Thermal stabilization of poly(vinyl chloride) treated with organoaluminium compounds:
2. Effect of solvents

Katsuo Mitani, Takayuki Ogata, Michio Nakatsukasa and Yukio Mizutani
Research and Development Division, Tokuyama Soda Co. Ltd, Mikage-cho, Tokuyama 745, Japan
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Poly(vinyl chloride) was treated with organoaluminium compounds in various solvents. The strong Lewis acids, alkyl-aluminium chlorides, predominantly cause the decomposition of PVC rather than the alkylation of the polymer regardless of solvents. In non-polar hydrocarbons, the treatment of PVC with trialkylaluminiums leads to increased heat sensitivity. In 1,2-dichloroethane solution and in benzene slurry, the trialkylaluminium-treated PVC exhibits significant improvement in thermal stability over unmodified PVC due to the exchange of the labile chlorines inherent in the polymer for relatively more stable alkyl groups. The apparent activation energy of the reaction of PVC with triethylaluminium in benzene slurry is the same as that in 1,2-dichloroethane solution, but the initial rate of alkylation of the polymer in benzene is about 10 times faster than that of the polymer in 1,2-dichloroethane. The aluminium concentration in the PVC particles is about twice that calculated from the swelling ratio of the PVC particles in benzene, suggesting that triethylaluminium not only penetrates into the swollen particles but is also adsorbed on the surface of the PVC particles to cause the increase in the aluminium concentration around the labile chlorines in the polymer chain. The alkylated PVC, compounded with only small amounts of zinc soap including an epoxidized oil and a chelating compound, shows excellent initial stabilization and long-term stability superior to the starting polymer even when this is compounded with 3 parts organotin stabilizers.

INTRODUCTION

Poly(vinyl chloride) (PVC) is subject to degradation by light and heat. The main manifestations of degradation are evolution of hydrogen chloride, darkening, and deterioration in physical and chemical properties. In commercial practice, such thermal degradation is retarded by the addition of suitable stabilizers. The disadvantages of the stabilizers include their potential toxicity, incompatibility, and extractability. Thus, the synthesis of thermal stable PVC has been the subject of many investigations[1-5].

Gaylord and Takashi[1] have found that treatment of PVC with a dialkylaluminum halide followed by treatment with a lower alkanol yields a polymer with greatly improved thermal stability. Thame and coworkers[2,3] have reported that alkylation of toluene with PVC or grafting of isobutylene and butadiene onto PVC by use of alkylaluminium compounds results in products of improved thermal stability compared to PVC. Kennedy and Ichikawa[4] have indicated that enhanced thermal stability of PVC results by introducing phenyl groups into the polymer chain using triphenylaluminium. Kolinsky *et al.*[5] have discussed the heat stability of PVC prepared with alkyllithium catalyst.

In the first paper of this series[6] we were concerned with the thermal stability of PVC prepared with triethylaluminium–Lewis base–carbon tetrachloride catalyst, suggesting that the labile chlorines in the polymer chain are converted into thermally stable structures on the polymerization process, and in the second paper[7] the mechanism of reaction of PVC with triethylaluminium in 1,2-dichloroethane solution was elucidated.

This paper deals with the effect of solvents on the alkylation of PVC with trialkylaluminium compounds, and the reaction mechanism of triethylaluminium with PVC in benzene slurry is proposed from a quantitative analysis for the rate of dehydrochlorination of the modified PVC decomposed at 180°C. Furthermore, the thermal stability of the modified PVC compounded of calcium soap–zinc soap as a non-toxic stabilizer was investigated.

EXPERIMENTAL

All experiments were carried out with commercial PVC (San Arrow Co. Ltd, Japan, $P_w = 820$), prepared by suspension polymerization. Organoaluminium compounds (Japan Alkylaluminum Co. Ltd) were used without further purification. Organic solvents were dried, distilled by standard methods, and stored under argon atmosphere.

The reaction of PVC with organoaluminium compounds was carried out in a glass flask with stirrer. To a stirred solution or suspension of PVC in organic solvents was added a solution of organoaluminium compounds in benzene solution. After the reaction the product was poured into a large amount of methanol which was slightly acidified with hydrochloric acid. The precipitated po-

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Table 1 Thermal stability of PVC treated with organoaluminium compounds[a]

Sample No.	Organoaluminium component	mmol	HCl[b] x 10^5 (mol/g PVC)
1	$(C_2H_5)_3Al$	0.1	–[c]
2	$(C_2H_5)_3Al$	3.0	2.4
3	$(iso\text{-}C_4H_9)_3Al$	3.0	5.7
4	$(C_2H_5)_2AlCl$	0.5	–
5	$(C_2H_5)_3Al$ $(C_2H_5)_2AlCl$	0.5 0.5	–
6	$C_2H_5AlCl_2$	0.5	–
7	$AlCl_3$	0.5	–
8	$Al(o\text{-}iso\text{-}C_3H_7)_3$	1.0	18.9

[a] A 2.0 g portion of PVC in 20 ml EDC was treated with organoaluminium compounds at 40°C for 1 h

[b] A quantity of hydrogen chloride eliminated from PVC decomposed at 180°C for 150 min. Virgin PVC; 19.5 x 10^5 mol HCl/g PVC

[c] Sample was decomposed during the reaction

lymer was washed several times with methanol, and dried under vacuum at 50°C.

The PVC samples were thermally decomposed at 180°C in a stream of pure nitrogen, 50–60 ml/min. The quantity of hydrogen chloride evolved, which was absorbed in water, was read off on a pH meter.

The double bond of PVC was determined on the basis of the method proposed by Morikawa[8]. PVC was dissolved in 1,2-dichloroethane, and bromine and mercury acetate were added. After the mixture had reacted at 25°C for 20 h in the dark, the reactant was poured into aqueous solution of potassium iodide with stirring, and free iodide was titrated with sodium thiosulphate.

The swelling ratio of PVC was reported as the ratio of the swollen weight to the weight of the initial polymer. After the PVC powder was stirred in benzene or in toluene, the swollen powder was filtered and weighed. The weight of the swollen powder was plotted against time. The time-swelling curves exhibit maxima within 15 min at temperatures above 40°C and level off. The time required to reach the swelling maximum decreases greatly with an increase in temperature.

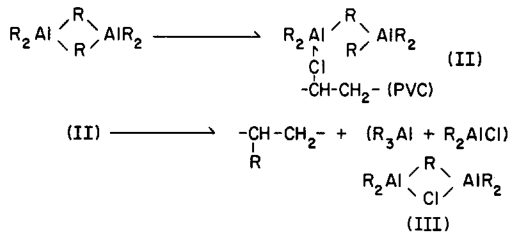
The aluminium concentration in the PVC particles was determined by X-ray fluorescence spectroscopy (Cr target). The calculated aluminium concentration in the PVC particles at each reaction temperature was obtained from the ratio of the quantity of benzene contained within the swollen PVC particles to the quantity of benzene used, which was calculated from the swelling ratio of the polymer in benzene. It was assumed that the aluminium concentration in the swollen PVC particles is the same as that in benzene solution.

Stabilizer, lubricant, with or without dioctyl phthalate (DOP) were mixed with PVC. Compositions were milled for 5 min at 160°C by using a two roll mixing mill to produce 1 mm thick sheets for heat ageing. Pieces of 3 cm × 5 cm size were cut from these sheets and placed on aluminium foils, aged in a 180°C circulating air oven, and samples were removed periodically to record the increasing discolouration of the materials.

RESULTS AND DISCUSSION

Table 1 lists the thermal stability of PVC treated with various organoaluminium compounds in 1,2-dichloroethane (EDC) solution. It shows that trialkylaluminium compounds, in particular triethylaluminium(Et_3Al), gives products of enhanced thermal stability. Molecular weight and the number of double bonds of the Et_3Al-treated PVC was the same as those of the starting polymer, suggesting that crosslinking, degradation, and addition of Et_3Al to the double bonds of PVC has not occurred. Thus, increased heat stability of PVC is attributed to the exchange of the labile chlorines inherent in the polymer for relatively more stable alkyl groups[7]. Alkylaluminium chlorides and aluminium chloride, stronger Lewis acids than trialkylaluminium, function to catalyse the rapid degradation of PVC. On the other hand, the rate of dehydrochlorination of PVC after aluminium isopropoxide treatment is negligibly smaller than that of the virgin polymer.

The enhancement in the heat stability of PVC treated with trialkylaluminium could be explained by the following possible mechanism of the reaction of PVC and trialkylaluminium[4,7]:



(1)

(2)

where R_3Al is trialkylaluminium. Et_3Al is dimeric in the liquid state and in solution, and an exchange reaction of ethyl groups in both bridging and terminal positions occurs at a sufficiently high rate. The final step in the alkylation, that is, the transfer of the ethyl group to the methine carbon in PVC, is assumed to occur through the half-bridged intermediate(II) formed between Et_3Al and the labile chlorines such as allylic chlorines and tertiary chlorines because of the stability of their carbenium ions.

In the presence of excess Et_3Al to the labile chlorines in the starting polymer, Et_2AlCl produced in the reaction of Et_3Al with PVC (equation (2)) is assumed to form complex III which is more stable on PVC than Et_2AlCl dimer under the mild reaction conditions. PVC treated with dilute Et_3Al concentration starts to decompose with the progress of reaction under the deleterious effect of Et_2AlCl when the concentration of Et_2AlCl accumulated is more than that of Et_3Al (sample No. 1 in *Table* 1). Regardless of reaction temperature, addition of Et_3Al at levels below 0.16 mmol to 2 g PVC (32 mmol) induces the decomposition of PVC. Therefore, assuming the formation of complex III between Et_3Al and Et_2AlCl in equation (2), the amount of labile chlorine present in the initial PVC may be estimated to be 0.25%.

Guyot *et al.*[9] have reported that modification of PVC with Et_3Al in carbon tetrachloride or in n-heptane increased the heat sensitivity. On the other hand, Thame and coworkers[2] have found increased stability upon treatment of PVC by n-pentane solution of Et_3Al at −30°C. *Table* 2 shows the effect of solvents in the Et_3Al-treatment on the heat stability of PVC. PVC treated in EDC solution exhibits improved thermal stability over untreated PVC, but in carbon tetrachloride PVC decomposes slowly due to the accumulation of Et_2AlCl gene-

Table 2 Reaction of PVC with Et_3Al in various diluents[a]

Diluent	Et_3Al (mmol)	HCl x 10^5 (mol/g PVC)
1,2-Dichloroethane	3.0	4.3
Carbon tetrachloride	1.0	41.7
Cyclohexane	1.0	67.5
n-Heptane	1.0	61.1
Benzene	1.0	4.2
Toluene	1.0	13.9
Cyclohexanone	2.0	23.7
Methyl ethyl ketone	2.0	25.5
Di-isopropyl ether	2.0	19.0
Tetrahydrofuran	2.0	19.2
Ethyl acetate	2.0	20.4
Triethylamine	1.0	—[b]
Aniline	1.0	—

[a] 2 g of PVC in 20 ml diluent was treated with Et_3Al at 40°C for 1 h
[b] Sample was decomposed during the reaction

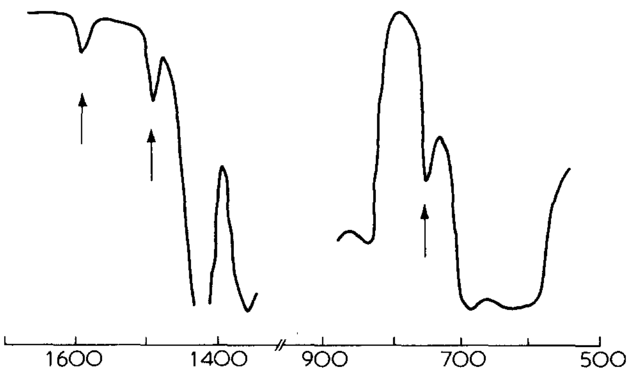


Figure 1 I.r. spectrum of PVC treated with triphenylaluminium in EDC solution

rated in the reaction of Et_3Al with carbon tetrachloride. In non-polar hydrocarbons, PVC starts to discolour gradually with increasing reaction time.

Significant improvement in thermal stability is obtained by treating in benzene slurry, and in toluene slurry the Et_3Al-treatment slightly increases heat stability of PVC. Thame *et al.*[2] have suggested that Friedel–Crafts alkylation in toluene by PVC occurs under the influence of the Lewis acid, Et_3Al, owing to the fact that the modified PVC shows peaks ascribed to the phenyl groups in the i.r. spectra. However, we could not find the characteristic band for the phenyl groups in i.r. on any of the samples which were treated with Et_3Al in toluene in temperatures between 30° and 90°C, when this was followed by pouring into a methanol–hydrogen chloride acid mixture, washing several times with methanol, and drying under vacuum at 50°C.

Figure 1 shows an i.r. spectrum of PVC treated with triphenyl-aluminum in EDC solution. The characteristic bands assigned to the phenyl groups were observed at 750, 1400, and 1600 cm^{-1}, suggesting that phenylation of PVC occurs according to equations (1) and (2).

These data may suggest that treatment of PVC with Et_3Al in benzene slurry leads to increased heat stability owing to the alkylation of the labile chlorines in the polymer with Et_3Al, and is not due to Friedel–Crafts alkylation of benzene. Furthermore, since PVC treated with Et_3Al in benzene exhibits significant improvement in the thermal stability over that in toluene, it seems likely to be attributable to the difference in degree of swelling of the polymer in the two solvents.

More nucleophilic solvents such as ethers, esters, and ketones which form donar–acceptor bonds with Et_3Al invariably appear to retard exchange between alkylaluminiums, and result in negligible alkylation of PVC. Amines among the strongest of Lewis bases not only form a stable complex with Lewis acid, Et_3Al, but also induce the dehydrochlorination of PVC at high temperatures.

Reaction in benzene slurry

Thermogravimetry programmed at a heating rate of 10°C/min in air of PVC samples which were treated with Et_3Al at two different temperatures is illustrated in *Figure* 2. On heating virgin PVC to above 230°C a first-stage weight loss of about 2–3% is observed, and a major loss ensues above 270°C, corresponding to the evolution of hydrogen chloride. On the other hand, dehydrochlorination of the treated PVC proceeds slowly with a rise in temperature; an improvement in thermal stability of 20–30°C for the modified PVC is observed. The kinetics of decomposition at the first stage of weight loss in *Figure* 2 is difficult to determine quantitatively due to uncertainties in locating the base line.

Figure 3 shows the kinetic curve of dehydrochlorination of PVC samples, treated with Et_3Al at 40°C for 1 h in benzene slurry and then decomposed at 180°C in nitrogen, as a function of Et_3Al concentration. Owing to the presence of an induction period the slope of the plots in *Figure* 3 were taken as a measure of thermal stability. This increases with increasing Et_3Al concentration. Evolution of hydrogen chloride from well stabilized PVC is negligible on heating at 180°C for 150 min in nitrogen. If the rate of dehydrochlorination is proportional to the concentration of labile chlorine, the ratio of the stabilized PVC $(PVC)_s$ to the original labile concentration $(PVC)_0$ is expressed as follows[7]:

$$\frac{(\mathrm{PVC})_s}{(\mathrm{PVC})_0}=\frac{K^0_{\mathrm{HCl}}-K_{\mathrm{HCl}}}{K^0_{\mathrm{HCl}}} \qquad (3)$$

Using equation (3), $(K^0_{\mathrm{HCl}}-K_{\mathrm{HCl}})/K^0_{\mathrm{HCl}}$ was plotted against the reaction time as a function of the reaction temperature in *Figure* 4. Thermal stability of PVC treated with Et_3Al in benzene increases significantly with reaction temperature, and levels off at a short reaction time. For example, at a reaction temperature of 85°C, more than

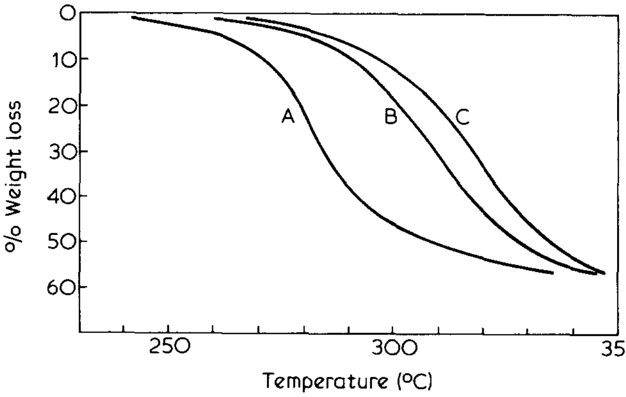


Figure 2 Thermogravimetry of PVC samples treated with Et_3Al in benzene: (A) purified original PVC; (B) 60°C; (C) 80°C

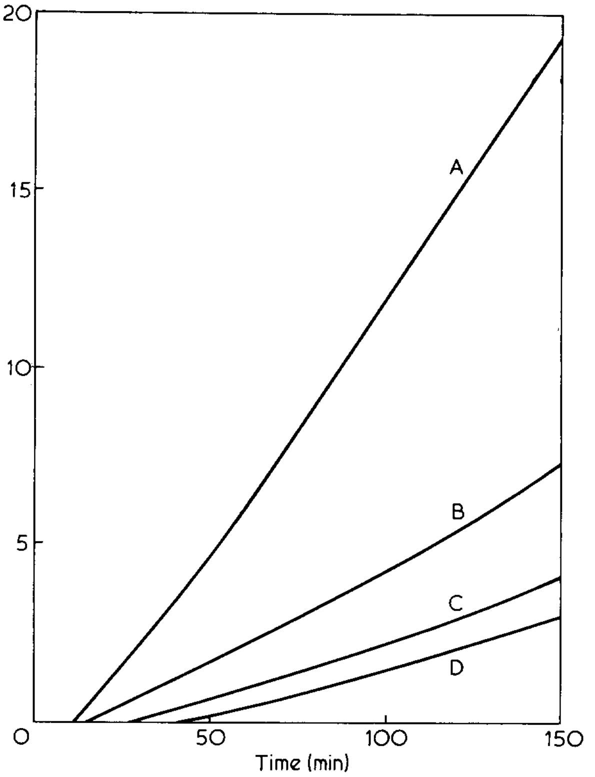


Figure 3 Thermal decomposition at 180°C in nitrogen of PVC samples treated with Et_3Al: (A) purified commercial PVC; (B) Et_3Al = 5 mmol; (C) Et_3Al = 10 mmol; (D) Et_3Al = 20 mmol. A 20 g portion of PVC in 60 ml benzene was treated with Et_3Al at 40°C for 1 h

90% of the labile chlorine in the original PVC is stabilized within 5 min of reaction time; for a sample treated at 85°C for 30 min, very small quantities of hydrogen chloride are evolved at 180°C in a nitrogen atmosphere even after 150 min.

Figure 5 shows the Arrhenius plots of the initial rate of reaction in EDC solution and benzene slurry. The apparent activation energies of the reaction of PVC with Et_3Al in the former and in the latter are 8.3 and 8.5 kcal/mol, respectively. However, the initial rate of alkylation of PVC by slurrying in benzene is more than 10 times faster than that of PVC in EDC solution in spite of the heterogeneous reaction condition.

Table 3 summarizes the aluminium concentration in PVC particles after treatment with Et_3Al in benzene, filtering, washing with benzene, suspending in methanol, stirring for 30 min, and drying under vacuum at 50°C. The aluminium concentration in the PVC particles increases with reaction temperature but levels off within 15 min regardless of reaction temperature. In addition, the observed aluminium concentration is about twice that which was calculated from the quantity of benzene within the swollen PVC particles at each temperature, assuming that the aluminium concentration in the swollen PVC particles is the same as that in benzene solution. This experimental evidence implies that the triethylaluminium not only penetrates into the swollen particles, but is also adsorbed on the surface to cause the increase in aluminium concentration around the labile chlorines in the polymer. Although we couldn't yet present a meaningful explanation for the adsorption of Et_3Al on the surface of the PVC particles, the ^{13}C-n.m.r. spectra of Et_3Al in toluene solution at 80°C reveal that the internal chemical shift between the methyl and methylene carbons of Et_3Al is 8.11 ppm, but in the presence of PVC that of Et_3Al is 6.78 ppm; in the presence of PVC the electronegativity of the aluminium atom of Et_3Al increases and the ionic character of the aluminium–carbon bond decreases. Thus, Et_3Al forms a dimeric complex with Et_3Al and in addition, coordinates to the chlorine atom in the PVC to induce the adsorption of Et_3Al on the surface of the swollen PVC particles.

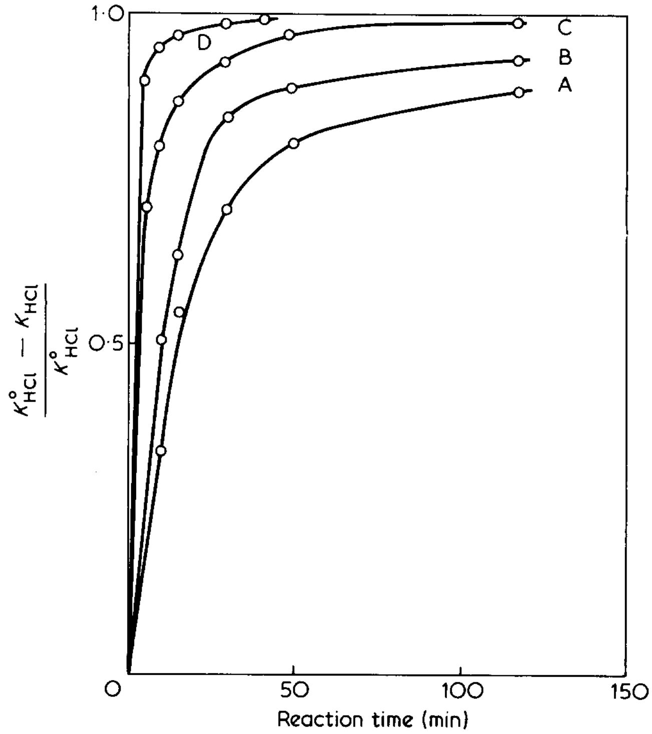


Figure 4 Effect of reaction time of Et_3Al-treatment on thermal stability of PVC at various temperatures: (A) 40°C; (b) 55°C; (C) 70°C; (D) 85°C. PVC concentration, 20 g/40 ml benzene. Et_3Al = 10 mmol

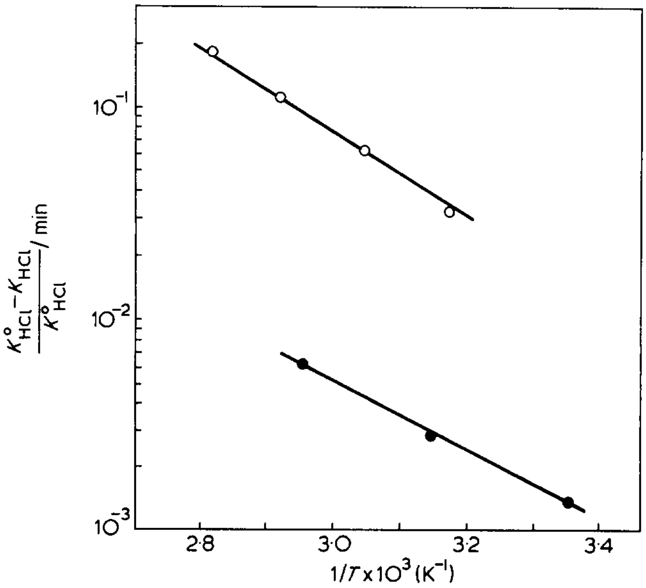


Figure 5 Arrhenius plots of initial rate of reaction: ○, benzene slurry; ●, EDC solution

Table 3 Al concentration in PVC particle[a]

Reaction temp. (°C)	Al concentration[b] Observed[c] (%)	Calculated[d] (%)
40	45	21
70	66	34
85	75	42

[a] 20 g of PVC in 60 ml benzene slurry was treated with 6.4 mmol Et_3Al
[b] It was assumed that the quantity of Et_3Al used in the reaction was 100%
[c] Obtained from X-ray fluorescence
[d] Calculated from the swelling ratio of PVC particle in benzene

Table 4 Effect of cooling on Al concentration in PVC[a]

Cooling temp. (°C)	Al concentration[b] (%)
70	62
50	50
35	41
20	34

[a] Treated with Et_3Al at 80°C
[b] It was assumed that the amount of Et_3Al used in the reaction was 100%

The fact of the penetration of Et_3Al into the PVC particles was confirmed by the experimental results listed in *Table* 4 and *Figure* 6. PVC was treated with Et_3Al at 80°C for 1 hour in benzene. It was cooled to a lower temperature (the second temperature) and the resultant mixture was poured into a large amount of methanol, filtered and dried. The aluminium concentration in the PVC particles decreases with a decrease in this second temperature, indicating the concentration of Et_3Al that had penetrated into the PVC particles increases with the reaction temperature because of the swelling of PVC in benzene, and upon cooling to low temperatures the swollen particles shrink to expel Et_3Al contained in their particles.

Figure 6 shows the kinetic curves of dehydrochlorination of PVC samples, treated with Et_3Al at 75°C for 1 hour in benzene and then cooled at several temperatures for 1 hour in the same manner as described in *Table* 4. The dehydrochlorination reaction of the polymer poured into methanol immediately after treatment with Et_3Al proceeds rapidly in the first stage, but gradually levels off with an increase in heating time. With a decrease in the second temperature, the quantity of hydrogen chloride evolved from the reactant decreases, but the rate of dehydrochlorination at the steady state is constant regardless of the second temperature. Thus, since both the aluminium concentration and the initial dehydrochlorination rate decrease with decrease of the second temperature, the hydrogen chloride observed in the first stage of decomposition seems to arise from the products which result from the reaction of Et_2AlCl in the PVC particles with methanol.

Trialkylaluminiums are associated in hydrocarbon and aromatic solvents, and this has an important bearing upon the reactivity of the organoaluminium compounds toward redistribution. Williams and Brown[10] have argued that the rate-determining step of bridge–terminal exchange in trimethylaluminium is dissociation of the dimer to two molecules of monomer. This is followed by rapid reassociation of dimer, the overall result being an interchange of bridging and terminal methyl groups. In addition, they have reported that the rate of exchange of methyl groups between bridge and terminal positions in trimethylaluminium in toluene is much faster than that in cyclohexane. Ramey and coworkers[11] have also indicated that the rate of diassociation of dimer to monomer is greater for triethylaluminium than for trimethylaluminium. Thus, alkylation of PVC with triethylaluminium by the process in equations (1) and (2) should be likely to occur in aromatic solvents.

Effect of stabilizers

Stabilizers are added to PVC compositions to protect against degradation under the influence of heat and mechanical shear in processing, and also to afford longer-term protection in service, mainly against the effects of heat, light, oxidation. Stabilizers should be colourless, compatible, and non-migrating, relatively inexpensive, non-toxic, odourless, and tasteless.

A general assessment of heat stability can be obtained from the colour developed on heating of the materials in an oven. A sequence of colour change was established, by preparing a series of strips degraded to colours described; the strips were used as standards for a quantitative expression of the colour change in the subsequent assessment[12]: 0, clear; 1, barely detectable change; 2, very slight change; 3, slight yellow tinge; 4, pale yellow; 5, yellow; 6, faint tinge of red; 7, pale red; 8, red; 9, deep red; 10, very

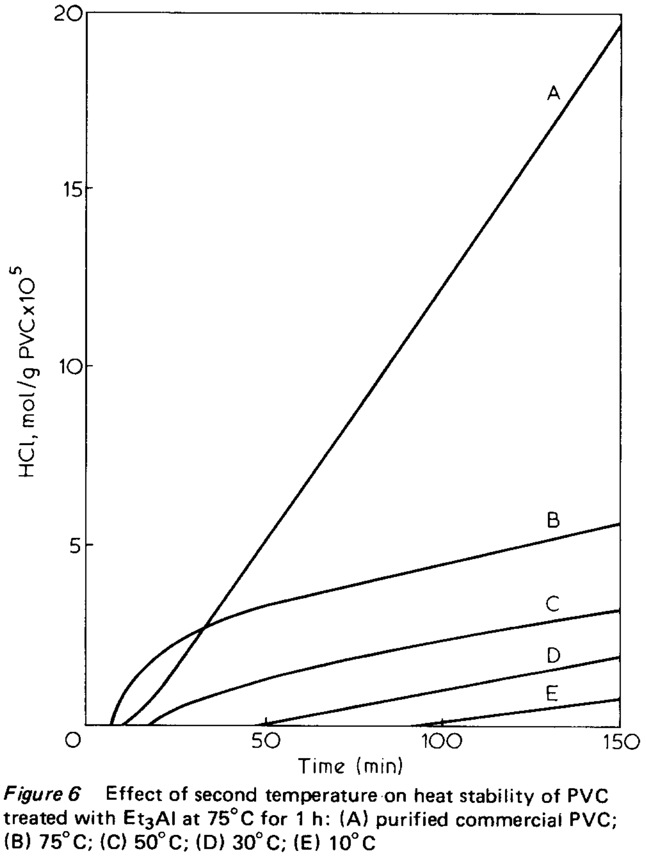


Figure 6 Effect of second temperature on heat stability of PVC treated with Et_3Al at 75°C for 1 h: (A) purified commercial PVC; (B) 75°C; (C) 50°C; (D) 30°C; (E) 10°C

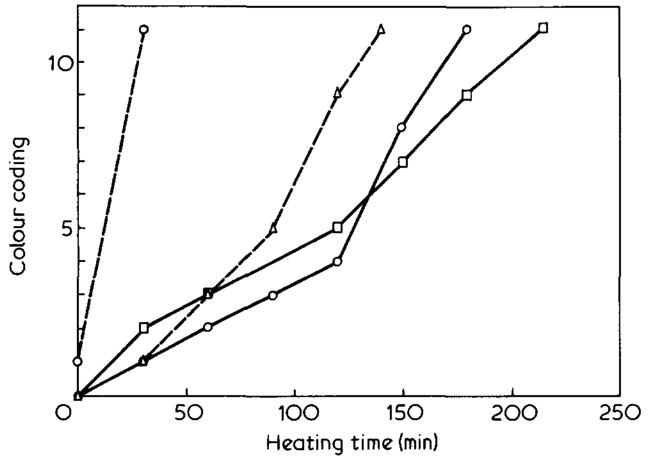


Figure 7 Colour change of PVC compounds on heating. Compositions were made up containing 100 parts PVC, 2.0 parts epoxidized soya bean oil, 0.3 parts chelater, and thermal stabilizers. — — — —, Untreated PVC: ○, 1.0 part zinc stearate—1.0 part calcium stearate; △, 2.0 parts dibutyltin maleate—1.0 part dibutyltin laurate. ———, Treated PVC: ○, 0.3 parts zinc stearate; □, 0.2 parts calcium stearate—0.3 parts zinc stearate

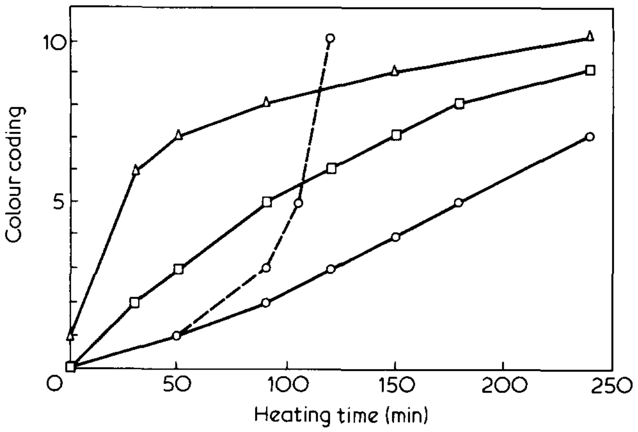


Figure 8 Colour change of plasticized PVC samples composed of 100 parts PVC, 40 parts DOP, 2.0 parts epoxidized soya bean oil, 0.5 parts tridodecyl phosphite, and thermal stabilizers. — — — —, Untreated PVC: ○, 1.0 part cadmium stearate—1.0 part barium stearate. ———, Treated PVC: △, non metal-soap; □, 0.2 parts triglycidyl isocyanurate; ○, 0.3 parts zinc stearate

deep red/black; 11, black. A series of strips were taken out at 15–60 min intervals in an air-circulating oven at 180°C and its colour number was determined.

Figure 7 shows plots of the results of rigid PVC samples compounded with calcium soap–zinc soap or with dibutyltin stabilizers. Dibutyltin maleate and dibutyltin laurate components produce significantly better long-term stability than calcium soap–zinc soap–epoxidized soyabean oil–dodecyl phosphite quaternary components. However, the alkylated PVC compounded with only small quantities of zinc stearate including epoxidized soyabean oil and tridodecyl phosphite, shows excellent initial stabilization and long-term stability superior to the starting polymer even when this is compounded with 3 parts organotin stabilizers; as the labile chlorines in the alkylated PVC was almost removed, it retards significantly the generation of zinc chloride responsible for catastrophic failure.

Figure 8 shows plots of colour coding of plasticized samples against degradation time. The organic and miscellaneous stabilizers such as epoxy compounds and alkylphosphites may be described as secondary or subsidiary stabilizers because they are never used alone but always in conjunction with metal-based stabilizers. For the plasticized alkylated-PVC blend of triglycidyl isocyanurate–epoxidized soyabean oil–tridodecyl phosphite system without addition of metal soap offers fairly good long-term stabilization. In practical terms, these could lead to a low-cost, efficient, non-toxic stabilizers system for plasticized PVC treated with trialkylaluminium compounds.

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