

Effect of Zinc Stearate and/or Epoxidized Soybean Oil on Gelation and Thermal Stability of PVC-DOP Plastigels

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ABSTRACT: The effects of zinc stearate (ZnSt_2) and/or epoxidized soybean oil (ESO) on mechanical properties and on thermal stability of plastigels obtained from polyvinylchloride (PVC) and dioctylphthalate (DOP) plastisols were studied using calorimetric, spectroscopic, and tensile-testing techniques. Plastigels having 2.5 or 5.0 part ZnSt_2 and/or 5 part ESO and 60 part DOP per 100 part PVC (phr) were gelled by heating at 140°C. The tensile strength of plastigels with no additive and having 5 phr ZnSt_2 , ESO, and both ZnSt_2 and ESO were 0.79, 0.46, 0.98, and 0.58 kN/cm², respectively. The decrease of tensile strength of plastigels with ZnSt_2 could be explained by the existence of ZnSt_2 in the solid phase in plastigels, as shown by differential scanning calorimetry (DSC). ESO helped better fusion of the plastisols without any additive and with ZnSt_2 . Higher tensile strengths of ESO containing plates indicated more complete gelation of the plastisols. The thermal stability of plastigels in terms of color and their yellowness index (YI) were higher for ZnSt_2 containing plastigels. Conjugated polyene concentrations were calculated from UV spectra of the films heated at 140°C. The reaction rate constant of the dehydrochlorination of PVC changed with the additives. Faster dehydrochlorination than control gels occurred in gels having ZnSt_2 at long heating times due to the autoaccelerating effect of ZnCl_2 formed by reaction of eliminated hydrogen chloride and ZnSt_2 . Organic acid formation reaction between ZnSt_2 and HCl formed by dehydrochlorination is investigated from the IR band at 1540 cm⁻¹ and 3400 cm⁻¹ during heating of the plastigel films. A synergistic effect of ESO and ZnSt_2 was observed when the mechanical strength and heat stability were considered together. Although ESO increased tensile strength, ZnSt_2 increased thermal stability of the plastigels at early times when they were present simultaneously in plastisols. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2488–2498, 1999

Key words: plastisol; heat stability; gelation; mechanical strength; yellowness index

INTRODUCTION

Poly(vinyl chloride), PVC, plastisol is a suspension of a small particles of PVC resin in a plasticizer. Plastigels in the form of coatings, films, sheets, foams, and rotational casting are obtained

by heating the plastisols.¹ As the plastisol is heated, diffusion of the plasticizer into particles of PVC resin take place.² Obtaining PVC dissolved in the plasticizer is the process of gelation.^{3,4} Ulutan et al.⁵ reported that even if 5–10 min were predicted for the gelation of 1.5- μ PVC particles with DOP, the time needed for complete gelation was 42 min due to the formation of agglomerates of 30 μm size for plastisols having 60 parts DOP per hundred parts (phr) resin.

PVC decomposes at a temperature lower than its processing temperature, which varies between

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140 and 200°C. Its decomposition produces almost exclusively hydrogen chloride, and is accompanied by polymer coloration going from yellow to orange, red, brown, and finally black.⁶

Thermal stabilizers are basic additives to PVC in its technological processing. The role of different types of stabilizers are to bond the eliminated hydrogen chloride, to replace the labile chlorine atoms in PVC chains and thus prevent further dehydrochlorination and to preserve color of polymer.^{7,8}

At present, the carboxylates of metals of the second group of the periodic system such as Ca^{2+} , Mg^{2+} , Ba^{2+} , and transition metals such as Zn^{2+} salts of phthalic, sebacic, lauric, stearic, and other acids come to the fore in the wide series of thermal PVC stabilizers.⁹ The synergetic mixtures of metal soaps have most frequently been used. Synergetic mixtures presenting no health hazard are worthy of mentioning. They are mixed zinc-based compounds. Zinc containing stabilizers function only at a very low concentration in PVC. Epoxide compounds should be used as HCl acceptors in conjugation with the stabilizer mixture.⁶ Epoxide compounds are widely used in a range of food-contact plastics as plasticizers, secondary heat stabilizers, and lubricants.^{10,11} Epoxide compounds (3–10 phr) are used in PVC foil.¹² The use of epoxides with metal soaps such as Cd, Ba, and Zn increases the stability to both heat and light.¹³

PVC undergoes dehydrochlorination reaction by heat, resulting in the formation of conjugated double bonds. Coloration occurs when the sequence length exceeds four and five units.¹⁴ The concentration of conjugated polyene sequences has been determined by using UV-visible spectroscopy. The polyene sequences absorb in the region of 300–600 nm.^{15,16} Volka et al.¹⁷ studied the effect of thermal stabilizers in the thermal treatment of PVC by IR spectroscopy. Zinc stearate added to PVC are characterized by an absorption band at 1540 cm^{-1} , corresponding to the antisymmetrical stretching vibration of the carboxylate group.

Oremusova et al.^{9,17,18} investigated the thermal stability of calcium, magnesium, zinc, and lead stearates. The effective rate constant of dehydrochlorination increased with increasing the ZnSt_2 concentration, and had an order of 10^{-4} min^{-1} .⁹ They reported that rate constant of the dehydrochlorination reaction of PVC stabilized with $3.2 \times 10^{-4}\text{ mol}$ of ZnSt_2 was $1.56 \times 10^{-4}\text{ min}^{-1}$. Levai et al.¹⁹ found ZnCl_2 formed from ZnSt_2 and HCl increased the rate of the dehydro-

chlorination reaction, but that the catalytic effect was eliminated with addition of pentaerythritol to zinc salts. Patel et al.²⁰ found the first-order rate constants of virgin and HCl-treated PVC at 150–190°C. Rate constants of the dehydrochlorination reaction at 140°C for virgin PVC and HCl-treated PVC are $1.66 \times 10^{-4}\text{ min}^{-1}$ and $4.64 \times 10^{-4}\text{ min}^{-1}$, respectively. Lerke et al.¹⁵ investigated effects of gamma irradiation on pure PVC and PVC stabilized with epoxidized soybean oil, and found that the concentration of conjugated polyene sequences of PVC stabilized with epoxidized soybean oil was lower. Housell²¹ investigated the coloration of PVC exposed to gamma radiation. When PVC mixtures containing 5 and 10 phr ESO were exposed to gamma radiation, it seemed that coloration had been decreased compared to control samples. Troitskii et al.²² observed that the addition of polyols to PVC mixtures containing ZnSt_2 and epoxy created a synergetic effect.

The mechanical properties of PVC do not change appreciably as pyrolysis goes on. The type of PVC affects the mechanical properties of PVC.²³ The mechanical properties such as tensile, flexural, and impact property of the mixtures cured with epoxy monomer was examined by Chin and Chen,²⁴ and was found better than that of mixtures without the epoxy monomer. Ghersa²⁵ found that the tensile strength and the elongation at break of PVC including 30% DOP were 2 kN/cm^2 and 275%, respectively. Gilbert et al.^{4,26} reported the tensile strength and the elongation at break of PVC having 60% Diisooctyl phthalate were 1.74 kN/cm^2 and 500%, respectively. The literature values of tensile strength, elongation at break percent, and modulus of soft PVC are in the range of $0.70\text{--}2.4\text{ kN/cm}^2$, 200–450%, and $0.25\text{--}2.0\text{ kN/cm}^2$, respectively.^{27,28}

The synergistic effect of ZnSt_2 and ESO on thermal stability of rigid and plasticized PVC processed with conventional methods such as solvent casting or extrusion was reported by previous workers.^{7,8} The present work aimed to study the effect of ZnSt_2 and ESO on sol-gel-processed plasticized PVC, which has commercial applications.¹ Determination of kinetics of thermal dehydrochlorination, effect of adding ZnSt_2 , and/or ESO on the mechanical properties and heat stability of plastigels are investigated. Dioctylphthalate (DOP) was used as the plasticizer. Although the reaction of the metal soap was followed using IR spectroscopy, the total number of conjugated polyenes was determined by UV spectroscopy.

Table I Parts by Weight of Stabilizer per 100 Parts of PVC in 60 phr DOP

Experimental	ESO	ZnSt ₂
1	0	0
2	0	5
3	5	0
4	5	5
5	0	2.5
6	5	2.5

EXPERIMENTAL

Materials

PVC (Petvinil, P, 38/74, Petkim) was used in preparation of plastisols. The viscosity molecular mass was 50,000. DOP (Sankim), with a refractive index of 1.4399, density of 0.993 gr/cm³, and epoxidized soybean oil ((Akdeniz Kimya) with oxirane oxygen content of 6%), and commercial zinc stearate, Akstab Zn, (Akdeniz Kimya) were used in preparation of the plastisols.

Preparation of Plastisols

Plastisol mixtures having compositions given in Table I were obtained by mixing the ingredients at 20°C for 45 min in a home-type Rowenta kneader.

Preparation of Plastisol Films

Thin-layer samples from plastisols were spread onto glass microscope slides. They were then evacuated in a vacuum dessicator for 1 h to get rid of the air entrapped in them.

Preparation of Plastigel Films

All of the prepared plastisol films were heated for 15 min in an air-circulating oven at 140 C ± 2°C. Thus, plastigel films having a 7–15-μm thickness were obtained.

Plastigel Plate Formation

Prepared plastisols were spread on the stainless steel circular plate of the die of the hot press developed for this study. Then they were placed into a vacuum dessicator and evacuated for 1 h to get rid of the entrapped air. Then they were pressed with 50 bars pressure for 15 min at the hot press and at 140°C. The thickness of the gels

were about 2 mm. Obtained plastigel plates were heated in an air-circulating oven for a time period of 15–60 min at 140°C.

Heating of Plastigel Films and Study of Films with IR and UV Spectroscopy

Films heated at 140°C for different time periods were studied by using IR-spectroscopy and UV-spectroscopy. Transmission IR-spectrum of the films was obtained with a Shimadzu IR-470 IR spectrophotometer. A Jasco 7800 UV spectrophotometer was used in obtaining the UV spectra of the films.

Yellowness Index

The yellowness index of the heated plastigel plates were measured by using a Data Color Tex-flash UV-visible spectrometer.

DSC Studies

DSC curves of PVC, ZnSt₂, and plastigels were obtained with 10°C/min heating and a cooling rate under N₂ atmosphere using a Setaram DSC 92. *T_g* was taken as midpoint of the step change in the heat flow–temperature curve.

Mechanical Tests

The stress–strain diagrams of plastigel plates were obtained using an Instron Tensile Tester 1114 according to TS 1398, with a 5 cm/min strain rate and recorder rate.

RESULTS AND DISCUSSION

Characterization of PVC, ZnSt₂, and Plastigels

There are two consecutive step changes in the heat-flow–temperature curve of PVC in Figure 1. The corresponding *T_g* values are 75 and 80°C, respectively. Because PVC used in this study was obtained by spray drying the emulsion, it contained additives such as emulsifiers. The additives caused observation of two *T_g* values for PVC. Melting temperature of ZnSt₂ determined as 121°C, as seen from the DSC curves of ZnSt₂ in Figure 1. ZnSt₂ was crystallized at 110°C upon cooling.

Melting enthalpy of ZnSt₂ calculated from the DSC melting endotherm of ZnSt₂ was determined as 54 kJ/mol. This value was comparable with melting enthalpy of metal(II) stearates. For ex-

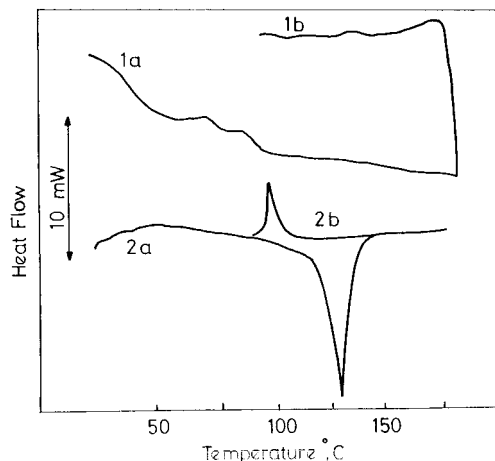


Figure 1 DSC curves of the 36.1 mg of PVC (1) and 4.6 mg of ZnSt₂ (2) (a) heating, (b) cooling.

ample, melting enthalpy of the cupric distearates prepared in various solvents were between 50–66 kJ/mol.²⁹

DSC curves of plastigels heated for the time periods of 15 and 60 min at 140°C are shown in Figure 2. The samples containing ZnSt₂ give a melting endotherm about 120–125°C. These peaks are due to presence of crystalline ZnSt₂ in

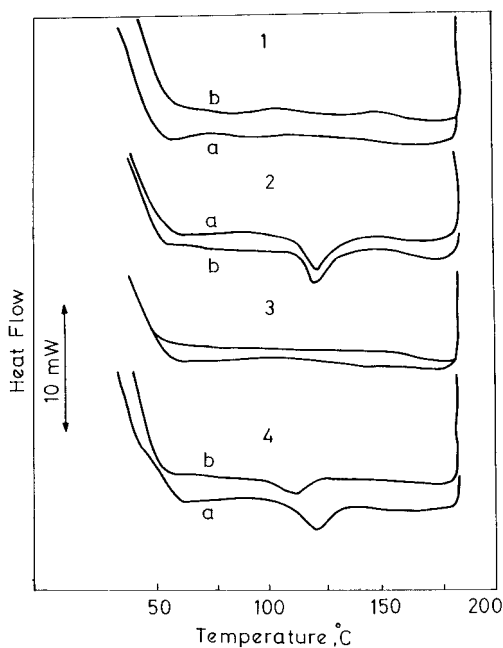


Figure 2 DSC curves of plastigels with 1: control, 2: ESO, 3: ZnSt₂, 4: ESO and ZnSt₂ at 5 phr level. The plastigels were heated in a time period of (a) 15 min (b) 60 min at 140°C.

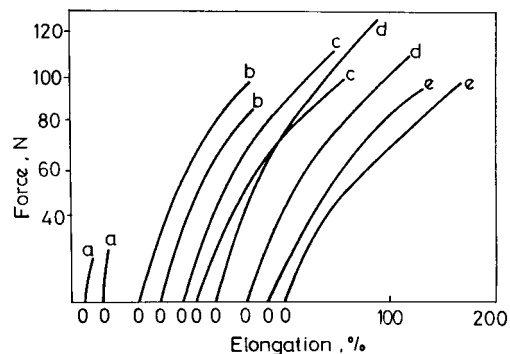


Figure 3 Stress–strain diagrams for control plastigel heated for different time periods at 140°C: (a) unheated, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min. The strain % starts from zero for each curve.

plastigels, indicating ZnSt₂ in plastigels was in the solid form.

Gelation Behavior of the Plastisols

The average particle size of the PVC used in this study was 1.5 μm .⁵ The agglomeration of PVC particles to a size of 30 μm when mixed with DOP caused longer gelation times than expected from the small size of the PVC particles.^{5,30} ZnSt₂ was liquified and dissolved in DOP at the gelation temperature, and was recrystallized upon cooling of the plastigel plates.³⁰ Mixing of PVC, DOP, and ZnSt₂ at the molecular level was not possible in the sol-gel technology. For thorough mixing, conventional high-shear processing techniques such as roll milling or extrusion should be used. An ESO addition to plastisols made gelation easier because it is a good plasticizer for PVC. Gelation means formation of a stable solution of PVC in plasticizers. It is controlled by the rate of diffusion of plasticizers in PVC agglomerates.³⁰ Because the presence and the distribution of the additives affects the state of agglomeration of PVC particles, it may not be possible to obtain plastigels with reproducible properties by the sol-gel processing. On the other hand, because the sol-gel process has industrial applications such as fabric or metal coating, dip molding, or slush molding,³¹ improvement of their thermal stability of plastigels are important.

Mechanical Behavior

Stress–strain diagrams of plastigels shown in Figure 3 indicated they were viscoelastic rather than rubbery.³¹

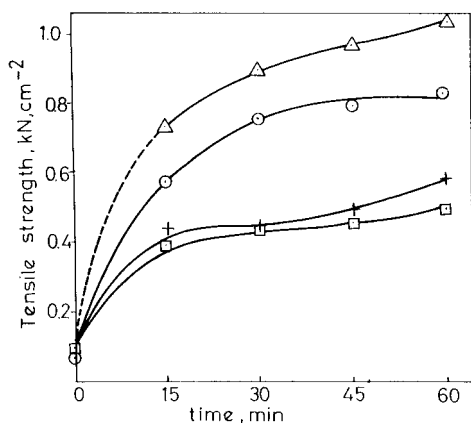


Figure 4 Change of tensile strength of plastigel plates with heating time 140°C. (○: control, with △: ESO, □: ZnSt₂, +: ESO and ZnSt₂ at 5 phr level.

Although the tensile strength and elongation at break % of plastigels, shown in Figures 4 and 5, increased during the 45-min heating time at 140°C, no change was observed for further heating. Gelled fraction increased and, therefore, the mechanical strength increased with heating time. If heating is continued after complete gelation, mechanical strength will not increase. Complete gelation in 45 min at 140°C is in agreement with the 42 min found from microphotographic studies.^{5,30} Agglomeration of PVC particles caused a longer gelation time than expected.

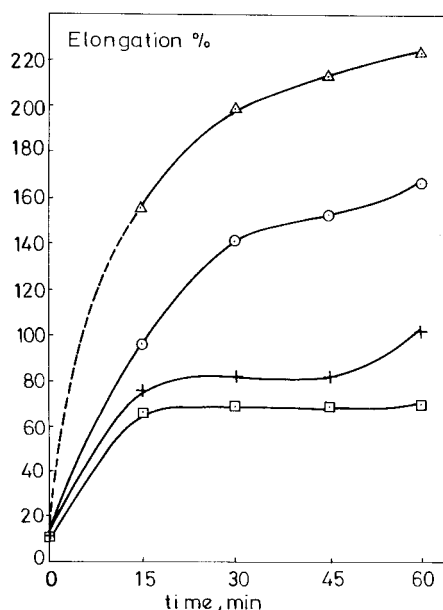


Figure 5 Change of elongation at break of plastigel plates with heating time at 140°C. (○: control, with △: ESO, □: ZnSt₂, +: ESO and ZnSt₂ at 5 phr level.

Table II Ultimate Mechanical Properties of the Gels at the End of 45 Min Heating

Content of Plastigel	Tensile Strength, kN, cm ²	Elongation at Break (%)
Control	0.79	154
5 phr ZnSt ₂	0.46	68
5 phr ESO	0.98	213
5 phr ESO and 5 phr ZnSt ₂	0.58	103

At the end of the 45-min heating time at 140°C, tensile strength and elongation at break of the plastigels were as shown in Table II. These are in the range of mechanical properties of the flexible PVC reported by other workers.^{4,24-26}

The obtained results showed that gelation was completed at 140°C in 45 min. Although addition of ZnSt₂ into the plastisol decreased the mechanical strength from 0.79 kN/cm² to 0.46 kN/cm², addition of ESO increased it to 0.98 kN/cm². ESO also has a plasticizing and lubricating effect in addition to its stabilizing effect.^{10,11} When ESO was used with ZnSt₂, the mechanical strength was decreased to a lesser extent, to 0.58 a kN/cm² value. The presence of ZnSt₂ as a solid phase in plastigels caused lowering in the tensile strength. The presence of ESO provided higher mechanical strength to ZnSt₂ containing plastigels. Tensile strength is a measure of cohesion of PVC particles swollen with plasticizers. The higher the particle size, the lower the forces holding them together.³² Aggregation of PVC particles in plastisols caused longer gelation times.^{5,30} The presence of ZnSt₂ and ESO in plastisols may also create a change in state of aggregation of the particles, effecting the tensile strength of the gels. Using the method of low-shear low-temperature mixing of plastisol ingredients, it was not possible to obtain the dispersion of ZnSt₂ at the molecular level in the present study. Even if ZnSt₂ melted and dissolved in DOP upon heating the plastisols at 140°C, it was recrystallized upon cooling of the plastigels, creating weak points of cohesion between PVC agglomerates.

Heat Stability of Plastigels

The color of PVC, yellowness index, the number, and the length of the conjugated diens, and total mol of HCl released are all measures of the thermal stability of PVC.

Table III The Change of Colors of Plastigels with Heating Time at 140°C

Heating Time, min	Control	5 phr ZnSt ₂	5 phr ESO	5 phr ESO and 5 phr ZnSt ₂
0	Light yellow	Light yellow	Light yellow	Light yellow
15	Yellow	Yellow	Yellow	Yellow
30	Yellow	Yellow	Yellow	Yellow
45	Brown	Yellow	Yellow	Yellow
60	Dark brown	Yellow	Dark yellow	Yellow

PVC, DOP, ESO, and ZnSt₂ are used as 100, 60, 5, and 5 parts, respectively.

The colors of plastigels heated at 140 and 160°C are shown in Table III. Although the control film became brown in 45 min, other plastigels having stabilizers remained yellow. The stabilizing effect of ZnSt₂ was seen on samples heated for 60 min. While ZnSt₂-containing gels were still yellow, the control and ESO-containing gels become dark yellow.

The change of the yellowness index of these plastigels with a heating time at 140°C are shown in Figure 6. The addition of ZnSt₂ into plastisol mixtures prevented the coloration during the heating of the plastigels at 140°C, but it caused sudden darkening of the plastigels at a further heating at higher temperatures.³⁰ This is explained by the catalytic effect of products from the reaction between PVC, HCl, and stabilizer.⁶ These products accelerate PVC dehydrochlorination.

The rate of the change of the yellowness index of the plates were very close to each other until 30 min heating time, as seen in Figure 6. Although

the control films were darkened, the films having ZnSt₂ or ESO-ZnSt₂ kept their yellow color upon further heating. ESO-containing films were darker than the ones with ZnSt₂, but lighter than the control gels.

Dehydrochlorination Kinetics of PVC

The HCl formed by dehydrochlorination and resulting in up to conjugated 8 units in PVC was determined by using UV spectra of the films.

It is very difficult to exactly determine the distribution of values of conjugated polyenes in the dehydrochlorinated PVC, but not impossible. It is generally accepted that the fine structure in the absorption spectra of dehydrochlorinated PVC is due to the formation of conjugated polyenes of the type H-(—CH=CH—)_n-H or CH₃-(—CH=CH—)_n-CH₃.³³ Table IV summarizes the absorption coefficient of the type H-(—CH=CH—)_n-H for each wavelength where the strongest absorption occurs.^{34,35}

The distribution of values of *n* in the dehydrochlorinated PVC was determined from the ab-

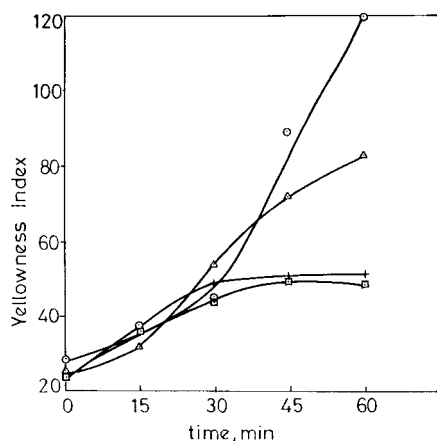


Figure 6 Change of yellowness index of plastigels with heating time at 140°C ○: control, with 5 phr △: ESO, □: ZnSt₂, +: ESO and ZnSt₂.

Table IV Molar Absorption Coefficient of H-(—CH=CH—)_n-H

Number of Conjugated Double Bonds <i>n</i>	Wavelength Where the Strongest Absorption Occurs λ (nm)	Molar Absorption Coefficient ε _λ · 10 ⁻³
3	268	34.6
4	304	72.0
5	334	121.0
6	364	138.0
7	390	174.0
8	410	203.5
9	428	232.0
10	447	261.0

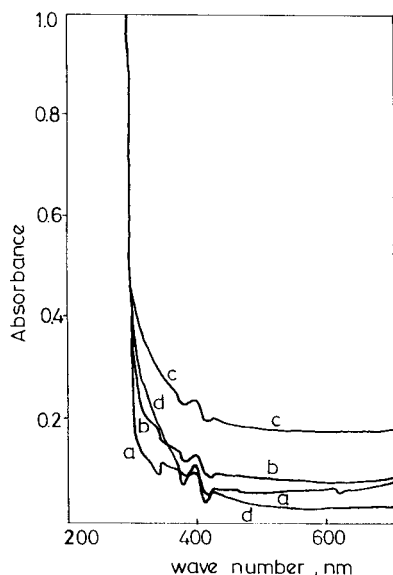


Figure 7 Absorption spectra of dehydrochlorinated PVC-DOP plastigel films at 140°C: (a) 15, (b) 30, (c) 45, (d) 60 min heated at 140°C.

sorption spectra of dehydrochlorinated PVC with the data given in Table IV. The distribution of values of conjugated double bonds, n , was found by using UV spectra of the plastigel films. As an example, the absorption spectra of PVC-DOP plastigel films heated at 140°C for different periods are shown in Figure 7.

The concentration of polyene sequences, C_n , is given by

$$C_n = A(\varepsilon_\lambda/d) \quad (2)$$

where A is the absorbance at wavelength λ , ε_λ is the molar absorption coefficient, and d is thickness of the plastigel films. As an example, change of polyene sequences of plastigel film containing 2.5 phr ZnSt₂ and 5 phr ESO vs. heating time at 140°C are shown in Figure 8. The data for other cases are reported in ref. 30.

The mol fraction of polyene sequences containing n conjugated double bonds can be determined from C_n as

$$N_n = C_n/C \quad (3)$$

where C is the concentration of vinyl chloride repeat units in 60 phr DOP plastigel, 11.5 mol/L. The mol fractions of polyene sequences and of double bonds, N_T and N_D , respectively, are given by

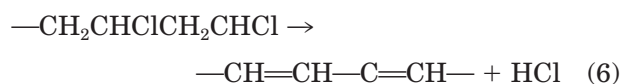
$$N_T = \sum N_n \quad (4)$$

$$N_D = \sum n \cdot N_n \quad (5)$$

The mol fractions of conjugated double bonds formed by dehydrochlorination are calculated using their UV spectra of the films for plastigels having different composition.

The total number of double bonds of the polyene sequences is practically equal to the hydrogen chloride molecules split off.²⁰

Thermal dehydrochlorination of PVC is a first-order reaction.^{9,20,21} The reaction can be represented by



Equation (7) was obtained by the integration of rate expression of reaction 6.

$$-\ln(1 - N_D) = k_1 t \quad (7)$$

where k_1 is reaction rate constant, t is time, and N_D is the mol fraction of conjugated double bonds. Equation (7) for small values of N_D can be written as

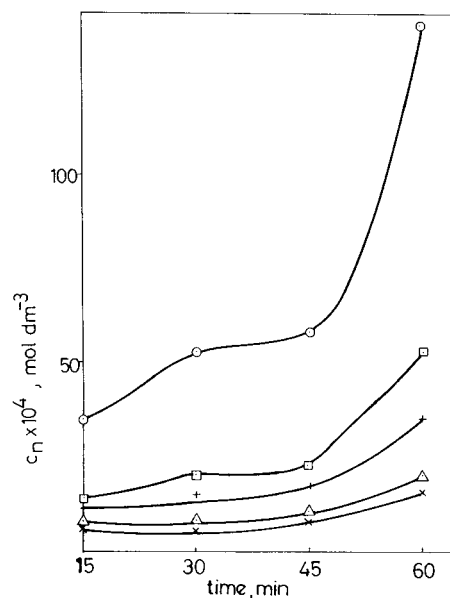


Figure 8 Concentration of polyene sequence as a function of heating time at 140°C for plastigel film containing 2.5 phr ZnSt₂ (○: 4, □: 5, +: 6, △: 7, ×: 8 conjugated double bonds).

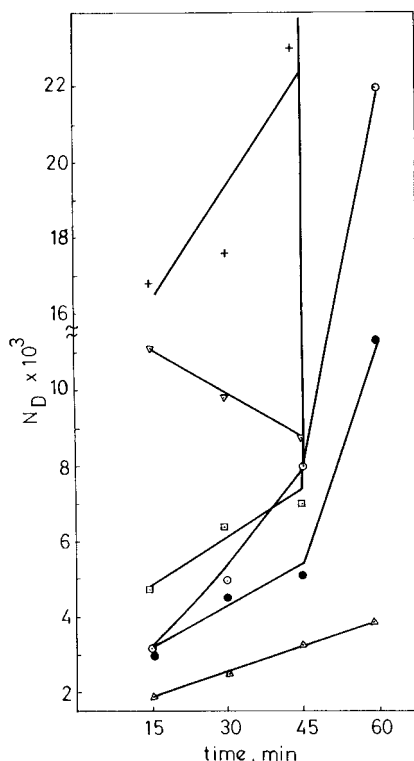


Figure 9 Change of total fraction of the double bonds with heating time 140°C for plastigels having (○: control, □: 2.5 phr ZnSt₂, +: 5 phr ZnSt₂ and 5 phr ESO, △: 5 phr ESO, ▽: 5 phr ESO, and 5 phr ZnSt₂, ⊗: 5 phr ESO and 2.5 phr ZnSt₂).

$$N_D = k_1 t \quad (8)$$

The change of mol fraction of the double bonds, N_D , with time during heating at 140°C is shown in Figure 9. The long heating times required for complete gelation of the films⁵ and recrystallization of ZnSt₂ in the films upon cooling created problems in determination of the correct N_D values. N_D vs. t lines should pass through the origin. Only the control film and maybe the film with ESO meet this requirement. The N_D values at

time zero found by extrapolating N_D vs. t lines were 3.8 and 9.0 for 2.5 and 5 phr ZnSt₂-containing films. Because no conjugated double bond existed in unheated PVC, this indicated ZnSt₂ present in the solid form in the films prevented light transmission from the films in proportion with their concentration. In Figure 9, it seems clear that the number of double bonds of PVC-DOP samples containing 5 phr ZnSt₂ and 5 phr ESO decreased with heating time. Decreasing the number of double bonds during heating may be due to a reaction of oxygen with air. Increasing transparency or decreasing absorbance of the films with complete gelation may be another explanation of the decrease of the calculated N_D values from absorbances with heating time. The number of double bonds of samples containing ZnSt₂ were sharply increased after 45 min. It can be said that ZnCl₂ formed during dehydrochlorination is an accelerating dehydrochlorination reaction as an autocatalyst, as also suggested by other workers.^{9,20} Dehydrochlorination rate constants, k_1 of eq. (8) from the slopes of the first 45-min part of the lines in Figure 9 and eq. (8) were determined using the least square method. The rate constants of the autoaccelerated reaction 6 due to either ZnCl₂ accumulation or HCl formation, k_2 was found from the slopes of N_D vs. t lines in a 45–60 min heating range. The values of k_1 and k_2 were as reported in Table V.

Even if there are problems in determination of correct values for N_D due to interfering effects of crystallization of ZnSt₂ and gelation of the films, a relative change of N_D with respect to heating time can be taken as indicator of the dehydrochlorination reaction.

Conjugated polyene concentrations were calculated from UV spectra of samples, which were taken during heating them at 140°C. k_1 for dehydrochlorination of the PVC-DOP plastigel was $1.62 \times 10^{-4} \text{ min}^{-1}$, close to the $1.66 \times 10^{-4} \text{ min}^{-1}$ value from Patel et al.'s data.²⁰ Although adding

Table V Determined Rate Constants for Steps of the Suggested Reaction Mechanism

Content of Plastigel	k_1 (min ⁻¹)	k_2 (min ⁻¹)	k_3 (lt mol ⁻¹ min ⁻¹)
Control	1.62×10^{-4}	6.60×10^{-4}	—
2.5 phr ZnSt ₂	0.77×10^{-4}	∞	12.4
5 phr ZnSt ₂	2.11×10^{-4}	∞	—
5 phr ESO	0.47×10^{-4}	0.47×10^{-4}	—
5 phr ESO and 2.5 phr ZnSt ₂	0.70×10^{-4}	4.20×10^{-4}	7.4
5 phr ESO and 5 phr ZnSt ₂	cannot be determined	∞	5.5

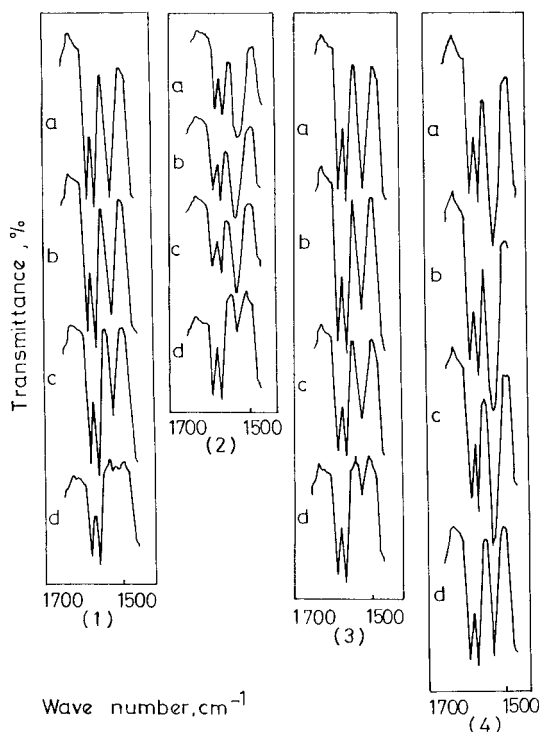


Figure 10 The IR absorption bands of the films having [(1): 2.5 phr ZnSt₂, (2): 5 phr ZnSt₂, (3): 2.5 phr ZnSt₂ and 5 phr ESO, (4): 5 phr ZnSt₂ and 5 phr ESO] (a) 15, (b) 30, (c) 45, (d) 60 min heated at 140°C in the 1400–1700 cm⁻¹ range].

ZnSt₂ at 5 phr level increased this value to $2.11 \times 10^{-4} \text{ min}^{-1}$, adding 2.5 phr ZnSt₂ decreased it $0.77 \times 10^{-4} \text{ min}^{-1}$. In other words, ZnSt₂ slowed down the dehydrochlorination reaction when it was present in low concentration and it accelerated when it is present at a high concentration. However, addition of 5 phr ESO together with PVC–DOP and 2.5 phr ZnSt₂ decreased this value to $0.70 \times 10^{-4} \text{ min}^{-1}$.

k_2 values were very high, indicating an instant reaction for gels containing 2.5 phr ZnSt₂, 5 phr ZnSt₂, 5 phr ZnSt₂, and 5 phr ESO. The films having 2.5 phr ZnSt₂ and 5 phr ESO had lower k_2 value, 4.2×10^{-4} compared to other ZnSt₂ containing films. Thus, a synergistic effect of ZnSt₂ and ESO was observed at the 2.5 phr level. The high k_2 value for control film indicates an auto-accelerating effect of HCl eliminated from PVC. Observation of the same k_1 and k_2 values for ESO-containing films confirmed the HCl scavenging effect of ESO.^{6,10,11}

Reaction of ZnSt₂ in PVC upon Heating

ZnSt₂ added to PVC is characterized by an absorption band at 1540 cm⁻¹ in the IR spectra of

the films corresponding to the antisymmetrical stretching vibration of the carboxylate group.¹⁶ Intensity, the absorption band at 1540 cm⁻¹ was proportional to the concentration of ZnSt₂, and it decreased with increasing the heating time.³¹ The absorption bands at 1540 cm⁻¹ for the plastigel films heated for different time periods at 140°C are as shown in Figure 10. The absorption band observed at 1590 cm⁻¹ due to an aromatic ring of DOP for plastigel films was taken as an unchanging reference in the heated gels, neglecting a small decrease in DOP concentration with time due to evaporation at 140°C.³⁶ The ratio of absorbance at 1540 cm⁻¹ to 1590 cm⁻¹ vs. a heating time at 140°C are as shown in Figure 11. It seems clear that the amount of carboxylate anions was decreased with the heating time.

The dehydrochlorination reaction started with heating of the plastigel films. HCl formed with the dehydrochlorination reacted with zinc carboxylate and carboxylate anion was transformed into organic acid. The reaction can be shown as



or in simplified form



OH group of the organic acid is characterized by an absorption band at 3400 cm⁻¹ corresponding to its stretching vibration. Changes of the absorbance of the band at 3400 cm⁻¹ with a heat-

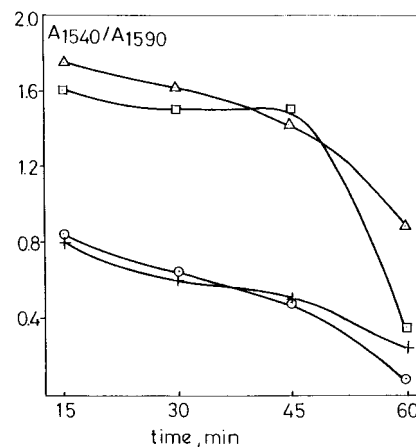


Figure 11 The ratio of absorbances at 1540 cm⁻¹ and 1590 cm⁻¹ vs. time for plastisols heated at 140°C and having (O): 2.5 phr ZnSt₂, (□): 5 phr ZnSt₂, (+): 2.5 phr ZnSt₂ and 5 phr ESO, (Δ): 5 phr ZnSt₂ and 5 phr ESO).

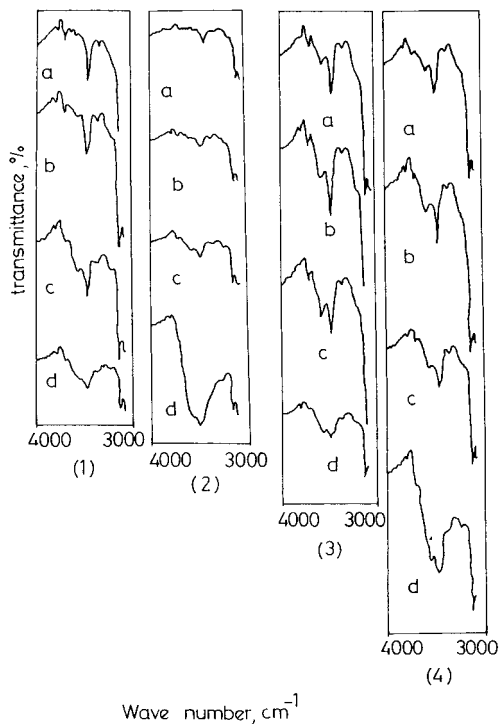


Figure 12 The IR absorption bands of the films having [(1): 2.5 phr ZnSt₂, (2): 5 phr ZnSt₂, (3): 2.5 phr ZnSt₂ and 5 phr ESO, (4): 5 phr ZnSt₂ and 5 phr ESO] (a) 15, (b) 30, (c) 45, (d) 60 min heated at 140°C in 3000–4000 cm⁻¹ range.

ing time at 140°C are as shown in Figure 12. The ratio of absorbances at 3400 cm⁻¹ to 1590 cm⁻¹ vs. a heating time at 140°C were as shown in Figure 13. Increase of the absorbance at 3400

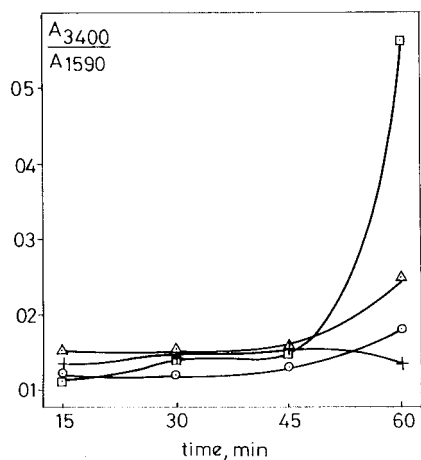


Figure 13 The ratio of absorbances at 3400 cm⁻¹ and 1590 cm⁻¹ vs. time for plastisols heated at 140°C and having (○): 2.5 phr ZnSt₂, (□): 5 phr ZnSt₂, (+): 2.5 phr ZnSt₂ and 5 phr ESO, (△): 5 phr ZnSt₂ and 5 phr ESO).

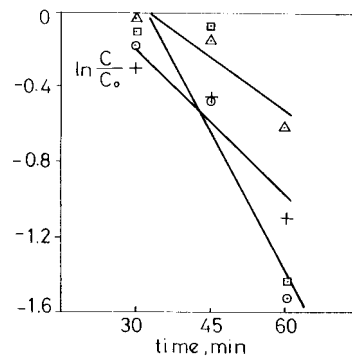


Figure 14 $\ln(C/C_0)$ vs. heating time for RCOO^- at 140°C.

cm⁻¹ with the heating time confirmed that RCOOH formed from the reaction between HCl and ZnSt₂. The overall rate of reaction 10 is first order with respect to both R—COO⁻ and H⁺. Because concentration of the dissolved HCl in films reaches its maximum value 3.68×10^{-3} mol dm⁻³ in a very short time,⁹ it can be taken as a constant in the rate equation. Thus, the integrated rate expression is

$$\ln(C/C_0) = -3.68 \times 10^{-3} k_3 t \quad (11)$$

where C_0 and C are the initial and instantaneous R—COO⁻ concentrations, respectively, and k_3 is the rate constant for reaction 10. C values were determined from absorbance values at 1540 cm⁻¹ and an experimental linear calibration line obtained with films having known concentrations of RCOO⁻ in the form of ZnSt₂. From the slopes of $\ln(C/C_0)$ vs. t lines in Figure 14 and eq. (11), k_3 values for reaction 10 were found. As seen in Table V, they are of the order of 10 dm³ mol⁻¹ min. In flexible PVC, a smaller second-order reaction constant than that found by Oresimova et al.⁹ for ZnSt₂ in pure PVC was found. The high value of the rate constant is the indication of the fast reaction between HCl evolved by dehydrochlorination and ZnSt₂.

CONCLUSION

Due to long heating times for complete gelation of PVC–DOP plastisols, heat stabilizers should be added to the mixture. The well-known synergistic mixture ZnSt₂ and ESO⁸ was effective at low ZnSt₂ levels in sol-gel processing. Crystallization of ZnSt₂ and incomplete gelation due to its pres-

ence in plastisols made the kinetic analysis of the dehydrochlorination reaction by the UV spectroscopic method complicated. The presence of ZnSt₂ caused faster dehydrochlorination due to ZnCl₂ accumulation following long heating times. Although the best heat stability and gelation effects were obtained with ESO for long heating times as confirmed by dehydrochlorination rate constants and tensile strengths, the highest color stability was observed for gels having ZnSt₂ and ZnSt₂ and ESO.

The synergistic effect of ESO and ZnSt₂ was observed when the mechanical strength and heat stability were considered together. Although ESO increased tensile strength, ZnSt₂ increased thermal stability of plastigels at early times when they were present simultaneously in plastisols.

REFERENCES

- Nakajima, N.; Yavornitzky, C. M.; Roche, E. J.; Harrel, E. R. *J Appl Polym Sci* 1986, 32, 3749.
- Guoguan, S.; Yioting, C. *Polym Testing* 1991, 10, 315.
- Gilbert, M.; Hemsley, D. A.; Miadonye, A. *Plastics Rubber Proc Appl* 1983, 5, 343.
- Gilbert, M.; Patel, S. V. *Plastics Rubber Proc Appl* 1985, 5, 85.
- Ulutun, S.; Baltacıoğlu, H.; Balköse, D. *Engineering Systems Design and Analysis Conference*, ASME, London, 1994, p. 153.
- Stepek, J.; Daoust, H. *Additives for Plastics*; Springer: New York, 1983.
- Owen, E. D. *Degradation and Stabilization of PVC*; Elsevier Appl Sci Publ: London, 1984.
- Wypych, J. *Polyvinyl Chloride Stabilization*; Elsevier Sci Publ Comp Inc: New York, 1986.
- Oremusova, J.; Simon, P.; Valko, L.; Kovarik, P. *Chem Papers* 1991, 45, 379.
- Demertzis, P. G.; Riganokos, K. A.; Akrida-Demertzi, K. *Eur Polym J* 1991, 27, 231.
- Howell, S. D.; Betso, S. R.; Meltzer, J. A.; Smith, P. B.; Debney, M. F. *Thermochim Acta* 1990, 166, 207.
- Sander, J. H. *Deut. Pat. DE 3720590 A1* (1986).
- Bredereck, P. *J Vinyl Technol* 1986, 8, 46.
- Abbas, B. K. I.; Szymanski, W. *J Appl Polym Sci* 1983, 28, 501.
- Lerke, G.; Lerke, I.; Szymanski, W. *J Appl Polym Sci* 1983, 28, 519.
- Volka, K.; Vymazal, Z.; Stavek, J.; Seidl, V. *Eur Polym J* 1991, 18, 219.
- Oremusova, J.; Simon, P.; Valko, L.; Kovarik, P. *Chem Papers* 1991, 45, 127.
- Oremusova, J.; Simon, P.; Valko, L. *Chem Papers* 1991, 45, 389.
- Levai, G. Y.; Ocskay, G. Y.; Niyatrai, Z. S. *Angew Makromol Chem* 1985, 137, 37.
- Patel, K.; Velazquez, H.; Calderon, H. S.; Brown, G. R. *J Appl Polym Sci* 1992, 46, 179.
- Housel, S. D. *Plastics Engineering*, September 47 (1985).
- Troitskii, B. B.; Troitskaya, L. S.; Denisova, V. N. *Prague Meetings on Macromolecules Prague* (1988).
- Katchy, E. M. *Kunststoffe* 1984, 74, 755.
- Chin, H. T.; Chen, C. B. *Advanced Composite Materials and Structures*; Sih, G. C.; Hsu, S. E., Eds. VNU Sci. Press BV: The Netherlands, 1987.
- Ghersa, P. *Mod Plast* 1958, 36, 135.
- Gilbert, M.; Patel, S. V. *Plastics Rubber Proc Appl* 1986, 6, 321.
- Perry, H. B.; Chilton, C. H. *Chemical Engineers' Handbook*; McGraw-Hill, New York, 1973.
- Nass, I.; Heiberger, A. *Encyclopedia of PVC*; Marcel Dekker: New York, 1987.
- Yürekli, M. *Chim Acta Turcica* 1989, 17, 377.
- Baltacıoğlu, H. Ph.D. Thesis, Ege University, İzmir, Turkey (1994).
- Rodrigues, F. *Principles of Polymer Systems*; McGraw Hill: London, 1983.
- Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience: New York, 1979.
- Bengough, W. I.; Varma, I. K. *Eur Polym J* 1966, 2, 61.
- Shindo, Y.; Hirai, T. *Makromol Chem* 1972, 155, 1.
- Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J Am Chem Soc* 1966, 83.
- Avdounin, B. D.; Metzger, G.; Verd, J. *J Appl Polym Sci* 1992, 45, 2091.