Pure & Appl. Chem., Vol. 49, pp. 539-567. Pergamon Press, 1977. Printed in Great Britain.

CHEMICAL MODIFICATION OF PVC

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ABSTRACT

The degradation of PVC at a processing temperature is mostly caused by its abnormal and unstable molecular structures. It has been pointed out that its allyl chloride structures play a significant role as the abnormal and unstable structures. Inasmuch as the allyl chloride structures are markedly more chemically active than the normal structure, the selective chemical treatments are applicable to the allyl chloride structures. The thermal stability of PVC can be remarkably improved by treating PVC with certain organo-aluminium compounds or protic solvents. Concretely, the results of analyzing the reaction mechanism with the low molecular model compounds of PVC or the tracer show that the selective stabilizing reaction on the allyl chloride structure takes place. On the other hand, the improvement of the mechanical properties of PVC, such as softening temperature, rigidity, anti-creep property, impact strength and tensile strength, is important for practical applications of PVC.

INTRODUCTION

Despite the fact that poly(Vinyl chloride) PVC has occupied the most important position among the general purpose plastics, its industrial applications are limited, due to its inferior thermal stability and mechanical properties. Many studies have been conducted to remedy these disadvantages, for which the following four remedial methods are conceivable :

a) improving PVC itself through polymerization during its production process ;
b) improving PVC itself through chemical modifications during its production process ;
c) improving the blending technology to develop new chemical ingredients of PVC ;
d) improving the processing machinery or technology.

It seems that the industrial advances on (a) and (d) have almost attained to the saturation level. Consequently, the industrial interest has recently shifted more and more to the applications on (b) and (c). The basic studies on (b) and (c) have already accumulated to a considerable degree and should be modified for industrial use hereafter.

In this paper, the above studies on (b) and (c) are reviewed with regard to the crosslinking chlorination, graft polymerization and stabilization as a group of the chemical modifications, which would be extremely useful to improve the mechanical properties and thermal stability of PVC.

IMPROVEMENT OF MECHANICAL PROPERTIES

Generally, the improvement of mechanical properties of plastics means to increase the abilities to withstand the heat deformation, etc... of the processed articles. It must be useful to increase the intermolecular force by introducing certain polar groups into polymer chains and to decrease the molecular chain mobility by combining the polymer chains with each other by certain chemical bonds. Typical examples concerning PVC are chlorination and crosslinking. On the other hand, grafting other kinds of polymer chain onto PVC means the addition of other properties without affecting the characteristics of PVC. Furthermore, the appearance of the new properties can be expected as a result of the formation of new chemical bonds between PVC and graft polymer quite different from polymer blends.

In this chapter, the outline of recent studies for crosslinking, chlorination and graft polymerization are reviewed from the viewpoints of the polymer reaction and the improvement of the mechanical properties.

Crosslinking of PVC

Many studies have been conducted for crosslinking of PVC through thermal degradation, UV or radioactive ray irradiation and chemical treatments (1∿12). The great many cases using these methods are industrially indesirable, because considerable dehydrochlorination and discoloration occur simultaneously with crosslinking reaction. Recently, the methods of radioactive ray irradiation with polyfunctional monomers have been developed, on which the industrial interest is being focused (13∿20).

The results of experiments by Salmon et al. are shown in Fig. 1 and 2 (17). The irradiation of high energy electron ray on PVC with crosslinkable monomers such as tetraethylene glycol dimethacrylate results in the remarkable improvement of the mechanical properties.

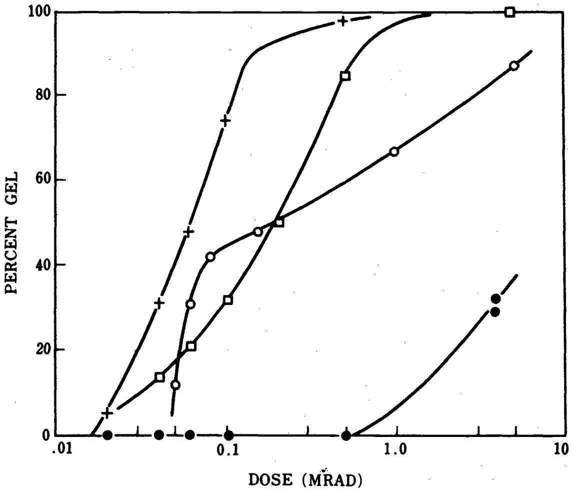


Fig. 1 The crosslinking behavior of blends of PVC with various monomers. Irradiated at 25°C. (BMG; n-butyl methacrylate, TEGDM; tetraethyleneglycol dimethacrylate, TMPTM; trimethylolpropane trimethacrylate, TMPTA; trimethylolpropane triacrylate). Monomer/PVC = 33.3/66.7 (wt.)

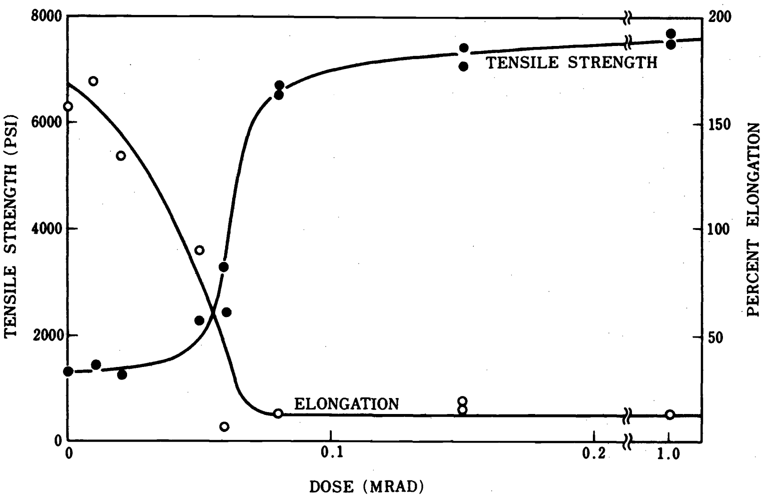
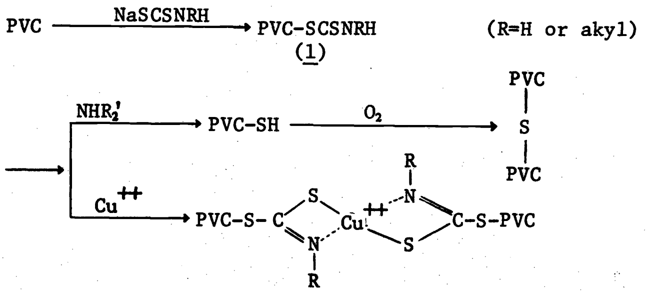


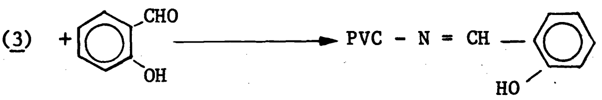
Fig. 2 The ultimate tensile strength and elongation vs. does (25°c) for TEGDM/PVC blends. TEGDM/PVC = 33.3/66.7 (wt.)

On the other hand, pure chemical crosslinking technology has recently advanced remarkably since the discovery of several kinds of the superior PVC displacement reactions. Okawara et al., for instance, found that the reaction of PVC with sodium dialkyldithiocarbamate in dimethylformamide at 50 ~ 60°C results in the introduction of alkyldithiocarbamate of about 35 mole % into PVC without dehydrochlorination (21).

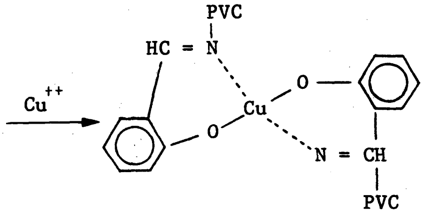


The amine treatments of (1) easily give PVC with thiol structures, which then causes crosslinking by air oxidation. Immersing the film of (1) into aqueous metal salt solution causes crosslinking through the chelate structure (22, 23).
Furthermore, the reaction of PVC with sodium azide introduces even an azide group of about 80 mole % into PVC, though azide anion has extremely weak nucleophilicity. The introduction of the chemically active groups such as azide group into PVC facilitate the secondary chemical modifications (24, 25). Namely, azide-PVC (2) gives phosphoimine polymer (3) by reacting with triphenylphosphine. The treatment of (3) with salicylaldehyde produces polyimine (4). The gel (5) is formed by mixing tetrahydrofurane solution of (4) with dimethylformamide solution of copper acetate at room temperature.

$$\underset{(2)}{\mathrm{PVC - N_3}} + \mathrm{P_3(C_6H_5)_3} \longrightarrow \underset{(3)}{\mathrm{PVC - N = P\ (C_6H_5)_3}}$$

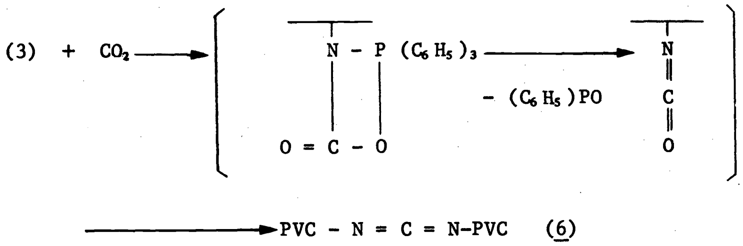


(4)



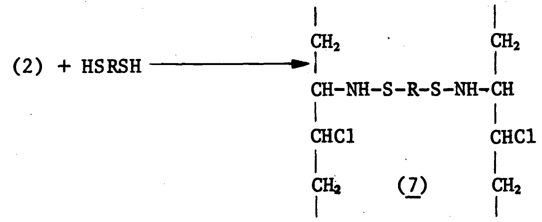
(5)

The rapid gel (6) formation can also be observed upon introducing a carbon dioxide into the tetrahydrofurane solution of (3).



(6)

The thermal treatment of (2) and thiokol on a mixing mill at 120 ~ 140° C gives the gel (7), which is almost insoluble to tetrahydrofurane (26).



(7)

On the other hand, starting from the studies on the reaction of PVC with morpholine (27 ~ 29), Nakamura et al. have found a lot of new crosslinking reaction of PVC with sulfur compounds. Morpholine is introduced into PVC by being heated with PVC at more than 100° C. The products easily causes crosslinking upon hot mixing with di- or tri-thiol compounds such as thiokol and tricyanuric acid on a mixing mill. The same reaction products seem to be caused when thermally mixing PVC with morpholine and the thio compounds at the same time (30).
Subsequently, the crosslinking methods were further improved to immersing the film of PVC and thiol compounds in liquid ammonia (31). In the old methods, the amount of morpholine is the same as that of PVC during the thermal treatment on a mixing mill, whereas the improved method is more practical because of just immersing the film in liquid ammonia. Furthermore, it was found that primary and secondary diamines are also useful as the crosslinking accelerators (32). The experimental results of PVC crosslinking with thiokol and ethylenediamine (EDA) are shown in Table 1 and 2 (33).

TABLE 1. Effect of temperature on the crosslinking reaction

Immersion temperature, °C	EDA permeated, wt-%	Crosslinked PVC: Color	Crosslinked PVC: THF-insoluble fraction, wt-%	Crosslinked PVC: Swelling ratio	Crosslinked PVC: N, wt-%
10	0	Colorless	0		(0.012)
20	4	"	30.0	6.10	(0.003)
25	11.6	"	76.0	4.50	(0.016)
30	16.7	"	100.0	2.90	(0.011)
40	25.6	"	"	2.86	(0.010)
50	32.6	Pale yellow	"	3.08	(0.067)
60	36.8	Orange	"	2.98	0.76
70	39.1	Reddish purple	"	3.00	2.39

All samples were obtained by immersing PVC blends containing 7g of EG-600 per 100g of PVC ($\bar{P}$ = 1450) for 60 min in EDA.
EG-600: $HSCH_2(CH_2OCH_2)_{11}CH_2SH$

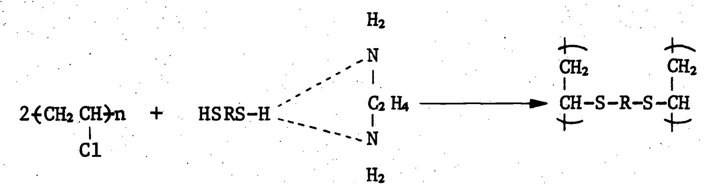
The immersion temperature of up to 30°C of PVC film in EDA seems efficient for the crosslinking judging from its THF insoluble fraction and swelling ratio. It can be mentioned from the nitrogen contents of the products that the crosslinking structures are hardly constructed with EDA itself. The EDA immersion remarkably improves the PVC mechanical properties. Namely, it has been clarified that crosslinking by the reagents of soft structures and long molecular chains causes the high tensile strength, impact strength and low brittle temperature, and that crosslinking by the reagents of short molecular chains gives the high yeild strengthes and high heat distortion temperatures.

TABLE 2. Structures of crosslinking agents and the properties of PVC crosslinked and uncrosslinked.

		Crosslinking conditions		Yield strength, kg/cm²		Tensile strength, kg/cm²		Elongation at break, %		Breaking energy, kg-cm/cm²		Heat distortion temperature, °C		Brittle Temperature, °C	
Crosslinking agents (CA)	CA, g/100g of PVC	Temp, °C	Time, min	PVC-X	PVC	PVC-X	PVC	PVC-X	PVC	PVC-X	PVC	PVC-X	PVC	PVC-X	PVC
EG-140	2.8	30	120	595	600	580	575	68	45	100	84	85	82	- 5	15
EG-600	8.8	30	60	535	500	600	500	135	46	262	90	83	70	-35	- 7
EG-1000	7.9	30	90	535	490	535	460	123	42	255	73	80	67	-32	- 5
$HSC_{10}C_{20}SH$	4.5	30	90	540	550	540	525	88	39	146	80	70	62	-20	- 3
$HSCH_2C_6H_4CH_2SH$	3.5	30	120	605	560	570	540	53	41	104	69	93	81	- 4	18
$HSCH_2C_6H_4CH_2$-$C_6H_4CH_2SH$	10.0	30	60	600	580	570	550	58	20	128	45	91	78	- 8	16
Dimercapto-dichloroparaffin	10.0	30	90	560	580	580	575	105	39	170	49	80	69	-20	- 1

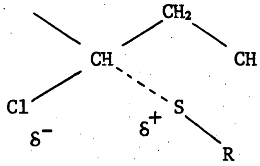
EG-140, EG-600, EG-1000 have n number of 1, 11, 21, respectively in $HSCH_2(CH_2OCH_2)nCH_2SH$

The reaction mechanism is a condensation reaction between PVC and thiol compound, which is accelerated by the formation of a complex of EDA with thiol compounds.

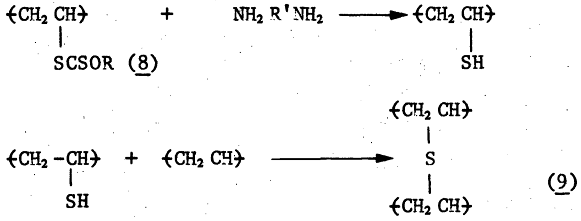


$$2\left(\underset{\displaystyle Cl}{CH_2CH}\right)_n + HSRS\text{-}H\cdots\begin{array}{c}H_2N\\|\\C_2H_4\\|\\NH_2\end{array} \longrightarrow \begin{array}{ccc}\vdash CH_2 & & \vdash CH_2\\ | & & |\\ CH & \text{-}S\text{-}R\text{-}S\text{-} & CH\\ \vdash & & \vdash\end{array}$$

The high reaction rates may depend on the neighboring group effect, under which the introduced sulfur atoms activate the neighboring chlorine atoms in PVC molecules.



These methods can be applied for crosslinking of PVC with other kinds of thiol compounds.
For example, the reaction product ($\underline{8}$) of potassium alkyl-o-xanthate changes into PVC with the sulfide crosslinking structure ($\underline{9}$) via the formation of the thiol structure by the EDA treatment (34).



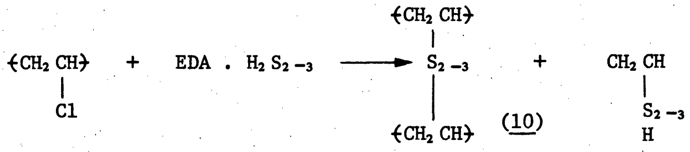
$$\underset{\substack{|\\ SCSOR\ (\underline{8})}}{(CH_2CH)} + NH_2R'NH_2 \longrightarrow \underset{\substack{|\\ SH}}{(CH_2CH)}$$

$$\underset{\substack{|\\ SH}}{(CH_2\text{-}CH)} + (CH_2CH) \longrightarrow \overset{\substack{(CH_2CH)\\ |}}{\underset{\substack{|\\ (CH_2CH)}}{S}} \quad (\underline{9})$$

However, the mechanical properties of the produced PVC are hardly improved, though the crosslinking occurs considerably. This unsatisfied improvement in the mechanical properties seems to be due to the formation of the short crosslinking chains.
Since then, a series of the studies has been developed in the direction of forming PVC crosslinking with polysulfide chains (36-39). The reaction of sulfur with dimethylamine forms the following complex molecule (35).

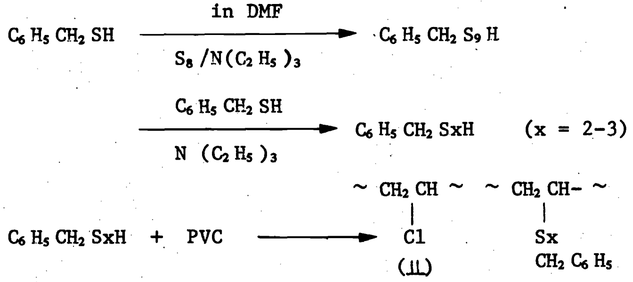
$$2\ (C_2H_5)_2NH + S_8 \longrightarrow (C_2H_5)NS_8H_2N(C_2H_5)_2$$

The similar reaction between sulfur and ethylenediamine gives the complex molecule (EDA • H_2S_{2-3} . Adding PVC powder to EDA • H_2S_3 solution of ethylenediamine results in forming the crosslinking structure ($\underline{10}$), which is almost completely insoluble to tetrahydrofurane. The same reaction can be observed upon immersing PVC film made by hot mixing of PVC and rubbery sulfur into ethylenediamine.



$$\underset{\substack{|\\ Cl}}{(CH_2CH)} + EDA\ .\ H_2S_{2-3} \longrightarrow \overset{\substack{(CH_2CH)\\ |}}{\underset{\substack{|\\ (CH_2CH)}}{S_{2-3}}}\ (\underline{10}) + \underset{\substack{|\\ S_{2-3}\\ H}}{CH_2CH}$$

On the other hand, the reaction between PVC and alkylhydropolysulfide gives PVC with side chains of alkylpolysulfide ($\underline{11}$) (40-42). Alkylhydrosulfide is synthesized in the dimethylformamide (DMF) solution through the reaction between thiol and amine-activated sulfur. ($\underline{11}$) Easily crosslinks and hardens by U.V or Gamma-ray (43).



$$C_6H_5CH_2SH \xrightarrow[S_8/N(C_2H_5)_3]{\text{in DMF}} C_6H_5CH_2S_9H$$

$$\xrightarrow[N\ (C_2H_5)_3]{C_6H_5CH_2SH} C_6H_5CH_2SxH \quad (x = 2\text{-}3)$$

$$C_6H_5CH_2SxH + PVC \longrightarrow \underset{\substack{|\\ Cl\\ (\underline{11})}}{\sim CH_2CH \sim}\ \ \underset{\substack{|\\ Sx\\ CH_2C_6H_5}}{\sim CH_2CH\text{-} \sim}$$

Chemical crosslinking might be developed industrially in the near future as one of the PVC processing technology, though a part of it has already been put to practical use. The reaction conditions of crosslinking should be industrially established to meet the required properties of PVC processed articles. Consequently, the recent basic studies on improving the mechanical properties can be highly evaluated so far as the crosslinking methods are concerned.

Chlorination of PVC

Chlorination has the longest history among the PVC polymer reactions which are used industrially. In the early stage, chlorinated PVC was used for paints because of its high solubility to organic solvents. Since then, chlorinated PVC has been utilized as molding material for processed articles of high temperature use, since the chlorination causes improving the mechanical properties of PVC. On the other hand, chlorination increases the fusion viscocity of the product. Therefore, chlorinated PVC requires undesirably severer processing conditions than PVC.

The physical and chemical properties of chlorinated PVC were reported by Fukawa et al. (44-49) and Bier et al. (50). One of the unsolved problems about chlorinated PVC is its chlorination mechanism. Fuchs et al. (5]) and Fukawa et al. (45) pointed out that the chlorination takes place in the methylenic group.

Later, Petersen et al. found that 1, 2-dichloride structure in the early stage and 1, 1-dichloride structure in the later stage occur preferably in the PVC chlorination reaction, but the continuous sequence of the latter unit does not occur (52). Then results are shown in Fig. 3.

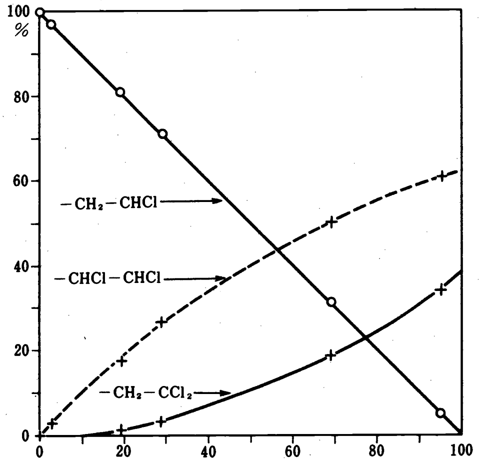
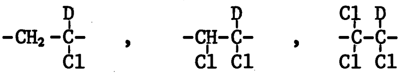


Fig. 3 The number of different nonomer units (in %) in chlorinated PVC chains at different chlorination numbers for the polymer samples as derived from NMR data.

Furthermore, Svegliado et al. pointed out that the number-average sequence length of 1, 2-dichloride units does not differ significantly from 1 besides confirming Petersen's results and that the chlorination is affected by stereoregularity or crystalinity of PVC (53).

Those studies described above are based on the assumption that not more than one chlorine atom can enter one monomeric unit. Kolinsky et al. found that the deuterium content in chlorinated PVC remains constant despite the increase in chlorine content during chlorination of α-deuterated PVC (54). Their results are shown in Fig. 4. In this chlorinated PVC, the expected amount of $-CH_2-$, $-CHCl-$, and $-CCl_2-$ certainly exist, though their ratio slightly differs from that in chlorinated ordinary PVC. These experimental results suggest that three kinds of monomeric units described below exist in the chlorinated PVC and two chlorine atoms can enter one monomeric unit.



$$-CH_2-\underset{Cl}{\overset{D}{C}}- \quad , \quad -\underset{Cl}{CH}-\underset{Cl}{\overset{D}{C}}- \quad , \quad -\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{D}{C}}-$$

This study is noteworthy, though the isotopic effect of the chlorination must be ascertained. Kolinsky et al. explained that two chlorine atoms enter only one methylenic group due to the conformation effect of PVC chain.

Influence of PVC stereoregularity in chlorination has been studied by Allen et al. (55) and Quenumi et al. (56). Chlorine radicals are presumed to attack preferably the middle carbon in the heterotactic triad.

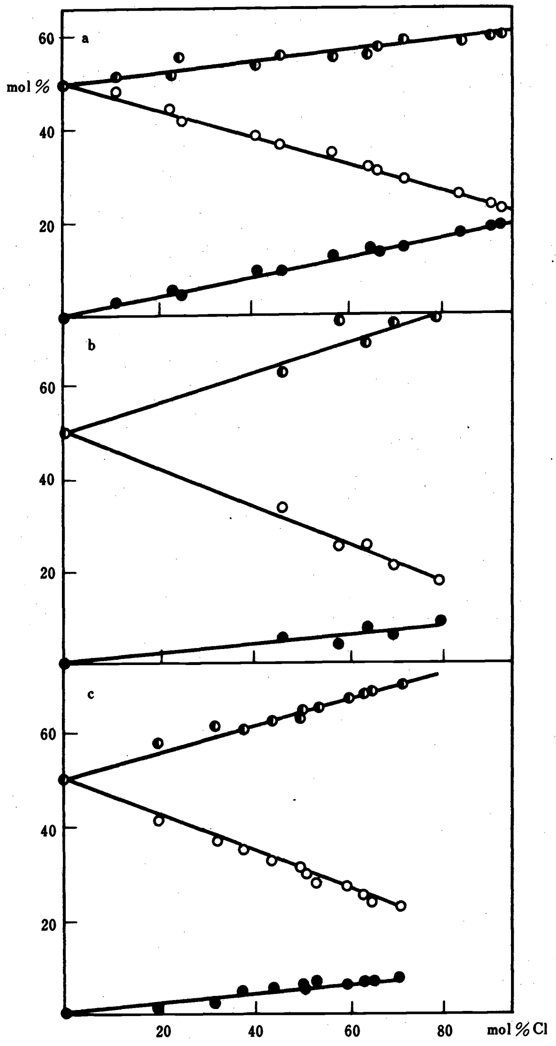


Fig. 4 Content of (○) CH_2, (◐) CHCl, and (●) CCl_2 groups in chlorinated poly-(vinyl chloride): (a) suspension-chlorinated CPVC; (b) solution-chlorinated CPVC; (c) suspension-chlorinated α-d-CPVC. Here y is defined as the sum of CHCl + CDCl groups, with the content of CDCl groups being constant and equal to 0.48 in the whole series. Both block polymerized and suspension polymerized samples are included.

The whole aspect of the chlorination mechanism might be clarified in the near future. Then, the improvement of the processability and the processing technology will be required in order to widen the application field of chlorinated PVC than at present.

Graft polymerization

There are four methods of graft polymerization, which are radical chain transfer, activating polymer, polycondensation, and jump reaction. Recent studies covering these four methods are introducted below:

Method of radical chain transfer. Prabhakara pointed out that PVC with the side chains of poly (methyl methacrylate)or poly (ethyl methacrylate) was synthesized by solution-polymerization of methyl methacrylate or ethyl methacrylate with PVC. Grafting efficiency of this reaction is 0.2 to 0.4 (57).
It was found by kawai et al. that the photo-induced graft polymerization of acrylate monomers shows the highest grafting efficiency of 0.2 to 0.4 at the mixed system of acrylic acid and n-butyl acrylate (58).
Okamura et al. tried to graft-polymerize ethyl acrylate, vinyl acetate, and styrene onto PVC

with benzoyl peroxide in dimethylformamide and cyclohexanone (59). The grafting efficiency of this reaction is more than 0.8, especially 1 with vinyl acetate (59). The thermal stability of the graft-PVC is shown in Table 3. The order of their thermal stability is PVC-g-ethyl acrylate>original PVC>PVC-g-vinyl acetate>PVC-g-styrene. The improvement of thermal stability seems to depend on decreasing carbon-carbon double bonds in the trunk polymer by graft polymerization.

TABLE 3. Percent reflectance (440 nm) of radical grafted PVC film (0.040 mm thick), 60% grafted in dimethylfolmamide.

Sample	Percent reflectance (%) Non-treatment	 Heat-treatment (140° C, 3hrs in air)	Color
Standard paper	69	-	White
PVC	69 (1.0$_0$)a)	45 (0.6$_3$)a)	Violet
PVC-g-EA	65 (0.9$_4$)a)	68 (0.9$_9$)a)	Pale yellow
PVC-g-VAc	63 (0.9$_1$)a)	42 (0.6$_1$)a)	Violet
PVC-g-St	59 (0.8$_6$)a)	35 (0.5$_1$)a)	Dark brown

a) Percent reflectance of non or heat-treated graftcopolymer film/Percent reflectance of non-treated PVC film.

Ultra-violet absorption spectra of the graft PVC, which show decreasing diene or triene in PVC by the graf polymerization, are shown in Fig. 5.

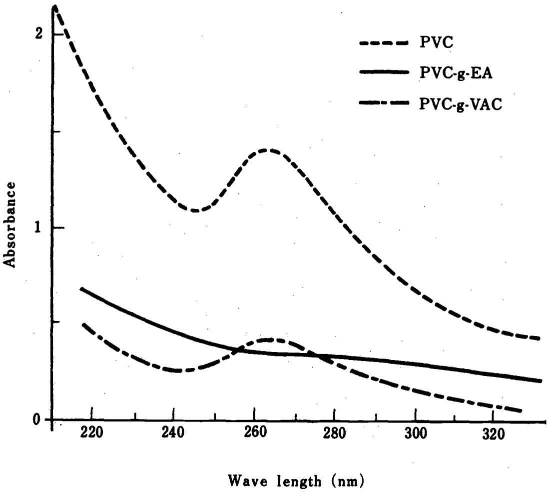
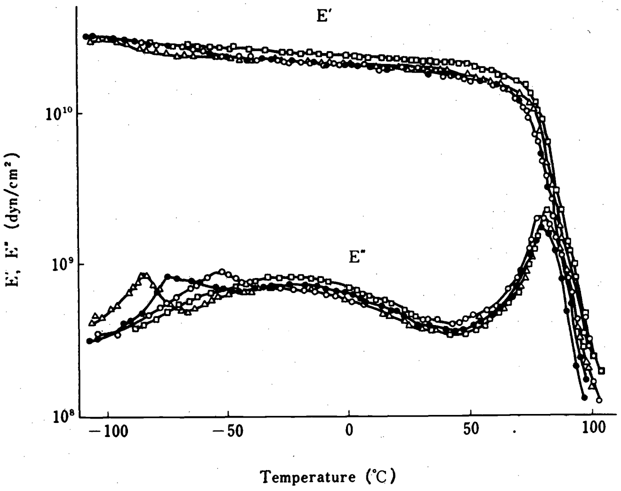


Fig. 5. Ultra-violet absorption spectra of radical grafted PVC film (coverted into 0.020 mm thick of PVC), 180% grafted in dimethylformamide.

It is quite interesting that this radical grafty polymerization simultaneously causes improving the PVC thermal stability by the saturation of the carbon-carbon double bonds in PVC. Besides, Chapiro et al. studied the graft primerization of methacrylic acid onto PVC film by Gamma-ray irradiation (60).

Method of activating polymers. Radical or cation formation in PVC molecule by Gamma-ray irradiation, redox reaction of PVC with metal ion, mechanochemical bond sission, and using PVC as co-calalyst in cationic polymerization catalyst systems have been studied. Morishima et al. studied to graft-polymerize butadiene onto PVC with Gamma-ray irradiation in gas-solid phase (61. 62). These reaction showed nearly 1.0 of the grafting efficiency and up to 25% of the grafting degree. The obtained PVC was studied about its morphology and its dynamic visco-elasticity. Fig. 5 shows the dynamic-elaciticily of the grafted PVC. A part of the grafted polybutadiene seems to be present in the heterogeneous phase in the grafted PVC when its graft-polymerization temperature is comparatively low (63).



● : Graft copolymer (degree of grafting 10%, polymerization temp. 30° C).
○ : Graft copolymer (degree of grafting 10%, polymerization temp. 60° C).
△ : Blendpolymer (PVC/PBD=100/10),
□ : PVC

Fig. 6 E' and E" vs. temperature for graft copolymer, blend polymer and PVC at 110 c/s.

Minoura et al. studied the radical graft polymerization of styrene onto PVC with cromium ion (Cr^{2+}) as the initiator, which can polymerize styrene with alkylhalide as the co-catalyst (63 ~ 65). The grafting effeciency is more than 0.88 and crosslinking also occurs through the recombination of polystyrene radicals with increasing the conversion. It has also been established with the model compounds that the grafty polymerization chiefly initiates from carbon atoms with the labile chlorines in PVC.

Guyot et al. have pointed out that the mechanochemical graft polymerization of methacrylate ester onto PVC in a Brabender-plastograph results in the considerable improvement of dynamic thermal stability (66). The improvement seems to be attained by scavengering free radicals with the vinyl monomers during mastication.

Gaylard et al. synthesized cis-1.4-polybutadiene grafted PVC with diethyl aluminium chloride (69), which can be used to polymerized cationically styrene and isobutene using organic halide as co-catalyst (67, 68). In this case, the graft polymerization seems to be cationically initiated from the PVC carbon atoms which carry the labile chlorine atoms. Actually, the graft PVC by this method exhibits extremely good thermal stability. The hydrochlorination characteristics are shown in Fig. 7.

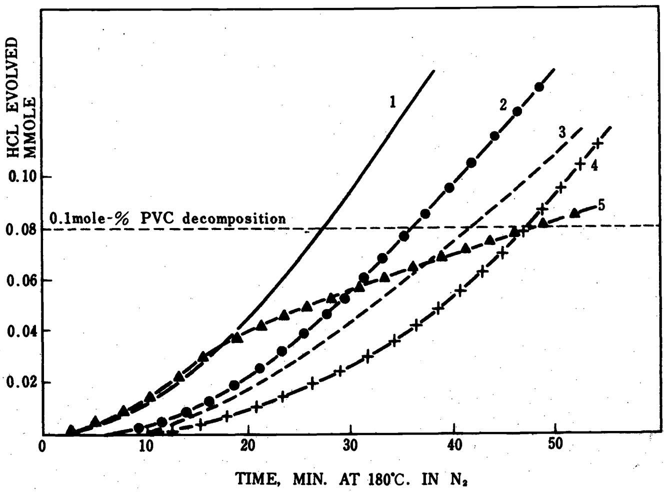


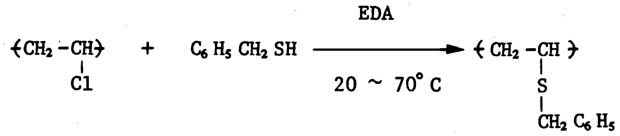
Fig. 7 Evolution of hydrogen chloride at 180° C (nitrogen as carrier gas) from suspension poly (vinyl chloride) (1), suspension PVC + stabilizer (2),

cis-1, 4-polybutadiene-poly (vinyl chloride) (suspension) graft copolymer from monomeric butadiene (Type M) (3), Type M graft copolymer + stabilizer (4), and graft copolymer from cis-1, 4-polybutadiene (Type P) (5).

		As shown	Normal
Stabilizer, phr:	Ferro 59-V-11 (ca-Zn)	0.10	2-3
	Ferro 5376 (organic)	0.05	1-1.5

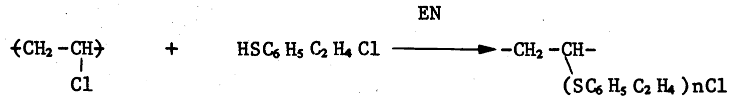
Kennedy et al. (70, 71, 73) and Abbås et al. (72) found that the above mentioned method can also be used for the graft polymerization of isobutene and styrene onto PVC.
As described above, the method of activating polymers can be used not only for synthesizing new graft PVC but also for stabilizing PVC.

Method of polycondensation. It is possible to innitiate the graft polymerization such as polycondensation from certain chemically active group previously introduced into PVC. Nakamura et al. found that the treatment of PVC with thiolcompounds and ethylenediamine (EDA) produces PVC with sulfide structures (74).



$$\text{-(}CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH}\text{)-} + C_6H_5CH_2SH \xrightarrow[20 \sim 70^\circ C]{EDA} \text{-(}CH_2-\underset{\underset{\underset{\underset{\displaystyle CH_2C_6H_5}{|}}{\displaystyle S}}{|}}{CH}\text{)-}$$

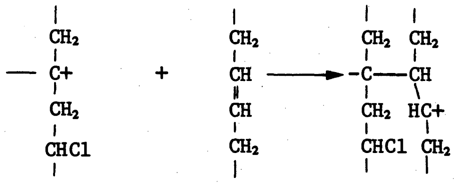
The reaction of PVC with p-(2-dichloroethyl) thiophenol (CETP) in EDA gives PVC with side chains of Poly (thioether) in the same way as the above reaction (75).



$$\text{-(}CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH}\text{)-} + HSC_6H_5C_2H_4Cl \xrightarrow{EN} -CH_2-\underset{\underset{\displaystyle (SC_6H_5C_2H_4)nCl}{\backslash}}{CH}-$$

The grafting efficiency was 0.2-0.4, though the homopoly condensation reaction of CETP was unavoidable. The properties of this grafted PVC were also studied.

Jump reaction. This covers the methods of combining PVC with anionic living polymer or other dead polymers.
Gallot et al. indicated that polystyrene grafted PVC can be produced by reacting PVC, as deactivator, with polystyrene anion-polymerized by phenylisopropyl potassium as the initiator in tetrahydrofurane (76).
Farthermore, Lechermeier et al. studied the graft polymerization with the living polymer initiated by n-butyl lithium (77). Then, the graft co-polymerization of styrene and butadiene onto PVC was studied (78, 79). These methods are useful to synthesize the samples for the polymer characterization because the polymerization degree of graft chains can be precisely controlled. On the other hand, a typical jump reaction can be seen in the reaction of polymeric carbonium ion of PVC with cis-1.4-polybutadiene (C-PB) (69). Namely, the reaction of PVC with diethylaluminium chloride, and C-PB generates the following crosslinking.



Diethylaluminium chloride react with labile chlorines such as tertiary or allylic chlorines in PVC to produce the carbonium ion, and then the crosslinking occurs between PVC and c-PB. Though the new chemical bonds between PVC and graft polymer, which are different from mere polymer blends may give the new mechanical properties of PVC, the industrial advantages of PVC applications have not yet been fully established.

IMPROVEMENT OF THE THERMAL STABILITY

PVC is too inferior in thermal stability to be thermally processed by itself. Therefore, the thermal stabilizers are used to avoid the decomposition but several problems are remaining unsolved.
Firstly, the use of thermal stabilizers increases the processing cost causing hygenic problems, the plate-out, the cloudiness and the like.
Secondary, because the thermal degradation of PVC is inevitable even by using thermal stabilizer, the processing temperature and speeds should be lower than other thermo-elastic

plastics. Consequently, the PVC processing efficiency has been low.
Thirdly, PVC is not suitable for certain uses. Namely, PVC can hardly be used for rigid injection molding of large articles which requires severe processing conditions. This application field, in which other thermo-elastic plastic have been preferably used, could create a large demand for PVC if its thermal stability were improved.
What PVC requires to avoid its thermal degradation during processing are its improved thermal stability, superior thermal stabilizers and well-designed processing equipment. The thermal degradation problems of PVC concern its gelation and melt-flow properties and the thermal stability of PVC itself. In this Paper, the studies on the latter are discussed. Of course, the use of thermal stabilizers is the most effective methods for avoiding the PVC degradation at present. Therefore, the essence in the stabilization mechanisms of thermal stabilizers must be utilized as a new method for the production technology of thermally improved PVC.
In this chapter, in which the improvement of PVC thermal stability is described from the viewpoint of the chemical modification, the thermal stability of the normal stracture and the thermal decomposition of PVC with stabilizers are discussed first. Secondly, the basic idea about improving the thermal stability with the polymer reaction method is described. Finally, several methods for improving the thermal stability are concretely shown.

Thermal decomposition of PVC

It is very important for improving PVC thermal stability to clarify the mechanisms of thermal decomposition, especially the initiation reaction.
The decomposition temperatures of PVC and the model compounds of the normal structure in inactive atmosphere are shown in Table-5. The results indicate that the thermal stability of PVC normal structure is extremely superior to that of real PVC, which suggests the possibility of improving PVC thermal stability to a large extent.

TABLE 5. Thermal decomposition temperature of PVC and its normal structure model compounds

Compounds	Decomposition temperature** (° C)	Phase	Remark
$CH_3\underset{Cl}{CH}CH_2\underset{Cl}{CH}CH_2\underset{Cl}{CH}CH_3$	257	liquid	80, 81 82)
$CH_3\underset{Cl}{CH}CH_2\underset{Cl}{CH}CH_3$	270	liquid	83
	360	gas	83, 84)
PVC*	~120	solid	***

* Comercial straight PVC by suspension polymerization.

** Under nitrogen flow or vacuum.

*** Indicate the temperature at which dehydrochlorination can be determined.

The normal structure of PVC, however, is not always stable against the oxidation degradation. The experimental results of decomposing 2,4, 6-trichloroheptane (P_3) under oxygen and nitrogen are shown in Table 6 (85).

TABLE 6 Thermal decomposition of 2, 4, 6-trichloroheptane (P_3) and PVC.

No.	Sample	Atmosphere	Decomposition temp. (° C)	Additive	Amount of Evolved HCl (mg/g-P_3 or PVC)	Color
1	P_3	N_2	200	-	~0	Colorless
2	P_3	O_2	200	-	0.9	yellow brown
3	P_3	O_2	200	TBMP*	0.2	yellow
4	P_3	O_2	200	DBTL**	0.1>	colorless
5	PVC	air	180	-	3.2	yellow brown
6	PVC	N_2	180	-	1.2	Dark red

1) No. 1 ~ 4 are degraded by blowing nitrogen or oxygen of 10cc/min. g-P_3.
2) No. 5, 6 is measured by Saeki's method (86, 87). Blowing rate of carrier gas is 100 ml/min g-PVC. *4, 4'-Thio-bis-(6-tert-butyl-3-methyl phenol): 0.1% **Di butyltin dilaurate: 0.1%.

Fortunately, the oxidative degradation rates of P_3 is considerably smaller than theat of real PVC and adding a small amount of anti-oxidant or thermal stabilizer can prevent such oxidative degradation.

Furthermore, P_3 is chemically inactive to thermal stabilizers in inactive atmosphere.

It is obvious from these results that PVC thermal degradation is hardly initiated from the normal structure during processing, if the oxidative degradation can be prevented by employing any suilable methods. Thus, it can be concluded that the thermal degradation of PVC during processing starts from the structures other than the normal structure, that is, the unstable abnormal structures.

Next, the results of PVC degradation with the thermal stabilizers are described below. Saeki et al. studied the degradation of PVC with cadmium stearate (Cd-St) stabilizer. The results are shown in Fig. 8 and 9. Cd-St apparently prevents the evolution of hydrogenchloride and the discoloration of PVC (86 ~ 88).

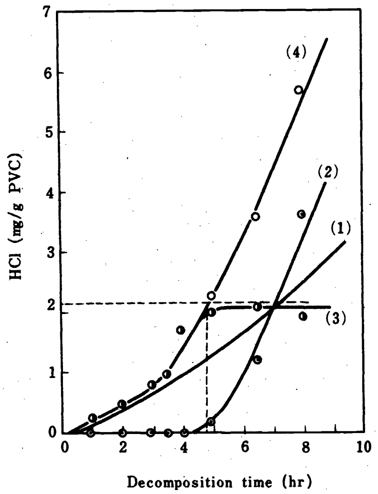


Fig. 8 The influence of Cd-st to dehydrochlorination of PVC.
(PVC: 5g + Cd-St: 0.1g, 150° C, under nitrogen)
(1) PVC only.
(2) Apparent dehydrochlorination amount.
(3) The amount of hydrogenchloride reacting with Cd-St.
(4) The real amount of dehydrogenchloride.
(   ): The theoretical amount of hydrogenchloride to react with the added Cd-St.

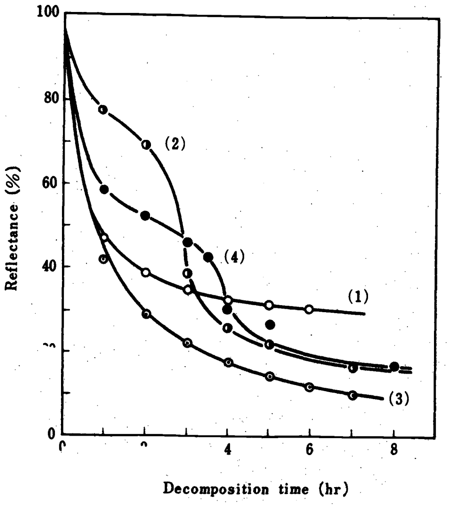


Fig. 9 The influence of Cd-St to discoloration of PVC (PVC : 5g + Cd-St: 0.1g, 150° C)
(1) PVC only (under air)
(2) PVC + Cd-St (under air)
(3) PVC only (under nitrogen)
(4) PVC + Cd-St (under nitrogen)

However, it is clear by measuring cadmiumchloride and hydrogenchloride that the evolution amount of hydrogenchloride in the case of degradation with stabilizer is equal to that of degradation without stabilizer. It is important that inhibiting the dehydrochlorination is not necessarily required to prevent the PVC discoloration.

Furthermore, thermal stabilizers can decrease the discoloration caused by previous degradation of PVC itself. The experimental results are shown in Fig. 10. (89). These results indicate certain chemical interaction between thermal stabilizer and the conjugated polyene in the degrated PVC.

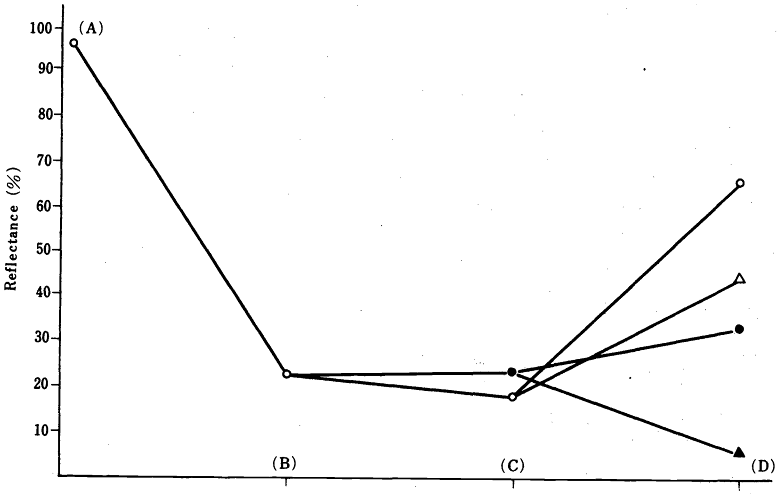


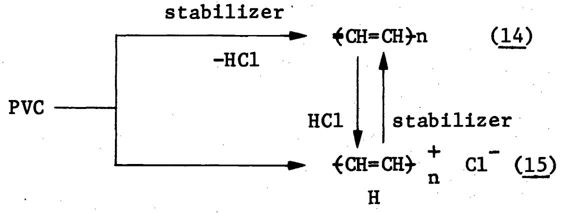
Fig. 10 The influence of thermal stabilizers to discolored PVC.
(A) Original PVC.
(B) PVC degraded at 170° C for 1.5 hrs under vacuum.
(C) ● : B polymer, ○ : Blend of dibutyltinditaurate 18 mg/PVC 1g
(d) △ ,▲: Redegrade at 170° C in N_2 for 1hr., ○ ● : Redegrade at 170° C in air for 1hr.

It should be concluded that thermal stabilizers can cause PVC degradation without discoloration and decreasing the discoloration, though the reaction mechanisms have been fully clarified.

Onozuka et al. found the reversible reaction of 2, 4-hexadiene with hydrogenchloride as described below (83):

$$\underset{\substack{\underline{(12)}\\ \text{Colorless}}}{CH_3-CH=CH-CH=CH-CH_3} + HCl \xrightarrow[\text{in } N_2]{175^\circ \text{ c/5min}} \underset{\underline{(13)}}{(CH_3-CH=CH-CH=CH-CH_3)^{+}_{H}} Cl^{-}$$

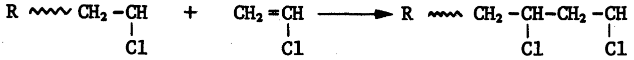
When the colored charge transfer complex (13) loses hydrogenchloride, colorless 2, 4-hexadiene occurs (12). This reaction suggests the following reactions between PVC and the thermal stabilizers:



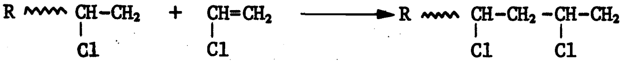
No discoloration of PVC occurs while n of (14) is comparatively small, though (15) with the same value of n may cause its discoloration. The thermal stability of PVC itself does not seen to be improved by this mechanism. The improvement of PVC thermal stability means to stabilize PVC itself structurally.
Therefore, the above mechanism cannot be used directly for improving the thermal stability of PVC itself. However, if the above reaction mechanism is used for the polymer reaction of PVC, the range of applicable reactions for PVC can be widened due to preventing its discoloration. Utilizing the mechanisms of thermal stabilizer to improve the thermal stability of PVC will be described later.

The initiation structures of PVC thermal degradation

The thermal degradation during PVC processing mostly begins from the unstable abnormal structure, except for the oxidative thermal degradation of its normal structures. Those structures can be predicted from the unit reaction of radical polymerization. Hayashi et al. pointed out that the propagation reaction occurs not by (17) but by (16) (90).

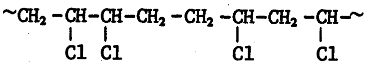


$$\mathrm{R}\sim\sim\mathrm{CH_2-\underset{Cl}{CH}} + \mathrm{CH_2=\underset{Cl}{CH}} \longrightarrow \mathrm{R}\sim\sim\mathrm{CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}} \quad (16)$$



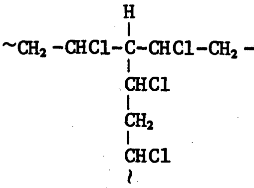
$$\mathrm{R}\sim\sim\mathrm{\underset{Cl}{CH}-CH_2} + \mathrm{\underset{Cl}{CH}=CH_2} \longrightarrow \mathrm{R}\sim\sim\mathrm{\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2} \quad (17)$$

The following abnormal structures of PVC can be assumed by combining the conclusion of Hayashi and other unit polymerization reactions. The head-to-head structure:

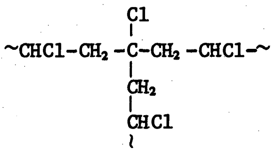


$$\sim\mathrm{CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}}-\sim \quad (18)$$

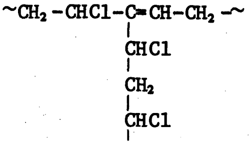
The branching structures:



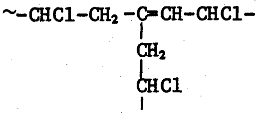
(19)



(20)

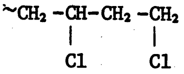


(21)



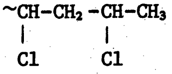
(22)

The saturated chain end structures:



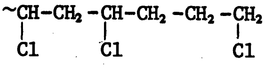
$$\sim\mathrm{CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH_2}}$$

(23)



$$\sim\mathrm{\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_3}$$

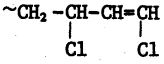
(24)



$$\sim\mathrm{\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-CH_2-\underset{Cl}{CH_2}}$$

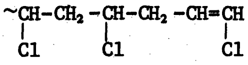
(25)

The unsaturated structures:



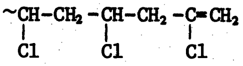
$$\sim\mathrm{CH_2-\underset{Cl}{CH}-CH=\underset{Cl}{CH}}$$

(26)



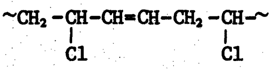
$$\sim\mathrm{\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-CH=\underset{Cl}{CH}}$$

(27)



$$\sim\mathrm{\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{C}=CH_2}$$

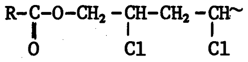
(28)



$$\sim\mathrm{CH_2-\underset{Cl}{CH}-CH=CH-CH_2-\underset{Cl}{CH}}-\sim$$

(29)

The catalyst fragment structures, fer example:



$R-\underset{O}{C}-O-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}\sim$

(30)

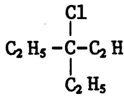
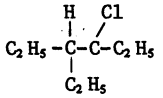
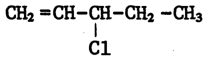
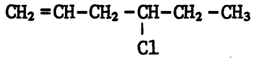
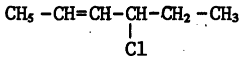
The thermal degradation during PVC processing certainly originates from some of the above structures.

The head-to-head structures can be excluded from the group of such unstable abnormal structures because chlorinated cis-polybutabiene is thermally more stable than PVC (91 92). The saturated chain end group can also be excluded by comparing the bond energy value of such structures with those of the normal structure.

The catalyst fragment structures can also be excluded based on the thermal stability of 2-chloropropyl acetate (94) and the industrial fact that the various radical catalyst do not give PVC having considerably different its thermal stability (93).

Furthermore, the existence of (22) itself can be denied, because the thermal treatment of 3-chloro-3-ethylpentane in vinylchloride does not cause its dehydrochlorination. Thus, the unstable abnormal structures in PVC can be limited to (19), (20), (26), (27), (28) and (29). The thermal stabilities have been tested using the low molecular model compounds. The experimental results are shown in Table 7.

TABLE 7 Decomposition temperature of model compounds of PVC unstable abnormal structures.

No.	Structure	Decomposition temperature (° C)	Phase	Remark
(1)	 $C_2H_5-\overset{Cl}{\underset{C_2H_5}{C}}-C_2H_5$	130	liquid	82)
		180	"	83)
		180	gas	84)
(2)	 $C_2H_5-\overset{H}{\underset{C_2H_5}{C}}-\overset{Cl}{C}-C_2H_5$	180	liquid	80, 82)
(3)	 $CH_2=CH-\underset{Cl}{CH}-CH_2-CH_3$	130 (9)	liquid	82)
		280	gas	84)
(4)	 $CH_2=CH-CH_2-\underset{Cl}{CH}-CH_2-CH_3$	200	liquid	82)
		325	gas	84)
(5)	 $CH_5-CH=CH-\underset{Cl}{CH}-CH_2-CH_3$	100>	liquid	82)
		140	"	83)
		160	gas	84)

Decomposition condition: under nitrogen or vacuum.

It should not always be considered that the thermal stability of the model compound is completely equal to that of PVC, because of their simplified structures.

However, all the model compounds of (1) ~ (5) in Table 7 are inferior to the normal structure in thermal stability, and especially, the thermal stabilities of tertiary chloride and allylic chloride structures are extremely poor.

Therefore, the tertiary and allylic chlorines should especially play an important role in PVC degradation, though the thermal degradation might be initiated from some or all of these unstable abnormal structures. Accordingly, confirming the presence and amounts of these chlorines and searching for the method of their thermal stabilization are significant problems to improve thermal stability of PVC.

The thermal stability and the unstable structure fo PVC.

The existence of carbon-carbon double bonds in PVC has been clarified by Baum et al. (94), Morikawa et al. (95), Suzuki et al. (82) and Michel et al. (96). The content of carbon-carbon double bonds is 0.02-2/1,000 monomeric units in PVC which is normally polymerized. These value do not seem to mean the amount of allylic chloride structures alone but mean the total amount of (26), (27), (28), (29) and others.

On the other hand, Cotman et al. confirmed the presence of branching structures in PVC. Since then, many studies have clarified that the number of branching is about 20/1,000 monomeric units in PVC which is normally polymerized (98 ~ 100).

Calaculacu et al. (101, 102) and Suzuki et al. (80) pointed out that the branching structures do not seem to have tertiary chlorine atoms but have tertiary hydrogen atoms. However, not all branching structures seem to have tertiary hydrogen atoms. Consequently, it should be considered that a small part of the branching has tertiary chloride structures, from which the thermal degradation of PVC starts as in the case of the allylic chloride structures. The branching and the unsaturation degree of PVC polymerized under various conditions are shown in Table 8 (80, 82). It can be said from these results that any PVC radically polymerized at more than 30° C has nearly the same branching number but has considerably different unsaturattion degrees, and that the ionically polymerized PVC has the branching degree of about zero.

TABLE 8 The branching number and unsaturation degree of PVC.

No	React temp (° C)	React time (hr)	Initiator amount (wt %)	Branching 1) number (mol/1,000	Unsatraction 2) degree monemeri units)
1	70	2.0	8	24	7.2
2	50	4.5	8	22	1.7
3	30	17.0	8	20	1.4
4	70	15.0	0.05	24	3.5
5	50	20.0	0.05	24	-
6	50	3.0	0.05	10	-
7 3)	25	20	3	0	1.2

1) Determined by Cotman's method (97)
2) Determined by Morikawa's method (95)
3) Anionically polymerized by n-butyllithium
4) No. 1 ~ 6 are polymerized by lauroyl peroxide

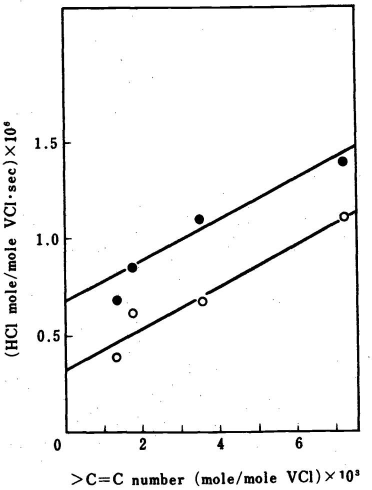


Fig.11 Dehydrochlorination characteristics and the unsaturation degree of PVC. (in nitrogen, 180° C, ○ : at 10 min., ● : at 90 min. after begining heating PVC, PVC radically polymerized)

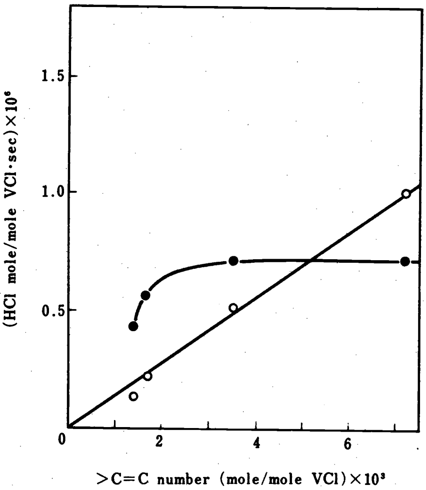


Fig. 12 Dehydrochlorination characteristics and the unsaturation degree of PVC. (in oxigen: 100 ml/min. g-PVC, 160° C, ○ : at 10 min., ○ : at 90 min. after begining heating PVC)

The relationship between the unsaturation degree and the thermal stability is shown in Fig. 11 and 12. The thermal stability of PVC is evidently dependent on its unsaturation degree. Especially, the rates of the oxidative thermal degradation at the early stage is closely related to the unsaturation degree.

The unsaturation degree means the total of the number of carbon-carbon double bonds in the polyene structure which should also exist in PVC plus the number of the isolated double bonds. The number of the carbon-carbon double bonds connected with only allylic chloride structures in the total structures have not yet been ascertained.

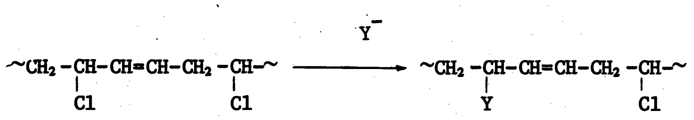
On the other hand, if all the branchings have the tertiary hydrogen structures, they would not play the so important role in the initiation reaction of the thermal decomposition during the PVC processing. However, it is undeniable that a small part of the branching structures has the tertiary chloride structure, though most of them would have the tertiary hydrogen structure. Even if a few parcent of the total branching number were caused by the tertiary chloride structure in radically polymerized PVC under usual conditions, number of branchings should be nearly equal to that of the allylic chloride structures. Actually, the ionically polymerized PVC without any branching is far more thermally stable than the radically polymerized PVC (80).

Anyway, though the branching and allylic chloride structures in PVC should be considered to play an important role in the initiation reaction of the thermal degradation during the PVC processing, the details of the role have not yet been clarified quantitatively.

The stabilization of the thermally unstable abnormal structures.

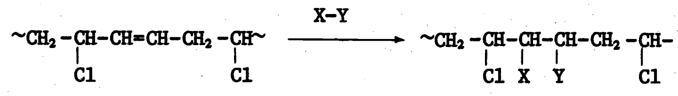
The thermal degradation of PVC during processing should be avoidable, if the unstable abnormal structures could be stabilized by certain methods. The allylic and tertiary chloride structure can be considered as the most important unstable abnormal structures, even though the several problems on such structures have been remaining unsolved. To stabilize these unstable structures by comparatively simple reactions, the following three ways are conceivable.

Firstly, the stabilization can be attained by certain displacement reactions of the labile chlorine atoms as described below:



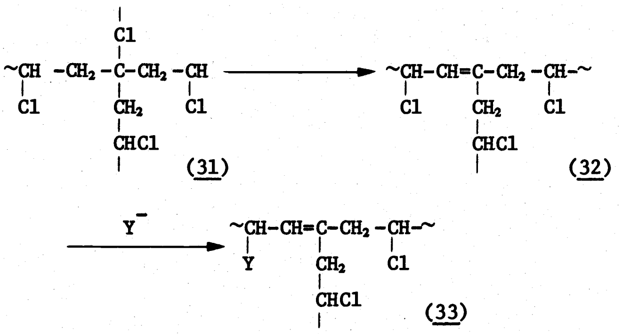
$$\sim CH_2-\underset{Cl}{CH}-CH{=}CH-CH_2-\underset{Cl}{CH}-\sim \xrightarrow{Y^-} \sim CH_2-\underset{Y}{CH}-CH{=}CH-CH_2-\underset{Cl}{CH}-\sim$$

Secondly, the stabilization can be attained by certain addition reactions of the carbon-carbon double bonds as described below:



$$\sim CH_2-\underset{Cl}{CH}-CH{=}CH-CH_2-\underset{Cl}{CH}\sim \xrightarrow{X-Y} \sim CH_2-\underset{Cl}{CH}-\underset{X}{CH}-\underset{Y}{CH}-CH_2-\underset{Cl}{CH}-$$

Thirdly, the stabilization can be attained by the displacement or addition reactions after changing the unstable structures into other structures which can be stabilized more easily than unchanged structures. For example, if a hydrogenchloride were eliminated from the branching (31), the structure with the allylic chlorine atom (32), which can be stabilized by the same reaction as the other allylic chloride structures, could arise.


(31) (32) (33)

These stabilization reaction should have high reaction selectivity only to the unstable abnormal structure in PVC. Fortunately, the allylic chlorine atoms, the tertiary chlorine atoms and the carbon-carbon double bonds should be far more chemically reactive than the normal chlorine atoms in PVC. The difficulties in stabilizing the unstable structures may be overcome by utilizing the chemical reactivities of the unstable structures, though their number in PVC is extremely small.

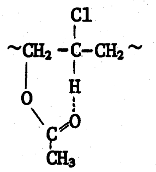
The decomposition temperature of the substituted derivatives of the tertiary chloride and allylic chloride model compounds are shown in Table 9. The decomposition temperature of all the derivatives are considerably higher than those of the original chloride compounds except the tertiary acetoxy derivative. Furthermore, the chlorohydroxy derivative, 3-hydroxy-5-chloro-n-heptene-1 gives almost the same thermal stability as the mere hydroxy derivative, though the neighboring group effects depending on the kinds of the introduced groups may be considered.

TABLE 9 Decomposition temperature of substituted derivatives of PVC unstable abnormal structures (°C).

X	$C_2H_5-C(X)(C_2H_5)-C_2H_5$	$CH_2=CH-CH(X)-C_2H_5$	$CH_3-CH=CH-CH(X)-C_2H_5$
-Cl	180[83)]	130[81)]	140[83)]
-OH	-	230	-
$-OCOCH_3$	170[83)]	180	230[83)]
$-SC_6H_5$	-	230	-
$-SC_2H_4COOC_2H_5$	220[83)]	-	215[83)]
$-OC_2H_5$	-	220	-

1) $CH_2=CH-CH(OH)-CH_2-CH(Cl)-CH_2-CH_3$: 220° C

Actually, Malhotra et al. pointed out that there is a neighboring group effect in the thermal degradation of vinylchloride-vinylacetate copolymer as follows (103):



Therefore, the displacement reaction applied for stabilizing PVC should be carefully selected, and at least the acyloxy groups seem unsuitable as the stabilization substituents, though they are widely used as thermal stabilizers. The actual examples of PVC stabilization by several chemical treatments are shown below.

Stabilization of PVC

Addition reaction. The unstable structures connected to the carbon-carbon double bonds can be stabilized by the suilable addition reactions.

Baum et al. (94) found that the slight chlorination of PVC in the dark results in improving its thermal stability by saturating the double bonds. The dehydrochlorination characteristics are shown in Fig. 13. This old methods for improving the thermal stability of PVC should be restudied, because the degree of its improvement is almost equal to that of the new methods described later.

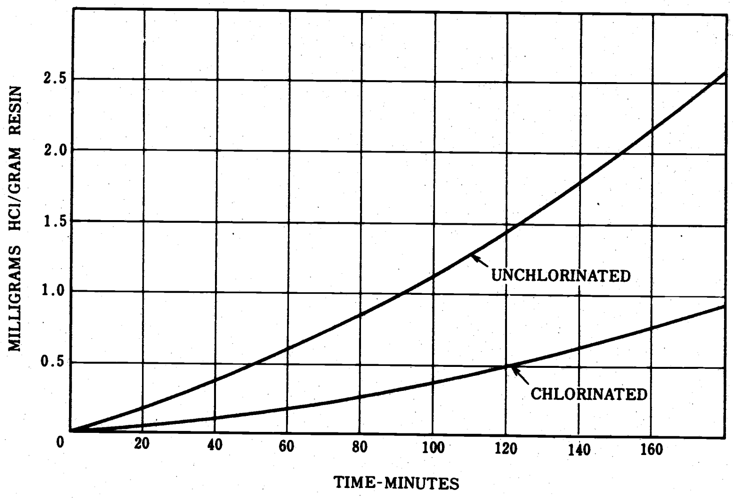
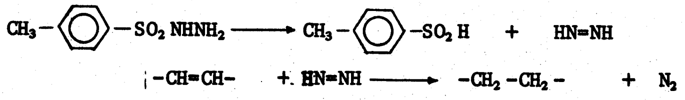


Fig. 13 Effect of chlorination on HCl loss at 150° C.

Okawara et al. showed that the reaction of PVC with diimide helps improve its thermal stability by saturating its double bonds (104). Namely, p-toluenesulfonylhydrazine (PSH) gives diimide through its gradual decomposition at 130-150° C as described below. Diimide can additionally react with carbon-carbon double bonds easily.



PVC also can react with PSH in dimethylformamide. The experiment results are shown in Fig. 14. PVC discolored by prior thermal degradation is decolorized and stabilized by being heated with diimide at 100° C for 4hrs. The thermal stability of PVC decolorized with diimide is superior to that of the original PVC.

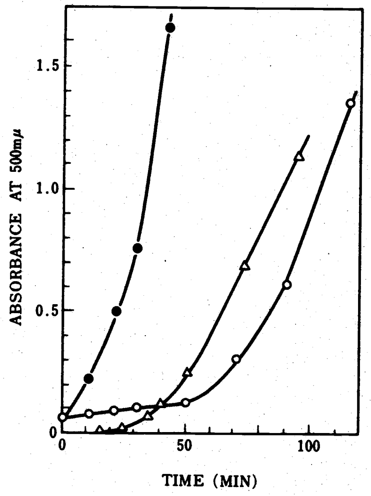


Fig. 14 Rediscoloration of decolorized PVC in DMF at 130° C; 0.30g. of PVC, 15 ml. of DMF: (O) decolorized PVC with diimide; (O) decolorized PVC with oxygen; ( ) original PVC.

The practical thermal stabilities of PVC by the addition reaction should be studied hereafter.

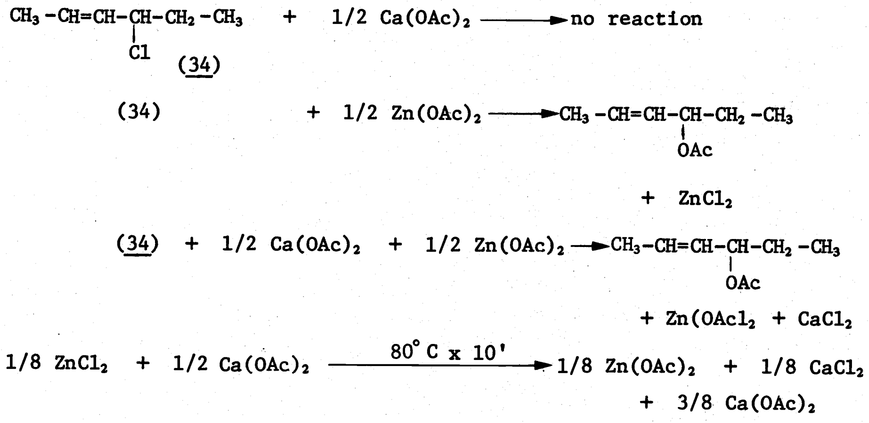
Stabilization by thermal stabilizers. The mechanisms of thermal stabilizers for PVC have not yet been fully elucidated. There should be some stabilizing mechanisms, wherein thermal stabilizers prevent PVC descoloration without hindering its dehydrochlorination during its processing, as described before. In these mechanisms PVC itself does not seem to be structurally thermally stabilized. On the other hand, it has been found that thermal stabilizers can react with certain unstable structures of PVC, besides the above stabilizatation mechanism. One of such selective reactions is the displacement reaction of the labile chlorine atoms in PVC with thermal stabilizers.

In this section, several studies are introduced regarding the stabilization of PVC through the displacement reactions of its labile chlorine atoms with thermal stabilizers.

Frye et al. found that the reactions of PVC with the thermal stabilizers result in introducing carboxylate groups into PVC, and suggested that these reactions should be connected with the stabilization mechanisms (105, 106).

Since then, it has been clarified that the stabilization mechanisms include the displacement reactions of the labile chlorine atoms with thermal stabilizers.

Onozuka et al. showed that the model compounds of PVC allylic chloride structures, 4-chlorolrexene-2 (34), react with calcium acetate ($Ca(OAc)_2$) and zinc acetate ($Zn(OAcl_2)$), which are the model compounds of metal soap thermal stabilizer causing an acetoxy derivative as described below (107):



$$CH_3-CH{=}CH-\underset{\displaystyle Cl}{CH}-CH_2-CH_3 \;\underset{(34)}{}\; + \; 1/2\ Ca(OAc)_2 \longrightarrow \text{no reaction}$$

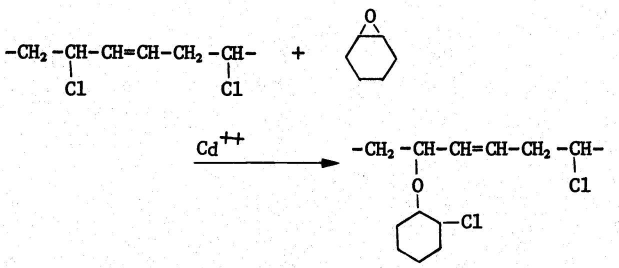
$$(34) \; + \; 1/2\ Zn(OAc)_2 \longrightarrow CH_3-CH{=}CH-\underset{\displaystyle OAc}{CH}-CH_2-CH_3 \; + \; ZnCl_2$$

$$(34) \; + \; 1/2\ Ca(OAc)_2 \; + \; 1/2\ Zn(OAc)_2 \longrightarrow CH_3-CH{=}CH-\underset{\displaystyle OAc}{CH}-CH_2-CH_3 \; + \; Zn(OAcl_2 \; + \; CaCl_2$$

$$1/8\ ZnCl_2 \; + \; 1/2\ Ca(OAc)_2 \xrightarrow{80^\circ C \times 10'} 1/8\ Zn(OAc)_2 \; + \; 1/8\ CaCl_2 \; + \; 3/8\ Ca(OAc)_2$$

Namely, it is not $Ca(OAc)_2$ but $Zn(OAc)_2$ that reacts with (34) causing an acetoxy derivative quantitatively. Furthermore, the reaction of (34) with the mixture of $Ca(OAc)_2$ and $Zn(OAc)_2$ gives the same product preventing the formation of zinc chloride, which remarkably accelerates the PVC thermal degradation. Zinc chloride, which is generated during the displacement reaction, reacts with $Ca(OAc)_2$ and changes into $Zn(OAc)_2$ again. Such metal soaps are chemically inactive to the ordinary secondary chloride compounds. These reactions should be an important part of the synergystic effect of Ca-Zn thermal stabilizer.

Anderson et al. clarified that the reaction of PVC with epoxide compounds such as cyclohexene oxide in conjunction with metal soaps causes the displacement reaction of the labile chlorine atoms (109) as described below:



Suzuki et al. showed that the reaction of 3-chloro-n-pentene-1 with dibutyltin dilaurate quantitatively gives the acyloxy derivatives, though this thermal stabilizer is chemically inactive to ordinary secondary chloride structures (110). Minagawa et al. indicated that such displacement reaction of the labile chlorine atoms with metal soaps can be adjusted by using certain chelating compounds (108). According to the above experimental results, thermal stabilizers should structurally stabilize PVC itself through the displacement reaction of its labile chlorine atoms. Though the substitution of the labile chlorine atoms by acetoxy groups does not necessarily result in remarkably improving the PVC thermal stability, the use of the other substitution reactions like the abovementioned mechanisms should be studied hereafter.

Stabilization by solvolytic displacement reactions. Besides utilizing the mechanisms of thermal stabilizers as described above using conventional displacement reactions should be considered to improve the PVC thermal stability. In this case, it is essential that the reaction selectivities should be highest possible without accompanying the side elimination reaction of dehydrochlorination. The solvolytic displacement reaction, which is a typical S_{N-1} reaction, should satisfy such requirements. S_{N-1} reaction is generally described in the following two step reactions.

$$RX \rightleftharpoons R^+ + X^- \qquad (1) \quad \text{(slow)}$$

$$R^+ + Y^- \longrightarrow R\text{-}Y \qquad (2) \quad \text{(fast)}$$

The rate of the reaction (1), which is the rate determining step, depends on the polar effect of the R-X bond and the ionizing effect of the used solvents. The polar effect of the R-X bonds varies with the kinds and structures of R and X. The solvolytic displacement reaction rate ratios of several organic halides are shown in Table 10 (111). It is obvious that the allylic and tertiary chloride structures corresponding to the PVC unstable structures are far more reactive than the secondary chloride structures corresponding to the PVC normal structure.

TABLE 10 The relative reaction rate of organic halides at solvolytic displacement reactions.

Compounds	Relative rate		
	C_2H_5OH (44.6° C)	50% C_2H_5OH (44.6° C)	HCOOH (100° C)
$CH_2=CHCH_2Cl$	1.00	1.00	1.00
$CH_2=C(CH_3)CH_2Cl$	1.26	1.53	0.47
$CH_3CH=CHCH_2Cl$	16	91	2069
$CH_2=CHCHClCH_3$	3.3	81	2940
$(CH_3)_2C=CHCH_2Cl$	1030	130000	-
$CH_2=CHC(CH_3)_2Cl$	2950	550000	-
$CH_3CH=CHCHClCH$	6600	-	-
$C_6H_5CH=CHCH_2Cl$	139	7700	-
$CH\equiv CCH_2Cl$	-	0.049	-
$CH_3CH_2CH_2Cl$	-	0.07	0.038
$(CH_3)_2CHCl$	-	0.12	~0.1
$(CH_3)_3CCl$	24	2100	-

On the other hand, the ionizing effects of the solvent depend on the conizing power (Y) theory of Grunwald-Ingold.

$$Y=\log (k_a/k_o)_{t\text{-}BuCl}$$

$$\log (k_a/k_o)_{RX} = mY$$

Wherein, $(k_a/k_o)_{t\text{-}BuCl}$ is the ratio of the rate constant (ka) in the used solvent to that (ko) in 80% aqueous ethanol in the solvolytic displacement reactions of tertiarybutylchloride at 25° C. $(ka/ko)_{R\text{-}X}$ is the ratio of the rate constant of R-X, to which the displacement reactions are applied. m Is the peculiar constant number determined by R-X.
Y value of several solvent systems are shown in Table 11 (111). Theoretically, water seems most suitable for such displacement reactions due to its largest Y value. But the solvent to be used should also be selected from the viewpoint of its affinity to PVC besides Y values. The solvolytic displacement reactions have been made upon PVC model compounds, which are isopropylchloride, 3-chloro-pentene-1 and 3-chloro-3-ethyl-pentance corresponding to the PVC normal, tertiary chloride and allylic chloride structures, respectively, based on the above ideas. The experimental results are shown Fig. 15.

TABLE 11 Y values of solvent systems

Volume % A	A Ethanol B Water	Methanol Water	Dioxane Water	Acetone Water	Acetic acid Water
100	-2.033	-1.090	-	-	-1.639
80	0.000	0.381	-0.833	-0.673	-
50	1.655	1.972	1.361	1.398	1.938
25	2.908	-	-	2.689	2.843
20	3.051	3.025	2.877	2.913	-
0	3.493	3.493	3.493	3.493	3.493

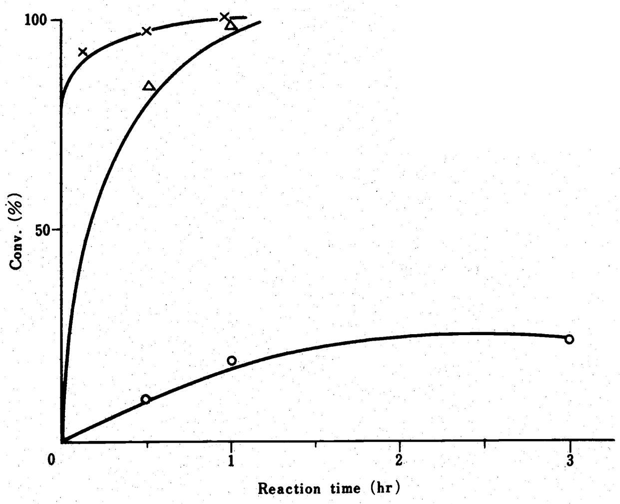
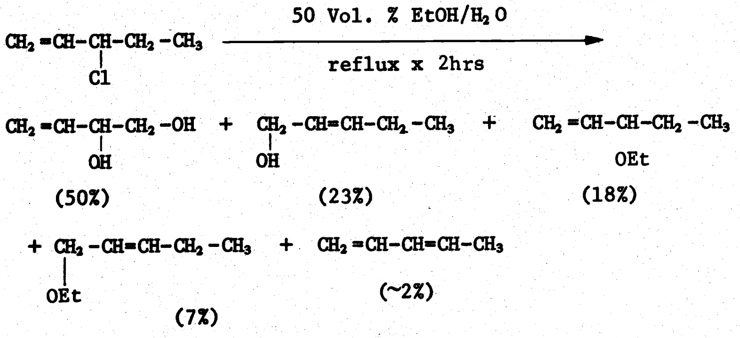


Fig. 15 The solvolytic displacement reactions of PVC model compounds by 50 vol. % aq. ethanol.
(○ : isopropyl chloride, △ : 3-chloropentene-1, X : 3-chloro-3-ethylpentane, at reflux temperature)

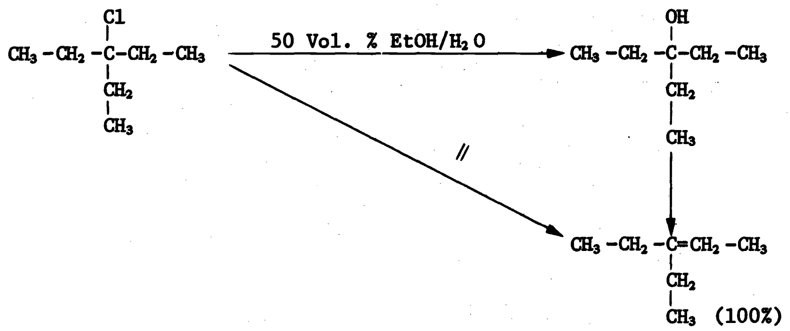
These results suggest that ethanolic solvolytic displacement reactions can be applied for the selective reactions of the PVC labile chlorine atoms beause of the considerably different reaction rates between the active chloride compounds and the secondary compounds. The final products and their ratios are described below:



$$CH_2{=}CH{-}\underset{\displaystyle Cl}{CH}{-}CH_2{-}CH_3 \xrightarrow[\text{reflux x 2hrs}]{\text{50 Vol. \% EtOH/H}_2\text{O}}$$

$$\underset{(50\%)}{CH_2{=}CH{-}\underset{\displaystyle OH}{CH}{-}CH_2{-}OH} + \underset{(23\%)}{\underset{\displaystyle OH}{CH_2}{-}CH{=}CH{-}CH_2{-}CH_3} + \underset{(18\%)}{CH_2{=}CH{-}\underset{\displaystyle OEt}{CH}{-}CH_2{-}CH_3}$$

$$+ \underset{(7\%)}{\underset{\displaystyle OEt}{CH_2}{-}CH{=}CH{-}CH_2{-}CH_3} + \underset{(\sim 2\%)}{CH_2{=}CH{-}CH{=}CH{-}CH_3}$$



3-chloropentene-1 gives four substituted derivatives and a small amount of pentadiene. 3-Chloro-3-ethylpentane promptly gives trisubstituted ethylene though a part of it goes through the hydroxy derivatives.

The suitable solvent systems seem to be $C_1 \sim C_3$ alcohol/water, because the use of other protic solvent-water undesirably increase the formation of pentadiene, which is the elimination products of 3-chloropentene-1. The experimental results, which are obtained by applying the above solvolytic displacement reactions on PVC, are shown in Table-12. The introduced amounts of ethoxy groups in PVC are determined by using C^{14} labeled ethanol in the aqueous ethanol. The total amounts of the introduce groups into PVC can be calculated based on the fact that the solvolytic displacement reactions of 3-chloropentene-1 in 50 vol. % gives the ethoxy and hydroxy derivatives at the ratio of 1 : 3. Introducing substituents into PVC and improving the PVC thermal stability cannot be done under the same conditions as those of model compounds. However, the raising the reaction temperature results in introducing the considerable amount of the substituents and improving the PVC thermal stability. Though using amine compounds as the reaction accelerators increases the amounts of the introduced substituents, the PVC thermal stability can not be improved. In these reactions, the substitution reaction should occur at the normal structure of PVC.

TABLE 12. Solvolytic displacement reaction of PVC with 50 vol % $EtOH/H_2O$.

No.	temp. °C	React time (hr)	Introduced amount of -OH & -OEt (mol/1000 monomer)	Additive	De-HCl Rate (mg/g-PVC.hr)
1	-	0	0	-	1.05
2	80	10	0	-	1.05
3	130	10	1.6	-	0.80
4	150	2	1.8	-	0.65
5	150	5	3.2	-	0.50
6	150	10	4.8	-	0.30
7	150	2	120	PDA	10<
8	150	2	5.2	O-AP	10<

1) PVC: 60mg, distilled water : 0.25cc, ethanol mixed by C^{14} label ethanol : 0.25cc.
2) PDA: phenylenediamine (0.1% to PVC), o-AP: o-aminophenol (1% to PVC)

Though PVC obtained under condition of 150° C-5hrs. has fairly good thermal stability, it can not be put to practical use because of the deep yellow discoloration. As described before, certain thermal stabilizers can prevent the PVC discoloration, although the dehydrochlorination of PVC cannot be inhibited during the thermal degradation. The mechanism seems to eliminate the hydrogenchlorides from the colored charge transfer complexes formed between hydrogenchloride and the short polyene structures in PVC.

The idea based on the above mechanism can be applied to prevent the discoloration in the solvolytic displacement reactions of PVC. Namely, the addition of a small amount of metal soap or epoxide compounds, as the hydrogenchloride scavenger, in the initial reaction system is quite useful for preventing the PVC discoloration. The UV and visible spectra of PVC obtained by using such hydrogenchloride scavengers are shown in Fig. 16. The use of such scavengers decreases the strength of the spectra absorption in the visible area.

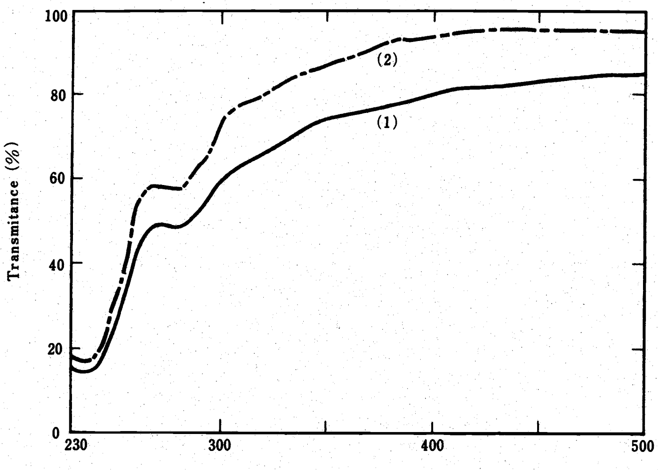


Fig. 16 The effect of the addition of hydrogenchloride scavengers to PVC stabilization reaction system. (1): without the scavengers, (2): with the scavengers.

Though the experiments described above are heterogeneously conducted, using the homogeneous reaction systems should moderate, the reaction conditions to prevent the side reactions of dehydrochlorination. The dynamic thermal stability of PVC obtained by the heterogeneous solvolytic displacement reactions is shown in Fig. 17. A Brabender-plastograph is used for the experiments.

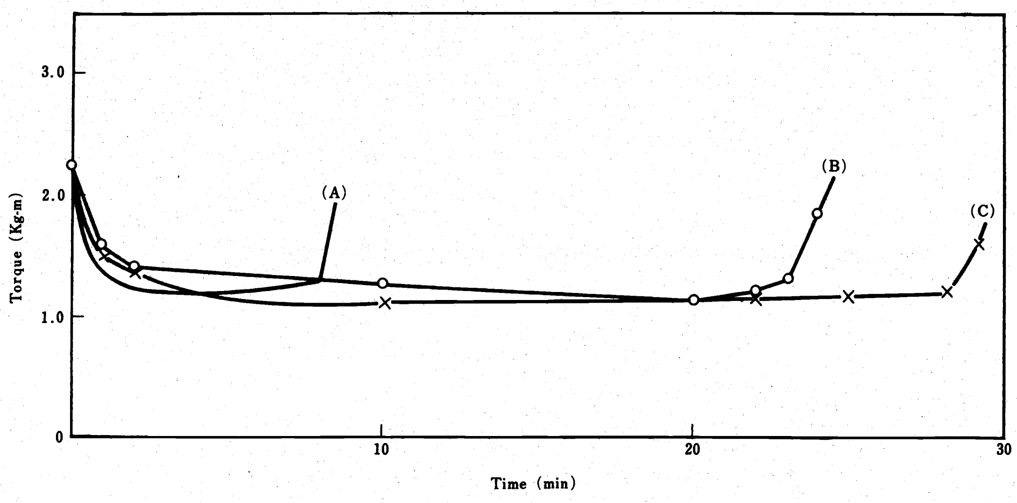


Fig. 17 Dynamic thermal stability of PVC improved by solvolytic displacement reaction.
(A) Conventional PVC under the calcium-zinc formulation.
(B) Conventional PVC under the organotin formulation.
(C) PVC stabilized by displacement reactions under the same formulation as (A).
Conditions of the plastograph: Cell volume (30 ml), specimen (30g) rotor speed (30 rpm), jacket temp. (216° C)

The thermal stability of PVC obtained by this method is about three times higher than that of the original PVC. This improvement method may be modified to prevent the side reactions of the dehydrochlorination almost completely.

Improvement by the substitution reaction with organo-aluminum

Recently, the improvement of the PVC thermal stability has been studied centering on the displacement reaction of the PVC labile chlorine atoms with organo-aluminum chlorides. Diethylaluminum chloride (DEAC) can selectively pull the chloride anion out of the unstable chloride structures in PVC and gives carbonium ion of PVC. Studies on the graft-polymerization starting from such PVC cation have already been reviewed before (66-68). Such a graft polymerization help to improve the PVC thermal stability.

In this section, improving the PVC thermal stability by displacement reactions via the formation of PVC cation with DEAC will be discussed. Gaylard et al. found that the reactions of PVC with DEAC followed by the treatments using the lower alcohols such as methanol, result in improving the PVC thermal stability (112). The hydrochlorination characteristics of PVC thus obtained are shown in Fig. 18. The dehydrochlorination amount of PVC treated DEAC/methanol is considerably smaller than that of the untreated PVC at the later stage of its thermal degradation, though the amount of the treated PVC exceeds that of the untreated PVC in the early stage.

Graft-polymerizing 1.4-cis-polybutadiene in place of the treatment with methanol onto PVC treated by DEAC also results in improving its thermal stability (69). These reaction mechanisms seem to work through the selective reactions of organo-aluminum compounds with the unstable chlorine atoms in PVC similar to the solvolytic displacement reaction as described before.

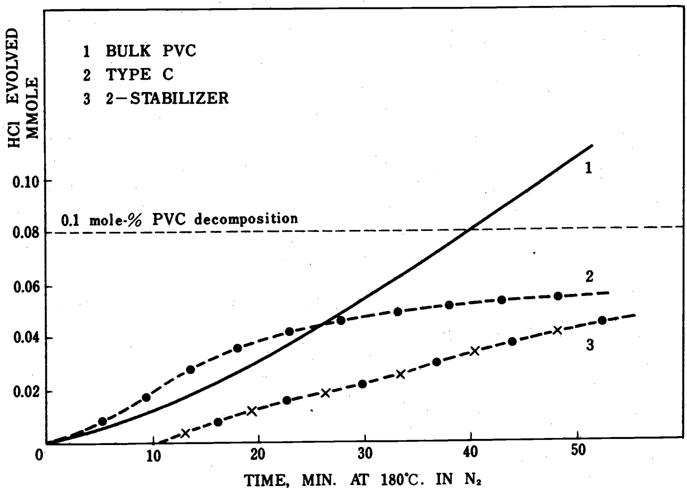
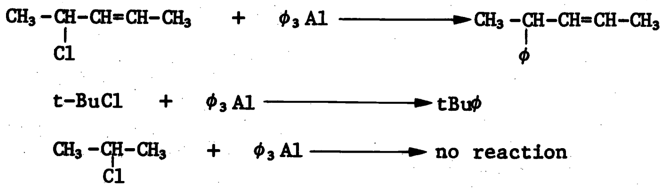


Fig. 18 Evolution of hydrogen chloride at 180° C (nitrogen as carrier gas) from bulk process poly (vinyl chloride) (1), diethylaluminum chloride-methanol treated bulk poly (vinyl chloride) (Type C) (2), and Type C + stabilizer (3).

		As Shown	Normal
Stabilizer, phr:	Ferro 59-V-11 (Ca-Zn)	0.10	2-3
	Ferro 5376 (Organic)	0.15	1-1.5

Kennedy et al. succeeded in improving the PVC thermal stability by the reactions of PVC with triphenyl aluminum in carbon disulfide (73). The reaction mechanisms were simulated by reactions of PVC model compounds as follow:



$$CH_3-\underset{Cl}{CH}-CH=CH-CH_3 + \phi_3Al \longrightarrow CH_3-\underset{\phi}{CH}-CH=CH-CH_3$$

$$t\text{-}BuCl + \phi_3Al \longrightarrow tBu\phi$$

$$CH_3-\underset{Cl}{CH}-CH_3 + \phi_3Al \longrightarrow \text{no reaction}$$

The dehydrochlorination characteristics of PVC obtained by this method are shown in Fig. 19.

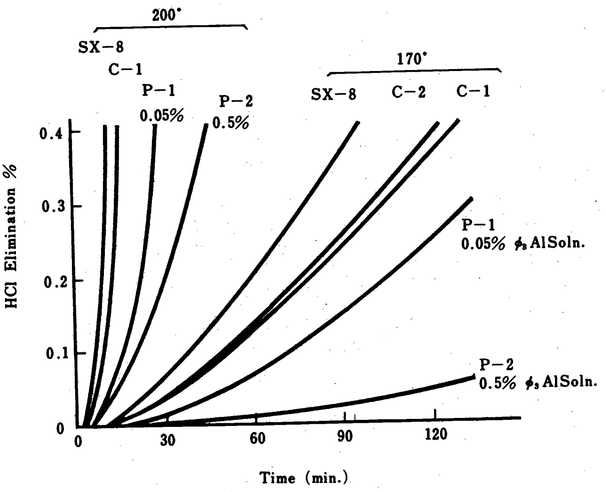


Fig. 19 Dehydrochlorination of ϕ_3 Al-treated PVC at 170° and 200° C in N_2 SX-8="out-of-bottle" resin; C-1=SX-8 suspended in CS_2 for 1 hr., filtered, resuspended in MeOH, stirred for 30 min, and dried; C-2=SX-8 suspended in CS_2 for 1 hr and dried. P-1=SX-8; 1.0g; ϕ_3 Al: 25 mg: CS_2: 50 ml. P-2= SX-8: 1.0g; ϕ_3 Al: 250 mg; CS_2: 50 ml. Treatment with ϕ_3 Al at 25° C for 1 hr. (Products were filtered, washed with CS_2, resuspended in MeOH and stirred for 30 min, filtered and dried at 50° C in vacuo for 15 hrs.)

PVC treated with a triphenyl aluminum solution of carbon disulfide is much more thermally stable than PVC treated with carbon disulfide free from triphenyl aluminum. However, the use of triisobutyl aluminum, triethyl aluminum or trimethyl aluminum instead of triphenyl aluminum, contrary to expectation, did not result in improving the PVC thermal stability. It seems that dehydrochlorination of PVC rather than alkylation occurred by the reaction of PVC with trialkylaluminum.

At any rate, the use of organo aluminum compounds, especially triphenyl aluminum, has been successful to a considerable extent in improving the thermal stability of PVC. The future application of these methods to the industrial uses is expected.

The remaining problems

The outline of the studies of improving the PVC thermal stability has been reviewed from the viewpoint of the chemical modification. Basically, these studies should be highly evaluated because of the considerable improvement which have been achieved. The method of the solvolytic displacement reactions has already been developed into an industrial technology. However, the improvement degree is till far from the theoretical completion, at which processing of PVC should be done without using any thermal stabilizers.

Therefore, the effect of improvement by several methods should be compared with one another and then the studies on some of these methods should be conducted for their industrial uses. Presently, it is not clear whether any of these methods can results in improving the PVC thermal stability to the theoretical value. Accordingly, the first requirement is that various PVC obtained by these methods would be evaluated for their Practical processing uses. It is after the accomplishment of such evaluation that the future direction of those studies could be determined.

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