Stabilization of Poly(vinyl Chloride). X. Synergisms between Epoxidized Polybutadienes and Metal Soaps on the Stabilization of Poly(vinyl Chloride)

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Synopsis

Effects of epoxidized 1,2- or 1,4-polybutadienes on the zinc stearate/calcium stearate synergetic soap-induced thermal stabilization of poly(vinyl chloride) (PVC) were investigated by colorimetry. The remarkable stabilization effects of epoxidized polybutadienes could not be observed on the PVC films without synergetic soaps, while the stabilization of PVC was markedly enhanced by combined use of epoxidized polybutadienes with synergetic soaps. Excessive coloration of cool color-producing zinc chloride-polyene complexes that were the source of abrupt discoloration of stabilized PVC was retarded by using epoxidized polybutadienes together with synergetic soap. The synergism of epoxidized polybutadienes was enhanced with increasing epoxy contents. Moreover, the effect is also clearly dependent on degree of dispersion of epoxidized polybutadienes in PVC. Further colorimetries, infrared (IR), and X-ray photoelectron spectroscopies on the various PVC-containing epoxidized polybutadienes and zinc chloride indicated that the epoxy groups capture the zinc chloride. The synergistic effect between epoxidized polybutadienes and metal soap was ascribed to epoxidized polybutadienes serving as acceptors for the excessive cool color-producing zinc chloride produced by zinc stearate to retard the abrupt discoloration of stabilized PVC. The plate-out phenomenon appeared during the molding process of PVC-containing epoxy compounds was considerably retarded by epoxidized polybutadienes which modified polyols. The polyol-modifying epoxidized polybutadienes also exhibited a marked effect on PVC stabilization with metal soap.

INTRODUCTION

The abrupt change from colorless to zinc chloride-polyene complex color (blue), observed on the poly(vinyl chloride) (PVC) films containing zinc stearate in early heating stages, markedly inhibited stabilization of PVC.[1,2] This phenomenon in the PVC-zinc stearate system has been called "zinc burning."

Marked effects on inhibition of the abrupt discoloration of PVC stabilized with the metal soaps could be observed by the combined use of some costabilizers with the metal soaps.[3-10]

As previously reported, epoxy compounds also exhibited the marked effects of delayed appearance of abrupt discoloration of stabilized PVC, owing to their abilities to capture the excessive cool color-producing metal chlorides which were a source of the abrupt discolorations.[11]

Some lower molecular costabilizers exhibited poor compatibility with PVC, and subsequently, increased the appearance of injurious phenomenon such as blooming and bleeding.

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In the present work, the effects of adding epoxidized polybutadiene (PB-EP) as a macromolecular costabilizer occurrence of stabilized PVC were investigated to prevent the injurious phenomena.

On the stabilization of PVC, PB-EP exhibited marked synergisms with the synergetic metal soaps, and the effects were increased with increased epoxidization degree. The heat efficiencies of synergetic soaps also depended on the compatibility of PB-EP with PVC.

Furthermore, PB-EP modified with polyols were used together with metal soaps to prevent the plate-out phenomenon which appeared through the molding process of PVC-containing epoxy compounds.

EXPERIMENTAL

Materials

PVC used in this work was Geon 103 EP (Nippon Geon Co. Ltd.); 1,4-polybutadiene and 1,2-polybutadiene were Nippol 1220 (Nippon Geon Co. Ltd.) and RB-820 (Japan Synthetic Rubber Co. Ltd.), respectively. Commercially available di(2-ethyhexyl)phthalate (DOP), metal stearates, and other materials were also used.

A mixture of two parts zinc stearate and 1 part calcium stearate [Zn/Ca(2/1)-st] was used as synergetic metal soap.

Epoxidation of Polybutadienes and Modification of Epoxidized Polybutadienes

Polybutadienes were epoxidized in benzene with formic acid by dropwise addition of hydrogen peroxide, *in situ* peracid reaction[12] at 40°C. The PB-EP were purified by dissolution in tetrahydrofuran and precipitation in methanol.

The modification of PB-EP was carried out by alcoholysis of epoxy groups in PB-EP with polyols, using sodium hydroxide as a catalyser.

The products were washed with water until sodium hydroxide was completely removed. PB-EP and polyol-modifying PB-EP were dried at 30°C in vacuo.

Epoxy content of PB-EP and polyol-modifying PB-EP was determined by titration with hydrochloric acid in 1,4-dioxane. For example, polybutadiene of which 40% of double bonds are epoxidized is abbreviated by PB-EP(40).

The amount of polyols added into the polymer backbone was indicated by the subtraction between epoxy contents of modified and unmodified PB-EP with polyols.

For example, the pentaerythritol-modifying PB-EP is also abbreviated by PB-EP(30)-Pen(10). The value in the second parentheses indicates the amount of pentaerythritol, which is added to 10% of double bonds in polybutadiene by alcoholysis of epoxy groups.

Infrared Spectrum and X-ray Photoelectron Spectroscopy (XPS)

Infrared absorbances of the modified polybutadiene films cast from benzene or 1,4-dioxane were obtained using a Shimadzu Seisakusho, Model IR-400 spectrophotometer.

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

Preparation of PVC Film

Mixtures of PVC, DOP, metal stearate, and PB-EP or polyol-modifying PB-EP 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 soap. The compound PVC film specimens (0.5 × 50 × 70 mm) were heated at 160 ± 2°C in Geer's oven. During compression of the roll film the process time was minimized to avoid a heat history.

Colorimetry

PVC films were investigated by colorimetry at room temperature using a Suga Shikenki, Model SM-4-CH color computer with Purity I-84 software 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.

Measurement of Dispersion

The dispersion degree of additives in the compounded PVC, which was evaluated by average area ($\overline{A}$) and average distance to nearest center of gravity ($\overline{NCG}$) of the shadows of additives obtained from an optical microscopic image of PVC films was measured by using a Nippon Avionics, Model TVIP-2000 image processor with Image Command 98 software.

RESULTS AND DISCUSSION

Effects of PB-EP

The stabilization effects of PB-EP used with Zn/Ca(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 heating time. Under the present conditions, W(Lab) of PVC films should be always less than 91 because W(Lab) of white color standard plate used as a reflector equals 91.0.

In PVC alone and PVC with only PB-EP, W(Lab) decreases with increased heating times owing to the formation, or coloration, of the longer polyene chains (λd = 580–610 nm; yellow orange).[1,2] Moreover, the decreases in W(Lab) of PVC with PB-EP alone is almost the same as that of unstabilized control.

PVC compounded with Zn/Ca(2/1)-st alone exhibited abrupt discoloration at 45 min, ascribing to the excessive coloration of zinc chloride-polyene complex (λd = 475 nm; blue).[1,2] These excessive colorations of polyene-zinc chloride complexes (π-complex) decreased W(Lab) markedly and remained almost invariable W(Lab) after attaining the minimum.

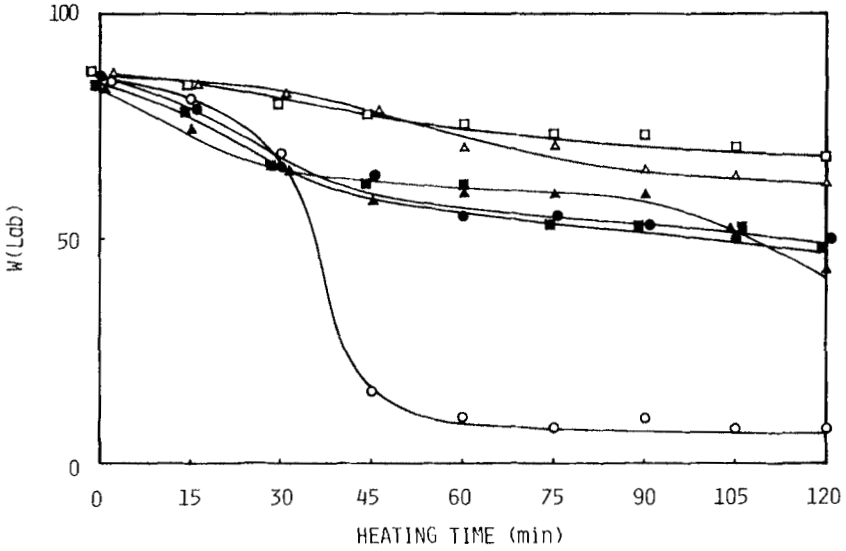


Fig. 1. Stabilization effect of PB-EP. PVC 100, and DOP 20 (●), PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0 (○), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(40)(1,4-dioxane solution) 2.0 (△), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(30)(1,4-dioxane solution) 2.0 (□), PVC 100, DOP 20, and 1,4-PB-EP(40)(1,4-dioxane solution) 1.0 (▲), and PVC 100, DOP 20, and 1,2-PB-EP(32) (1,4-dioxane solution) 1.0 (■) were milled at 150°C for 5 min and heated at 160°C.

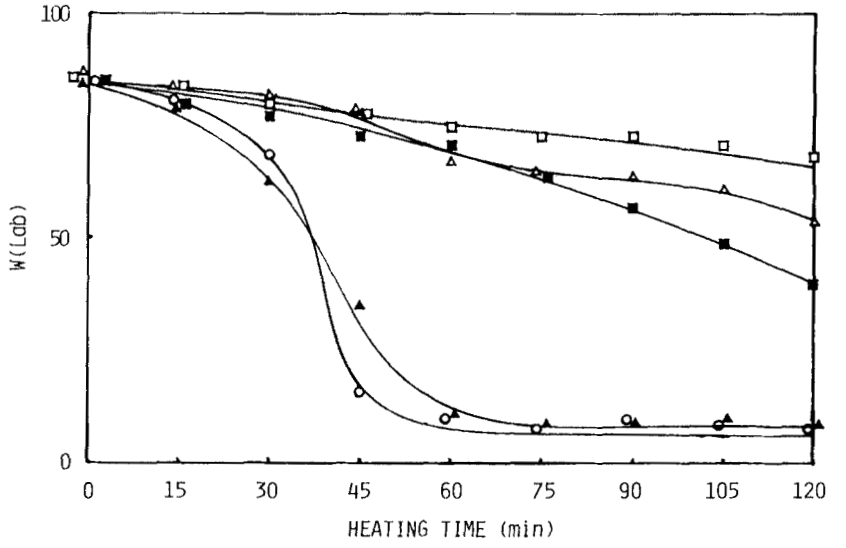


Fig. 2. Stabilization effect of PB-EP. PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0 (○), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(40)(1,4-dioxane solution) 1.0 (△), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(30)(1,4-dioxane solution) 1.0 (□), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(40) (solid) 1.0 (▲), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(33)(solid) 1.0 (■) were milled at 150°C for 5 min and heated at 160°C.

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

The synergetic effects of various PB-EP with synergetic metal soaps are summarized in Table I based on Figures 1 and 2.

The dominant wavelength (λd) which corresponds to hue in colorimetry for PVC alone and PVC with only PB-EP turns to 585–611 nm [$\lambda d(f)$] which correspond to the hue of the polyene color (yellow orange)[1,2] developed with increased heat treatments.

The abrupt color change from 574 nm to 475 nm, which is due to the excessive formation of the π-complexes is observed at 45 min (t_E) for stabilized controls. Tristimulus values were decreased to minute size by the appearance of excessive coloration of the π-complexes, such as zinc burning. Therefore, λd are of uncertain accuracy after the appearance of excessive cool color of the π-complexes.

On the other hand, PB-EP inhibit the formation of π-complexes and retard abrupt discoloration of PVC with the synergetic metal soaps, because the $\lambda d(f)$ does not approximate to 475 nm in the effective systems.

The synergetic effects of PB-EP with synergetic metal soaps are enhanced with increased additions or degrees of epoxidation.

Differing effects are observed in the case of 1,4-dioxane solution and solid particle of PB-EP as shown in Table I. The synergetic effects of 1,4-PB-EP and 1,2-PB-EP with Zn/Ca(2/1)-st are markedly enhanced by adding them to PVC as a 1,4-dioxane solution. Moreover, the synergetic effect of 1,2-PB-EP is superior to the effect of 1,4-PB-EP.

When adding them as solution, any undispersed granules could not be observed in microscopic images of all films. On the other hand, when employing the solid, undispersed particles were observed as shown in Figure 3. Additionally, $\bar{A}$ and $\overline{NCG}$ for compounded PVC with 1,2-PB-EP are smaller than those for 1,4-PB-EP.

Therefore, the synergetic effects of PB-EP also markedly depend on their dispersion degrees in PVC.

Influence of Dispersion Degree

The patterns of microscopic image of PB-EP and the relationships between number of particle ($\bar{N}$) and $\bar{A}$ are shown in Figures 4 and 5, respectively.

Figure 4 shows the plots of $\bar{N}$ versus $\bar{A}$ obtained by varying magnifications of microscope (many fine particles of PB-EP should be observed with increasing magnifications).

$\text{Log}\,\bar{N}/-\log\bar{A}$ as for differing amounts of PB-EP added, based on the relationship in Figure 4, are summarized in Table II.

1,2-PB-EP exhibit good compatibility and finely disperse into compound PVC in comparison with 1,4-PB-EP.

Moreover, the distances among the particles of 1,2-PB-EP in the PVC compound are shorter than those for 1,4-PB-EP as shown in Figure 5.

From these results, it should be concluded that the marked synergetic effect for 1,2-PB-EP is due to the fine dispersion into the PVC compound.

TABLE I
Stabilization Effect of Epoxidized Polybutadiene[a]

Additive[b]	phr	W_o	t_E (min)	W_M	t_L (min)	W_L	$(W_o - W_M)/W_o$ (%)	$(W_o - W_L)/W_o$ (%)	$\lambda d(i)$ (nm)	$\lambda d(f)$ (nm)
PVC	—	87	—	—	120	49	—	44	575	587
1,4-PB-EP(40)	1.0	86	—	—	120	42	—	51	572	586
1,2-PB-EP(30)	1.0	86	—	—	120	51	—	41	575	586
Zn/Ca(2/1)-st	3.0	87	45	73	120	8	16	91	574	486
1,4-PB-EP(11)[c,d]	0.4	86	45	76	120	8	12	91	567	481
	1.0	87	90	54	120	24	38	72	569	579
	2.0	87	120	52	120	45	40	48	569	581
	3.0	86	—	—	120	46	—	47	568	581
1,4-PB-EP(30)[c,d]	0.4	86	60	76	120	19	12	78	568	484
	1.0	87	105	55	120	32	37	63	570	578
	2.0	87	—	—	120	53	—	39	570	579
	3.0	86	—	—	120	54	—	37	572	580
1,4-PB-EP(40)[c,d]	0.4	87	75	65	120	20	25	77	569	484
	1.0	87	—	—	120	55	—	37	568	579
	2.0	86	—	—	120	62	—	28	568	579
	3.0	85	—	—	120	61	—	28	571	579
1,4-PB-EP(40)[c,e]	0.4	86	45	71	120	9	17	90	573	484
	1.0	84	45	63	120	9	25	89	573	482
	2.0	83	75	54	120	15	35	82	575	486
	3.0	83	75	50	120	18	40	78	574	487

TABLE I (*Continued from the previous page.*)

Additive[b]	phr	W_o	t_E (min)	W_M	t_L (min)	W_L	$(W_o - W_M)/W_o$ (%)	$(W_o - W_L)/W_o$ (%)	$\lambda d(i)$ (nm)	$\lambda d(f)$ (nm)
1,2-PB-EP(6)[c,d]	0.4	87	45	73	120	14	16	84	572	485
	1.0	87	45	70	120	17	20	80	572	487
	2.0	86	45	69	120	19	20	78	574	488
	3.0	86	45	55	120	19	36	78	573	487
1,2-PB-EP(12)[c,d]	0.4	87	75	72	120	12	17	86	572	482
	1.0	86	90	60	120	19	30	78	573	498
	2.0	86	—	—	120	49	—	43	573	577
	3.0	84	—	—	120	58	—	31	573	578
1,2-PB-EP(30)[c,d]	0.4	87	90	65	120	17	25	80	572	479
	1.0	86	—	—	120	66	—	23	574	578
	2.0	87	—	—	120	68	—	22	572	577
	3.0	87	—	—	120	65	—	25	574	579
1,2-PB-EP(33)[c,e]	0.4	87	60	60	120	9	31	90	572	481
	1.0	86	105	57	120	40	34	53	572	576
	2.0	86	—	—	120	64	—	26	572	577
	3.0	85	—	—	120	63	—	26	573	579

[a] Heated at 160°C. W_o represents W(Lab) of unheated film. t_E is heating time for onset of zinc burning. W_M represents W(Lab) at the heating time just before onset of zinc burning. t_L is heating time attaining the lowest W(Lab). W_L represents the lowest W(Lab). $\lambda d(i)$ represents the dominant wavelength of unheated film. $\lambda d(f)$ represents 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.

[d] 1,4-dioxane solution.

[e] Solid.

3-1

$\overline{NCG}=1.2\times10^{-1}$mm

$\bar{A}=7.3\times10^{-3}$mm^2

3-2

$\overline{NCG}=6.8\times10^{-2}$mm

$\bar{A}=3.9\times10^{-4}$mm^2

Fig. 3. Dispersion of PB-EP. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(40)(solid) 3.0(3-1), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(33)(solid) 3.0(3-2) were milled at 150°C for 5 min.

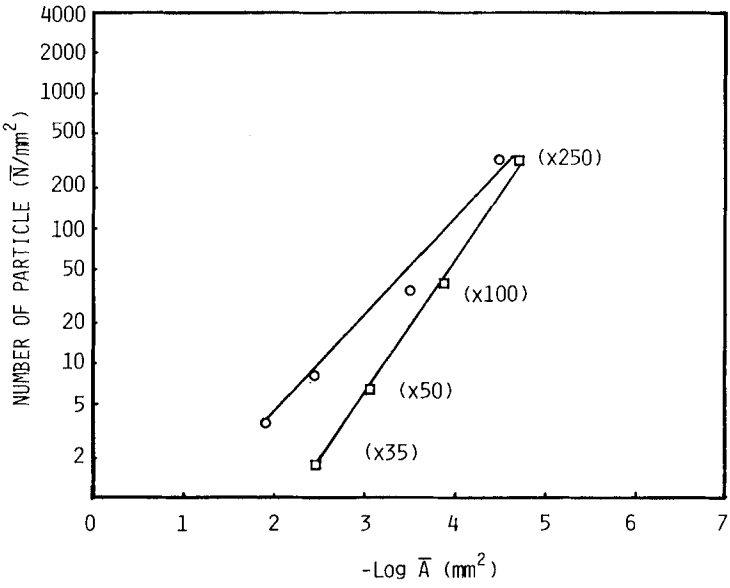


Fig. 4. Relationship between number of particle and area. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(40)(solid) (○), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(33)(solid) (□). Figures in parentheses are magnification of microscope.

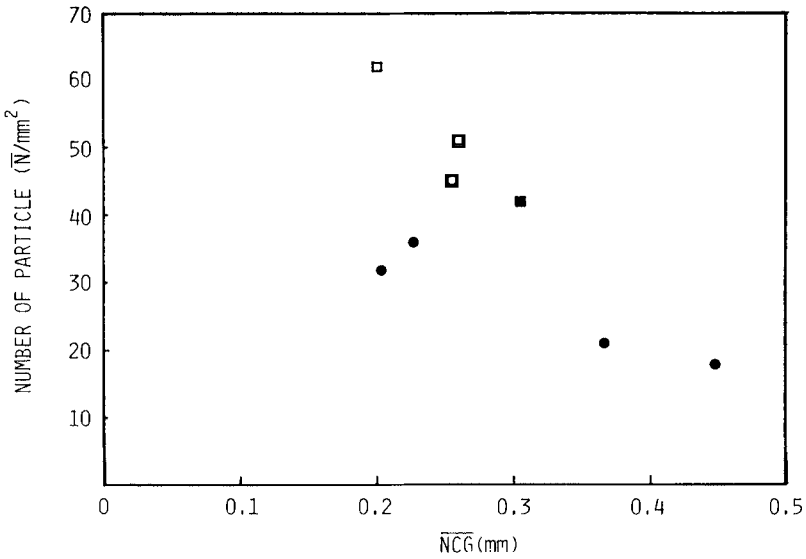


Fig. 5. Relationship between number of particle and $\overline{NCG}$. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP (○) or 1,2-PB-EP (□) were milled at 150°C for 5 min and heated at 160°C. Particles having $10^{-4} \sim 10^{-5}$ mm^2 area are processed to evaluate. ● and ■ indicate the system which appears the zinc burning at 90 min.

TABLE II
$\log \bar{N} / - \log \bar{A}$ as for PB-EP Particles in the Compounded PVC[a]

	$\log \bar{N} / - \log \bar{A}$	
phr	1,4-PB-EP(40)	1,2-PB-EP(33)
3.0	0.72	1.0
2.0	0.69	1.2
1.0	0.65	0.93
0.4	0.90	1.2

[a] PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and PB-EP were milled at 150°C for 5 min.

Synergetic Mechanism Between PB-EP and Metal Soaps

From the colorimetry of various aged PVC films, it is apparent that the remarkable stablization effects of PB-EP could not be observed on the PVC films without synergetic metal 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 complexes. Therefore, the synergism between PB-EP and synergetic metal soaps may be due to the interaction between PB-EP and cool color-producing zinc chloride, which would be easily converted from the corresponding metal soap in the aged PVC.

The influence of epoxy content on the synergetic effect of PB-EP with Zn/Ca(2/1)-st is shown in Figure 6. The higher W(Lab) appeared at higher epoxy contents, while abrupt decrease in W(Lab) is observed at lower epoxy contents and is due to the appearance of zinc burning. The maximum W(Lab) appears at $4.0 \sim 5.0 \times 10^{-3}$ mol/100 g PVC in epoxy content. These epoxy

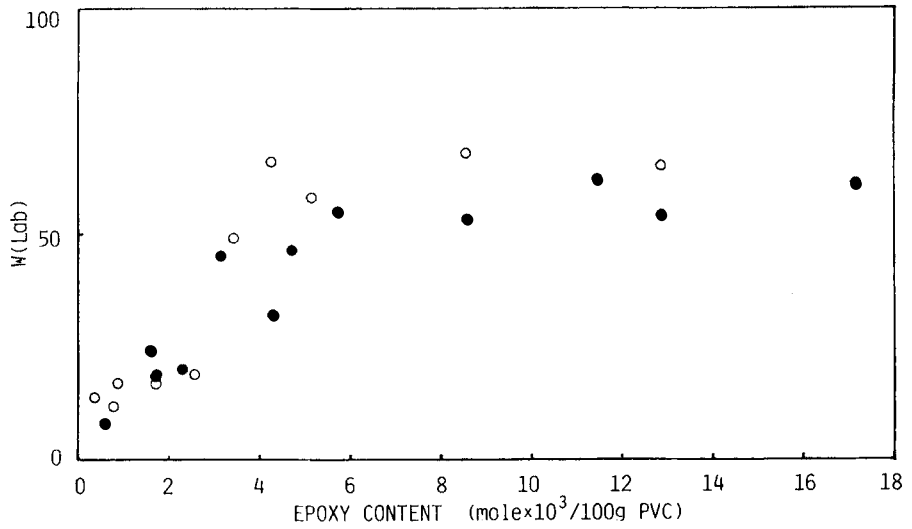


Fig. 6. Effect of epoxy content on the stabilization of PVC. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP (●), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP (○) were milled at 150°C for 5 min and heated at 160°C.

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 that the desirable interaction between epoxides and cool color-producing zinc chloride should be situated in the aging PVC compound.

The absorbance ratios between oxirane ring (1280–1260 cm^{-1}, 890 cm^{-1}, and 820 ~ 830 cm^{-1}) and methylene group (2860 cm^{-1}) for the products obtained by heating a mixture of zinc chloride and PB-EP at 150°C for 5 min are shown in Table III. The absorbances for oxirane ring are decreased or disappear by heating PB-EP with zinc chloride. These results indicate that oxirane rings of PB-EP are cleaved by zinc chlorides.

The binding energies (E) for Zn_{2p} of various samples are shown in Table IV. The binding energies of PB-EP and zinc chloride mixtures deviate from that

TABLE III
The Reaction Between Zinc Chloride and PB-EP

Sample	Absorbance ratio[a]		
	1280 cm^{-1} ~ 1260 cm^{-1}	890 cm^{-1} (trans-)	830 cm^{-1} ~ 820 cm^{-1} (cis-)
1,4-PB-EP(40)	0.2	0.2	0.2
1,4-PB-EP(40)/$ZnCl_2$[b]	—	—	—
1,2-PB-EP(30)	0.5	—	0.5
1,2-PB-EP(30)/$ZnCl_2$[b]	0.1	—	0.2

[a]Absorbance of oxirane ring/Absorbance of methylene group (2860 cm^{-1}).
[b]Rigid product obtained by heating a mixture of $ZnCl_2$ (0.08 mole) and PB-EP (0.05 mole) at 150°C for 5 min.

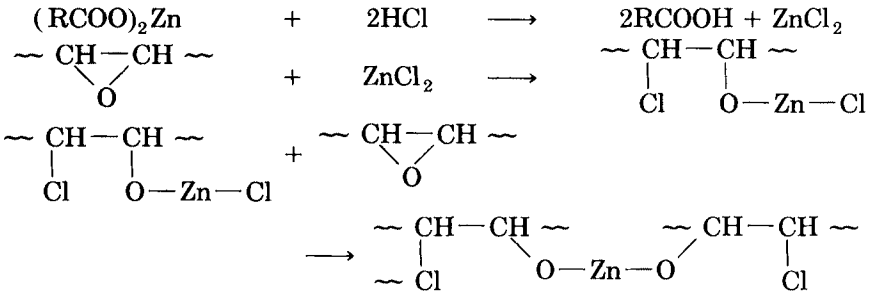
TABLE IV
Peak Shifts of Binding Energy for Aged PVC

Sample	Binding energy (eV)			
	Zn_{2p}	ΔE from $ZnCl_2$	ΔE from ZnO	ΔE from $Zn(OCOCH_3)_2$
$ZnCl_2$ alone	1024.0	—	+1.9	+1.4
$ZnCl_2$/PVC[a]	1023.6	−0.4	+1.5	+1.0
$ZnCl_2$/1,4-PB-EP(40)/PVC[b]	1022.7	−1.3	+0.6	+0.1
$ZnCl_2$/1,2-PB-EP(30)/PVC[b]	1022.6	−1.4	+0.5	0.0
$ZnCl_2$/1,4-PB-EP(40)[c]	1022.7	−1.3	+0.6	+0.1
$ZnCl_2$/1,2-PB-EP(30)[c]	1022.7	−1.3	+0.6	+0.1
ZnO alone	1022.1	−1.9	—	−0.5
$Zn(OCOCH_3)_2$ alone	1022.6	−1.4	+0.5	—

[a] PVC with $ZnCl_2$ (0.2 mol/100 g PVC) was milled at 150°C for 3 min on an open roll.
[b] PVC with $ZnCl_2$ (0.04 mol/100 g PVC) and PB-EP (0.4 mol/100 g PVC) was milled at 150°C for 3 min on an open roll.
[c] Rigid product obtained by heating a mixture of $ZnCl_2$ (0.08 mole) and PB-EP (0.05 mole) at 150°C for 5 min.

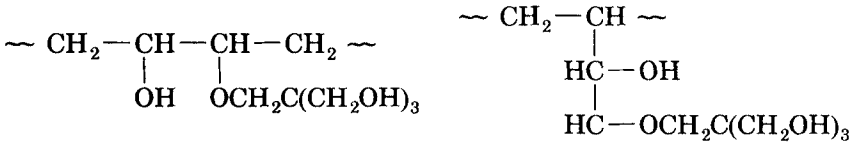
of zinc chloride and approximate to those of zinc oxide and zinc acetate. This means that Zn-O linkages are formed even in aging PVC compound.

From the various colorimetries, IR spectroscopies, and XPS the following reactions between PB-EP and zinc chloride which would be easily produced from zinc stearate should occur even in the PVC compound with heat treatments.



Effects of Polyol-Modifying Epoxidized Polybutadienes

The synergetic effects of various polyol-modifying PB-EP with synergetic metal soaps are summaried in Table V.



When polyol-modifying PB-EP were added into PVC as 1,4-dioxane solution, the synergetic effect is almost the same as those of each raw PB-EP. Especially when employing solid, polyol-modifying 1,4-PB-EP exhibited the remarkable synergetic effect than 1,4-PB-EP(40).

TABLE V
Stabilization Effect of Polyol-Modifying PB-EP[a]

Additive[b]	phr	W_o	t_E (min)	W_M	t_L (min)	W_L	$(W_o - W_M)/W_o$ (%)	$(W_o - W_L)/W_o$ (%)	$\lambda d(i)$ (nm)	$\lambda d(f)$ (nm)
Zn/Ca(2/1)-st	3.0	87	45	73	120	8	16	91	574	486
1,4-PB-EP(35)	0.4	87	75	62	120	8	29	91	571	487
-Pen(5)[c,d]	1.0	87	—	—	120	56	—	36	572	579
	2.0	87	—	—	120	60	—	31	572	579
	3.0	86	—	—	120	58	—	33	572	579
1,4-PB-EP(35)	0.4	85	60	66	120	8	22	91	572	480
-Pen(5)[c,e]	1.0	86	—	—	120	48	—	44	573	579
	2.0	86	—	—	120	58	—	33	572	579
	3.0	85	—	—	120	58	—	32	572	579
1,2-PB-EP(20)	0.4	84	60	72	120	12	14	86	574	489
-Pen(5)[c,d]	1.0	83	90	63	120	20	24	76	574	572
	2.0	83	120	51	120	44	39	47	575	579
	3.0	83	—	—	120	59	—	29	574	578
1,2-PB-EP(23)	0.4	86	45	71	120	5	17	94	572	482
-Pen(7)[c,e]	1.0	87	75	52	120	8	40	91	572	485
	2.0	87	105	66	120	55	24	37	573	579
	3.0	87	120	54	120	58	38	33	572	577

[a] Heated at 160°C. Definitions of abbreviations are same as in Table I.
[b] Each film contained 20 phr DOP.
[c] 3.0 phr Zn/Ca(2/1)-st was compounded in each film.
[d] 1,4-dioxane solution.
[e] Solid.

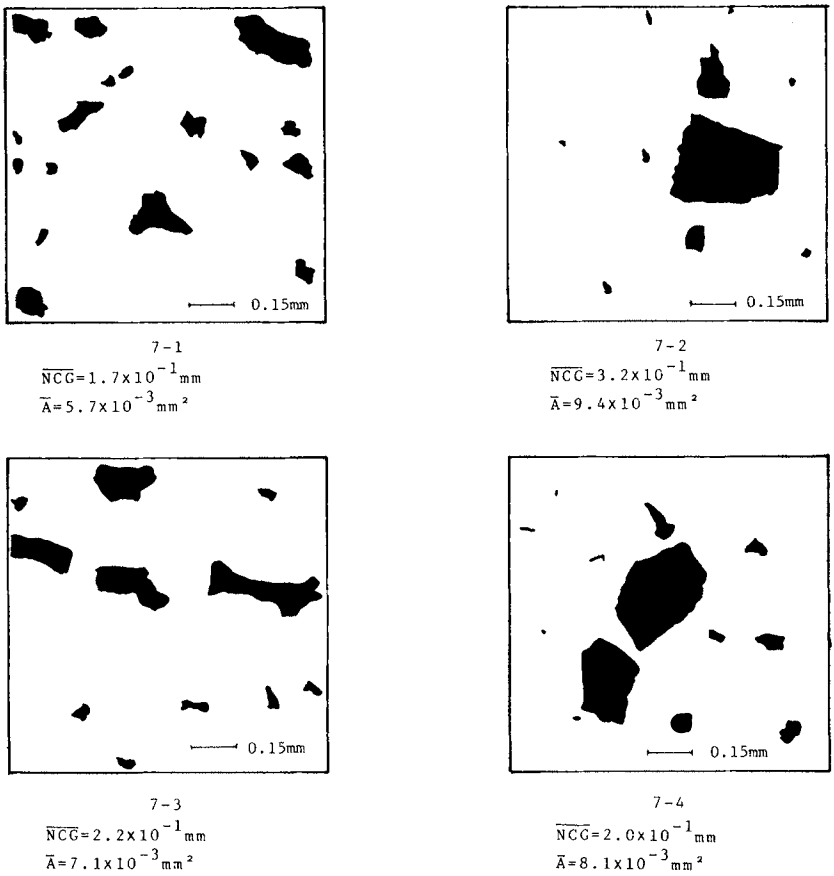


Fig. 7. Dispersion of additives in the compounded PVC. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,4-PB-EP(35)-Pen(5)(solid) 3.0(7-1), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and pentaerythritol(solid) 0.3(7-2), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2-PB-EP(23)-Pen(7)(solid) 3.0(7-3), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and pentaerythritol(solid) 0.4(7-4)

The patterns of microscopic image of each additive are shown in Figure 7.

Although the compatibility of 1,2-PB-EP with PVC is considerably decreased by modifying 1,2-PB-EP with polyols, the compatibility of polyols improved markedly.

The polyol-modifying PB-EP retard the plate-out phenomenon in comparison with PB-EP.

CONCLUSIONS

On the various colorimetries of aged PVC films, the strong and favorite interactions between PB-EP and cool color-producing zinc chloride are observed as for stabilization of PVC.

The marked stabilization effects of PB-EP with synergetic soaps depend mainly on their action as scavengers for the excessive cool color-producing zinc chloride in order to inhibit the unnecessary or injurious abrupt coloration of the π-complexes.

It is necessary to retain the efficient cool color-producing zinc chlorides which keep PVC colorless in complementary color relationship with polyenes.[1,2] Therefore, it is also necessary that suitable amounts of epoxy groups should be combined to retain the efficient zinc chloride. Excessive additions of epoxy groups 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 complementary colors with cool color of the π-complexes. This phenomenon is probably due to the excessive captures of cool color-producing zinc chloride with the excessive addition of epoxy groups.

The stabilization effects of PB-EP with synergetic soap also markedly depend on the dispersion degrees of PB-EP.

The outbreak of plate-out phenomenon is considerably retarded by using polyol-modifying PB-EP.

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