimadzu Seisakusho Model ESCA-750 with ESCAPAC-760 soft wear. MgK_{α} (1253.6 eV) was used as X-ray source.

Absorbance of Ultraviolet and Infrared Spectrum

Ultraviolet absorbance of heated PVC, dissolved in tetrahydrofuran (5 g/L), were obtained by using a Shimadzu Seisakusho Model MPX-50L spectrophotometer at room temperature.

Infrared absorbances of PVC which was powdered by using a fine file and then wafered with dried potassium bromide were obtained using a Shimadzu Seisakusho Model IR-400 spectrophotometer.

RESULTS AND DISCUSSION

Effects of Epoxides

The stabilization effects of bisphenol A type epoxides used with Zn/Ca(2/1)-st or Cd/Ba(2/1)-st are shown in Figures 1 and 2. These figures represent a plot of whiteness in Lab color system [W(Lab)] as a function of

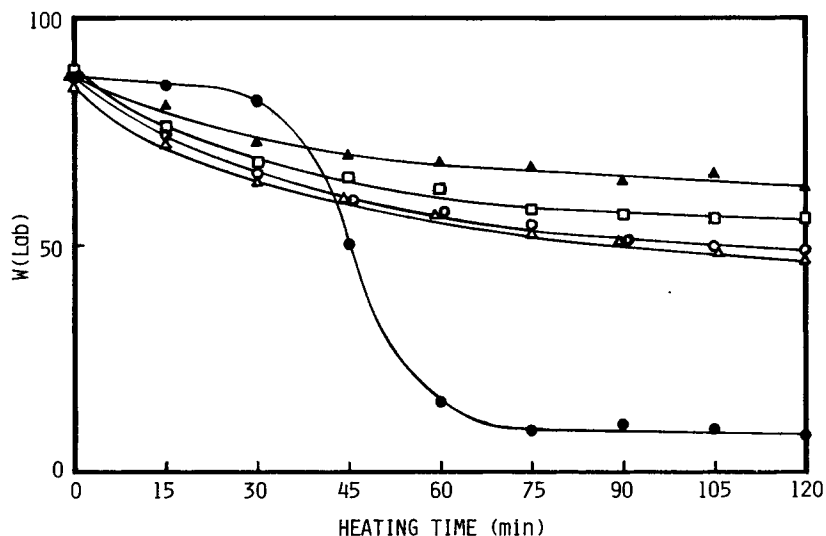


Fig. 1. Stabilization effect of epoxy compounds. PVC 100 and DOP 20 (○), PVC 100, DOP 20, and Zn/Ca(2/1)-St 3.0 (●), PVC 100, DOP 20, and EPX-380 1.0 (△), PVC 100, DOP 20, Zn/Ca(2/1)-St 3.0, and EPX-380 2.0 (□), and PVC 100, DOP 20, Zn/Ca(2/1)-St 3.0, and EPX-1100 2.0 (▲) were milled at 150°C for 5 min and heated at 160°C.

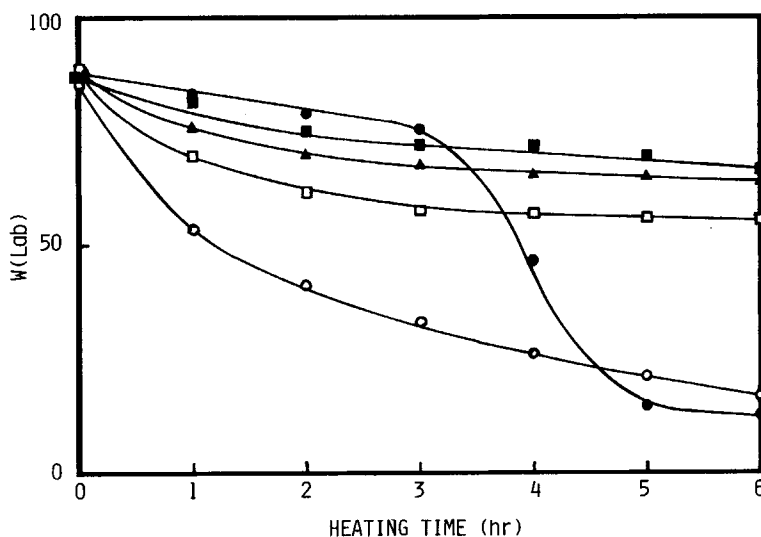


Fig. 2. Stabilization effect of epoxy compounds. PVC 100 and DOP 20 (○), PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0 (●), PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and EPX-380 3.0 (□), PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and EPX-1100 3.0 (▲), and PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and EPX-2500 3.0 (■) were milled at 150°C for 5 min and heated at 160°C.

heating time.¹⁷ Under the present conditions, $W(\text{Lab})$ of PVC films should be always less than 91 because $W(\text{Lab})$ of whitecolor standard plate used as a reflector equals 91.0.

In PVC alone and PVC with only EPX-380, $W(\text{Lab})$ decreases with increased heating times owing to the formation, or coloration, of the longer polyene chains ($\lambda_d = 580\text{--}610$ nm; yellow orange).^{15,16} Moreover, the decreases in $W(\text{Lab})$ of PVC with epoxide alone is almost the same as that of unstabilized control.

PVC compounded with Zn/Ca(2/1)-st alone and Cd/Ba(2/1)-st alone exhibit abrupt discoloration at 45 min and 4 hr, respectively, which is ascribed to the excessive coloration of the zinc chloride-polyene complex ($\lambda_d = 475$ nm; blue)^{15,16} and the cadmium chloride-polyene complex ($\lambda_d = 485$ nm; bluish green).^{15,16} These excessive colorations of polyene-metal chloride complexes (π -complex) decreased $W(\text{Lab})$ markedly and kept an almost invariable $W(\text{Lab})$ after attaining the minimum.

In the case of combined use with synergetic soaps, all epoxides inhibit the excessive coloration of the π -complexes and slow down the discoloration of PVC. Hence, the epoxy compounds do not stabilize PVC without the synergetic metal soaps.

The synergetic effects of various epoxides with synergetic soaps are summarized in Tables I and II based on Figures 1 and 2.

The dominant wavelength (λ_d) which corresponds to hue in colorimetry as for PVC alone and PVC with only epoxy compounds turns out to be 585–611 nm [$\lambda_d(f)$], which corresponds to the hue of the polyene color (yellow orange) with increased heat treatments.

The abrupt color changes from 574 to 475–486 nm, which is due to the excessive formation of the π -complexes are observed at 45 min and 4 h (t_E) as

TABLE I
 Stabilization Effect of Epoxy Compounds^a

Additive ^b	phr	W_0	t_E , min	W_M	t_L , min	W_L	$(W_0 - W_M)/W_0$, %	$(W_0 - W_L)/W_0$, %	$\lambda_d(i)$ nm	$\lambda_d(f)$ nm
PVC	—	87	—	—	120	49	—	44	575	587
EPX-380	1.0	85	—	—	120	47	—	45	575	585
EPX-2500	1.0	86	—	—	120	42	—	51	575	490
Zn/Ca(2/1)-st	3.0	87	45	73	120	8	16	91	574	486
EPX-380 ^c	0.4	86	120	69	120	58	20	33	575	576
	1.0	88	—	—	90	67	—	24	575	576
	2.0	88	—	—	105	56	—	36	574	579
	3.0	87	—	—	120	50	—	43	573	581
EPX-560 ^c	0.4	87	90	72	120	9	17	90	574	480
	1.0	88	—	—	120	67	—	24	572	575
	2.0	87	—	—	90	61	—	30	573	577
	3.0	87	—	—	120	56	—	36	573	579
EPX-1100 ^c	0.2	87	45	79	120	7	9	92	572	486
	0.4	87	60	73	120	10	16	89	572	490
	0.6	87	60	75	120	13	14	85	573	480
	0.8	86	105	63	120	13	27	85	572	505
	1.0	87	105	62	120	17	29	80	574	480
	2.0	87	—	—	120	63	—	28	573	576
	3.0	87	—	—	120	59	—	32	572	578
EPX-1900 ^c	0.2	87	45	81	120	13	7	85	575	492
	0.4	87	60	78	120	14	10	84	574	491
	0.6	86	60	79	120	15	8	83	575	488
	0.8	87	60	77	120	13	11	85	574	490
	1.0	86	90	70	120	17	19	80	574	575
	2.0	85	120	65	120	61	24	28	575	576
	3.0	88	—	—	120	60	—	32	574	578
EPX-2500 ^c	0.2	87	45	80	120	9	8	90	573	490
	0.4	87	60	73	120	11	16	87	571	485
	0.6	87	60	75	120	10	14	89	573	496
	0.8	86	60	75	120	13	13	85	573	491
	1.0	88	90	66	120	12	25	86	571	480
	2.0	88	105	67	120	54	24	39	570	575
	3.0	88	—	—	120	61	—	31	573	577
EPX-2600 ^c	0.2	87	45	80	120	11	8	87	574	486
	0.4	86	60	78	120	10	9	88	574	495
	0.6	87	60	76	120	10	13	89	572	490
	1.0	89	75	70	120	12	21	87	573	483
	2.0	89	90	70	120	25	21	72	572	574
	3.0	89	120	64	120	56	28	37	572	575

^a Heated at 160°C. W_0 represents $W(\text{Lab})$ of unheated film. t_E is heating time for onset of zinc burning. W_M represents $W(\text{Lab})$ at the heating time just before onset of zinc burning. t_L is heating time attaining the lowest $W(\text{Lab})$. W_L represents the lowest $W(\text{Lab})$. $\lambda_d(i)$ represents the dominant wavelength of unheated film. $\lambda_d(f)$ represent the dominant wavelength of aged film which is heated for 120 min.

^b Each film contained 20 phr DOP.

^c 3.0 phr Zn/Ca(2/1)-st was compounded in each film.

TABLE II
 Stabilization Effect of Epoxy Compounds^a

Additive ^b	phr	W_0	t_E , hr	W_M	t_L , hr	W_L	$(W_0 - W_M)/W_0$,	$(W_0 - W_L)/W_0$,	$\lambda_d(i)$,	$\lambda_d(f)$,
							%	%		
PVC	—	85	—	—	6	17	—	80	574	611
Cd/Ba(2/1)-st	3.0	87	4	74	6	13	15	85	574	482
EPX-380 ^c	0.4	87	—	—	6	68	—	22	573	576
	1.0	87	—	—	6	65	—	25	572	576
	2.0	87	—	—	6	60	—	31	573	575
	3.0	88	—	—	6	55	—	38	571	578
EPX-560 ^c	0.4	87	—	—	6	68	—	22	573	576
	1.0	87	—	—	6	66	—	24	574	576
	2.0	87	—	—	6	65	—	25	574	575
	3.0	87	—	—	6	62	—	29	573	575
EPX-1100 ^c	0.4	88	—	—	6	69	—	22	574	576
	1.0	88	—	—	6	69	—	22	574	576
	2.0	88	—	—	6	69	—	22	574	576
	3.0	88	—	—	6	64	—	27	575	576
EPX-1900 ^c	0.2	89	—	—	6	69	—	22	573	576
	0.4	89	—	—	6	70	—	21	573	576
	0.6	89	—	—	6	70	—	21	573	576
	0.8	88	—	—	6	69	—	22	573	576
	1.0	88	—	—	6	68	—	23	574	576
	2.0	88	—	—	6	68	—	23	572	575
EPX-2500 ^c	3.0	88	—	—	6	68	—	23	574	576
	0.2	88	—	—	6	69	—	22	573	576
	0.4	88	—	—	6	69	—	22	573	576
	0.6	88	—	—	6	70	—	20	573	576
	0.8	87	—	—	6	67	—	23	574	576
	1.0	87	—	—	6	66	—	24	573	576
	2.0	87	—	—	6	66	—	24	573	577
EPX-2600 ^c	3.0	88	—	—	6	66	—	25	573	577
	0.2	89	—	—	6	69	—	22	574	577
	0.4	88	—	—	6	69	—	22	573	576
	0.6	89	—	—	6	68	—	24	573	576
	0.8	89	—	—	6	69	—	22	573	576
	1.0	89	—	—	6	69	—	22	575	576
	2.0	90	—	—	6	69	—	23	573	577
3.0	89	—	—	6	67	—	25	572	577	

^a Heated at 160°C. t_E is the heating time for onset of excessive coloration of polyene-cadmium chloride complex. W_M represents $W(\text{Lab})$ at the heating time just before onset of excessive coloration of polyene-cadmium chloride complex. $\lambda_d(f)$ represents the dominant wavelength of aged film which is heated for 6 h.

^b Each film contained 20 phr DOP.

^c 3.0 phr Cd/Ba(2/1)-st was compounded in each film.

for stabilized controls, respectively. Tristimulus values were decreased to minute size by the appearance of excessive coloration of the π -complexes such as zinc burning. Therefore, λ_d is uncertain in accuracy after the appearance of excessive cool color of the π -complexes.

On the other hand, the epoxides inhibit the formation of the excessive π -complexes and retard the abrupt discoloration of PVC with the synergetic metal soaps, because $\lambda_d(f)$ does not approximate 475 or 485 nm in the effective systems.

The synergetic effects of epoxides with synergetic soaps are enhanced with the increased additions or increased epoxy contents. No significant prolongation of good initial color for these systems is observed in comparison with the polyols.¹⁷

Synergetic Mechanism between Epoxides and Metal Soaps

From the colorimetry of various aged PVC films, it is apparent that the remarkable stabilization effects of epoxides could not be observed on the PVC films without synergetic soaps. Moreover, the $\lambda_d(f)$ of the effective systems are not shifted to the lower wavelength corresponding to the color of zinc chloride-polyene and cadmium chloride-polyene complexes. Therefore, the synergism between epoxides and synergetic soaps may be due to the interaction between epoxides and cool color producing metal chloride such as zinc chloride or cadmium chloride, which would be easily converted from the corresponding metal soap in the aged PVC.

As shown in Figure 3, the differing effects are observed between two systems with or without which the epoxides and zinc chloride are premixed before mixing them with PVC. The synergetic effect in the case of premixed use of epoxide and zinc chloride is superior to the unpremixed system. This also means that the stabilization effects of epoxides should be enhanced by dispersing them in the vicinity of the compounded metal soaps.

The influence of epoxy content on the synergetic effect of epoxides with Zn/Ca(2/1)-st is shown in Figure 4. $W(\text{Lab})$ are dully decreased at higher epoxy contents owing to the appearance of polyene color. On the other hand, the abrupt decreases in $W(\text{Lab})$ are observed at lower epoxy contents and are due to the appearance of zinc burning. The maximum $W(\text{Lab})$ appears at

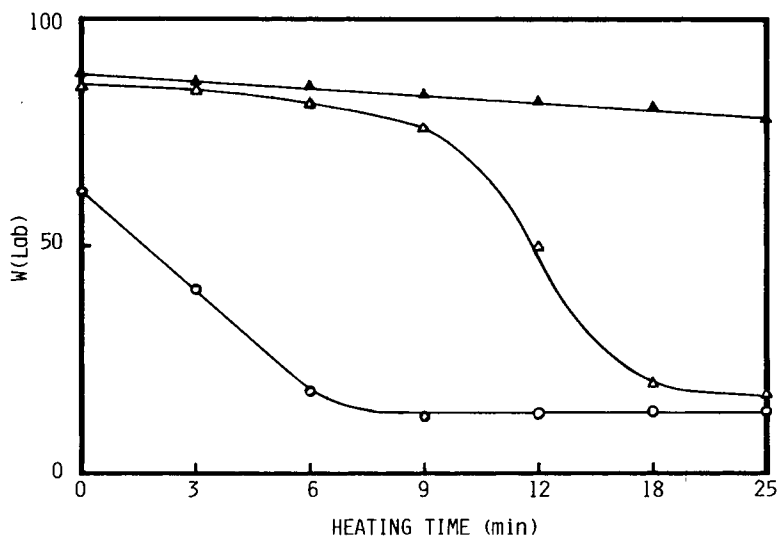


Fig. 3. Different effect between premixed and unpremixed systems. PVC 100, DOP 20, and unpremixed EPX-380 1.0 and ZnCl_2 0.2 (○), PVC 100, DOP 20, and premixed EPX-380 1.0 and ZnCl_2 0.2 (△), and PVC 100, DOP 20, and premixed EPX-380 3.0 and ZnCl_2 0.2 (▲) were milled at 150°C for 3 min and heated at 160°C .

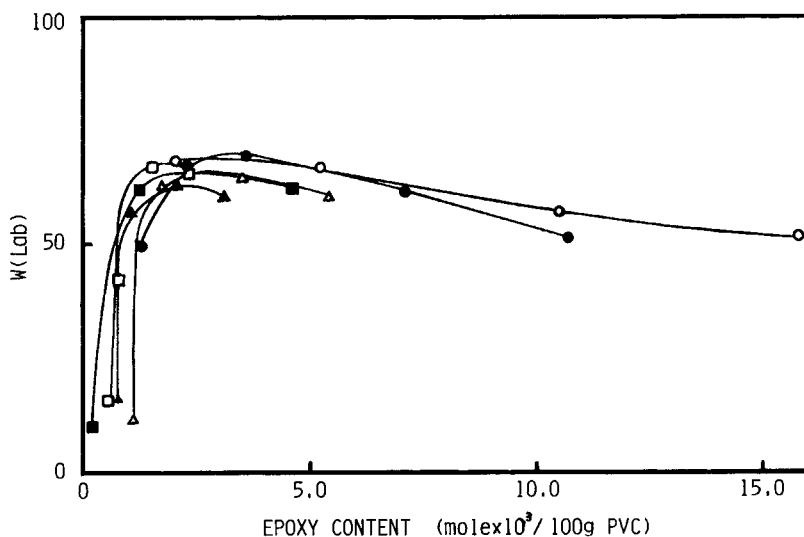


Fig. 4. Effect of epoxy content on the stabilization of PVC. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and EPX-380 (○), EPX-560 (●), EPX-1100 (△), EPX-1800 (▲), EPX-2500 (□), or EPX-2600 (■) were milled at 150°C for 5 min and heated at 160°C.

$3.0\text{--}4.0 \times 10^{-3}$ mol/100 g PVC in epoxy content. These epoxy contents approximate to the theoretical amount of zinc chloride (3.2×10^{-3} mol/100 g PVC), which would be produced from the zinc stearate added.

These results indicate the fact that the desirable interaction between epoxides and cool color producing metal chlorides should be situated in the aging compound PVC.

The binding energies (E) for Zn_{2p} of various samples are shown in Table III. The binding energies of EPX-380 and zinc chloride mixtures deviate from that of zinc chloride and approximate those of zinc oxide and zinc acetate. This means that Zn-O linkages are formed even in aging compound PVC.

TABLE III
Peak Shifts of Binding Energy for Aged PVC

Sample	Binding energy (eV)			
	Zn_{2p}	ΔE from ZnCl_2	ΔE from ZnO	ΔE from $\text{Zn}(\text{OCOCH}_3)_2$
ZnCl_2 alone	1024.0	—	+1.9	+1.4
$\text{ZnCl}_2/\text{PVC}^a$	1023.6	-0.4	+1.5	+1.0
$\text{ZnCl}_2/\text{EPX-380}/\text{PVC}^b$	1022.5	-1.5	+0.4	-0.1
$\text{ZnCl}_2/\text{EXP-380}^c$	1022.3	-1.7	+0.2	-0.3
ZnO alone	1022.1	-1.9	—	-0.5
$\text{Zn}(\text{OCOCH}_3)_2$ alone	1022.6	-1.4	+0.5	—

^a PVC with ZnCl_2 (0.2 mole/100 g PVC) was milled at 150°C for 3 min on an open roll.

^b PVC with ZnCl_2 (0.5 mole/100 g PVC) and EPX-380 (0.5 mole/100g PVC) was milled at 150°C for 5 min on an open roll.

^c Rigid product obtained by heating a mixture of ZnCl_2 (0.01 mole) and EPX-380 (0.03 mole) at 97°C for 6 hr in 100 mL 1,4-dioxane.

TABLE IV
 The Reaction between Zinc Chloride and Epoxy Compound

Composition ^a (mole/100g PVC)		Yield of gel (wt %)	[Zn]/[EPX-380] in gel ^d	Absorbance ratio (914 cm ⁻¹ /1608 cm ⁻¹)	Binding energy (eV)
ZnCl ₂	EPX-380				Zn _{2p}
0.25	0.53	5.2	0.37	0.1	1022.6
0.54	0.53	6.2	0.39	0.1	1022.5
1.06	0.53	23.1	0.34	0.1	1022.3
ZnCl ₂ /EXP-380 ^b		7.9 ^c	6.24	0.5	1022.3

^a PVC with ZnCl₂ and EPX-380 was milled at 150°C for 5 min on an open roll.

^b Rigid product obtained by heating a mixture of ZnCl₂ (0.01 mole) and EPX-380 (0.03 mole) at 97°C for 6 hr in 100 mL 1,4-dioxane.

^c This value was based on the amount of ZnCl₂ and EPX-380 mixed.

^d These values were calculated by assuming the reaction that the gel parts were formed with only ZnCl₂ and EPX-380.

The mixture of EPX-380 and zinc chloride turned to the rigid substance which is undissolved in 1,4-dioxane and tetrahydrofuran after heating it even at 97°C for 6 h in 1,4-dioxane under stirring.

The binding energy for Zn_{2p} of the rigid substance approximates to those of zinc oxide and zinc acetate.

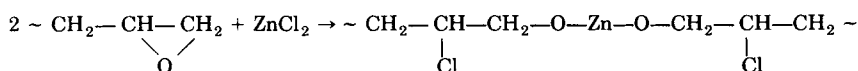
As shown in Table IV, the gel formations as for PVC admixed with epoxide and zinc chloride are enhanced with increased additions of zinc chloride. The zinc content in the gel is also increased with increasing additions of zinc chloride. The zinc burning does not appear in any system.

One mole of EPX-380 catches 0.3–0.4 mol of zinc chloride, by assuming the prerequisite that the gel parts are formed with only zinc chlorides and EPX-380. The zinc chloride would serve to crosslink the polymer backbones in the compound PVC with the highest addition of zinc chloride, because the gel formation is considerably greater than the other systems. On the other hand, considerable amount of zinc chloride may be confined in the gel parts of aged mixture of only zinc chloride and EPX-380.

In regard to the gels, IR absorbance of oxirane ring at 914 cm⁻¹ considerably disappears. The ratio of absorbance at 914 cm⁻¹ and absorbance of aromatic double bonds at 1608 cm⁻¹ (914 cm⁻¹/1608 cm⁻¹) concerning aged PVC are markedly decreased in comparison with the aged mixture of zinc chloride and EPX-380. This means that the liberated hydrogen chloride also acts against the cleavage of oxirane ring. The binding energies for Zn_{2p} also has a good approximation to those of zinc oxide and zinc acetate.

These results indicate the fact that the cleavages of oxirane ring, or the formations of Zn–O linkages, should take place even in aging PVC admixed with epoxides and zinc chloride.

From the various colorimetries, IR spectroscopies, and XPS, the following reactions between epoxy compounds and zinc chloride which would be easily produced from zinc stearate should undergo even in the compound PVC with heat treatments:



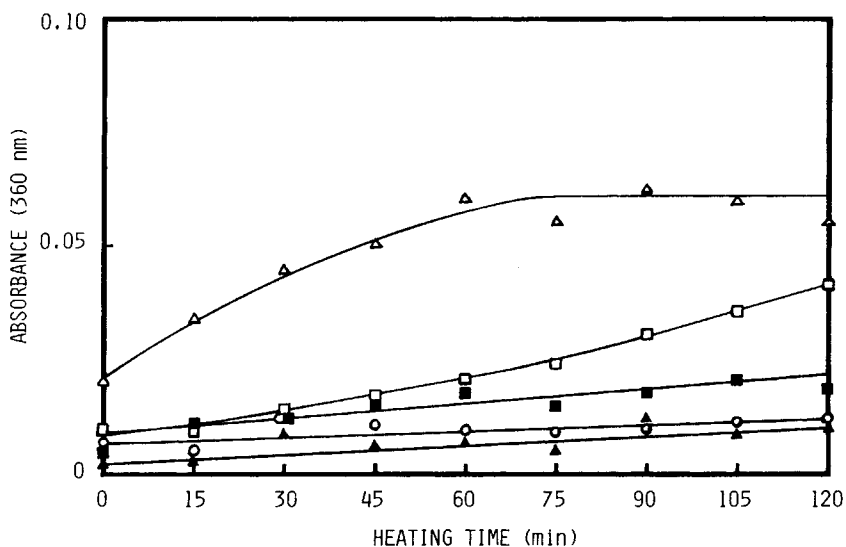


Fig. 5. Effects of epoxy compounds on the formation of longer polyene chains of aged PVC. PVC 100 and DOP 20 (○), PVC 100, DOP 20, and EPX-380 1.0 (▲), PVC 100, DOP 20, and EPX-1100 1.0 (■), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and EPX-380 2.0 (△), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and EPX-1100 2.0 (◻) were milled at 150°C for 5 min, heated at 160°C, and dissolved in tetrahydrofuran (5 g/L).

As shown in Figure 5, the epoxy compounds do not markedly slow down the formation of longer polyene chains which are a chromophore for yellow orange of aged PVC. Therefore, the stabilization effects of epoxy compounds should be based on the action as an acceptor for excessive cool color producing metal chlorides produced from the corresponding metal soaps, in addition to the usual stabilization mechanisms such as acceptor for the liberated hydrogen chloride and a retardant for the formation of longer polyene chains.⁹⁻¹⁴

CONCLUSIONS

On the various colorimetries of aged PVC films, the strong and favorite interactions between epoxy compounds and cool color producing metal chlorides are observed as for stabilization of PVC. Moreover, the epoxy compounds do not retard the formation of longer polyene chains of the aged PVC with or without metal soaps.

The marked stabilization effects of epoxy compounds with synergetic soaps depend mainly on their action as a scavenger for the excessive cool color producing metal chlorides in order to inhibit the unnecessary or injurious abrupt coloration of the π -complexes. But it is necessary to retain the efficient cool color producing metal chlorides which keep PVC colorless in complementary colors relationship with polyenes.¹⁸ Therefore, it is also necessary that suitable amounts of epoxides should be combined to retain the efficient zinc chloride. The excessive additions of epoxide injure the prolongation of good initial color of PVC with synergetic soaps, owing to the marked appearance of polyene color which is unable to extinguish by complementary colors with cool color of the π -complexes. This phenomenon should be due to the excessive

captures of cool color producing metal chlorides with the excessive addition of epoxides.

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