Synergistic Effect of Zinc Stearate and Natural Zeolite on PVC Thermal Stability

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ABSTRACT

At high temperatures (about 100 °C), PVC decomposes by the removal of hydrogen chloride (HCl) gas and the decomposition is accompanied by polymer discoloration going from yellow to orange, brown and black. In order to prevent decomposition of PVC, thermal stabilizers are added to PVC. The synergistic effect of zinc stearate ($ZnSt_2$) and/or natural zeolite (clinoptilolite) on PVC thermal stability was investigated in this project. For this purpose PVC plastisol was prepared by mixing poly(vinyl chloride) (PVC) and dioctyphthalate (DOP) and stabilized with different amounts of metal soaps and zeolite.

The materials and the prepared PVC plastisols were characterized by spectroscopic and thermal analysis techniques. The gelation of the plastisols was observed by optical microscopy and the photographs were taken by a digital camera. The complete gelation was observed at 185 °C. The morphology of PVC plastigel films were studied by scanning electron microscope (SEM). SEM with energy dispersive X-ray (EDX) analysis was used to obtain elemental compositions in polymer and particle phases. The thermal stability of PVC plastigels in terms of color were obtained by heating them in a static vaccum oven. When zeolite was used as a primary stabilizer it prevented the early blackening of the film. Kinetic study of dehydrochlorination was determined by 763 PVC Thermomat equipment for unstabilized and stabilized PVC plastigels. When PVC plastigels were heated in PVC Thermomat in the presence of nitrogen gas, the conductivity of water which nitrogen gas was passed due to the evolved HCl, changed with respect to time. The period when conductivity starts to increase is called as induction time, and the period when the conductivity value reaches to 50 µS/cm is called as stability time. The induction and stability time values of unstabilized and stabilized PVC plastigel films were obtained at 140 and 160 °C. The stabilizing effect of zeolite on the increase in the induction period of the sample was considered the result from the absorption of HCl which was thought to reduce the autocatalytic effect of HCl evolved at the initial stages of dehydrochlorination. Since the induction time of the sample having 0.53% $ZnSt_2$ and 0.53% zeolite was higher than the PVC plastigels having only $ZnSt_2$ or zeolite the synergistic effect on thermal stability was observed at low levels of them.

ÖZ

PVC yüksek sýcaklýklarda (100 °C) hidrojen klorür (HCl) gazý çýkararak bozunur ve bu bozunma polimerin renginin sarýdan turuncuya daha sonrada kahverengi ve siyaha dönüþmesiyle birlikte gerçekleþir. PVC’nin bozunmasýný önlemek için ýsýl kararlý kýlýcýlar PVC’ ye eklenir. Bu çalýþmada, çinko stearat ($ZnSt_2$) ve doðal zeolitin PVC’nin ýsýl kararlýlýðýna sinerjistik etkisi incelenmiþtir. Bu amaçla PVC ve DOP’un karýþtýrýlmasýyla PVC plastisolleri hazýrlanmýþ ve bu karýþýmlara farklý miktarlarda metal sabunlarý ve doðal zeolit eklenmiþtir.

Bu proje kapsamýnda kullanýlan malzemeler ve hazýrlanan PVC plastisolleri spektroskopik ve termal analiz teknikleriyle karakterize edilmiºtir. PVC plastisollerin jelleþme davranýþlarý optik mikroskopla incelenmiþ ve farklý sýcaklýklarda mikro fotoðraflarý çekilmiþtir. Jelleþmenin 185 °C’ de çok kýsa sürede gerçekleþtiði gözlemlenmiþtir. PVC plastijellerin morfolojisi elektron taramalý mikroskobu ile çalýþýlmýþ, elementlerin polimer ve tanecik fazýndaki kompozisyonlarýný elde etmek için EDX analizi yapýlmýþtýr. Ayrýca filmler vakumlu etüvde 140 ve 160 °C’ de farklý sürelerde ýsýtýlmýþ ve zamanla renk deðiþimleri gözlemlenmiþtir. Zeolit tek baþýna ýsýl kararlý kýlýcýsý olarak kullanýldýðýnda filmin erken sürede kararmasýný önlemiþtir. PVC plastijellerin ýsýl kararlýlýðý ve bozunma reaksiyon kinetiði 763 PVC Thermomat cihazý ile çalýþýlmýþtýr. Isýl kararlýlýk, PVC plastijellerini PVC Thermomat cihazýnda ýsýtýp, azot gazýnýn geçtiði suyun iletkenliði ölçülerek saptanmýþtýr. PVC ýsýtýldýðýnda HCl gazý çýkararak bozunur ve HCl azot gazý ile suya taþýnýr ve su tarafýndan absorplanýr. Böylece suyun iletkenliði deðiþir. Ýletkenliðin artmaya baþladýðý süre indüksiyon zamaný, iletkenliðin 50 µS/cm’e ulaþtýðý süre kararlýlýk zamaný olarak tanýmlanýr. Bu çalýþmada PVC plastijellerin 140 ve 160 °C’ deki indüksiyon ve kararlýlýk zamanlarý bulunmuþtur. Zeolit tek baþýna ýsýl kararlý kýlýcý olarak PVC plastisole eklendiðinde indüksiyon süresinde artýþ olmuþ ve bu artýþ PVC ‘nin bozunmasýyla ortaya çýkan HCl gazýnýn zeolit tarafýndan absorblanmasýyla açýklanmýþtýr. Böylece oluþan HCl gazýnýn tekrar PVC’nin bozunma reaksiyonuna girip, bozunmayý katalizlemesi engellenmiþtir. %0.53 $ZnSt_2$ ve %0.53 zeolit içeren PVC plastijelinin indüksiyon süresi (1.25 s) sadece $ZnSt_2$ ve sadece zeolit içeren örneklerin indüksiyon zamanlarýndan daha yüksek olduðu için $ZnSt_2$ ve zeolitin PVC’nin ýsýl karalýlýðýna sinerjistik etkisi bu malzemelerden düþük oranlarda kullanýldýðýnda gözlemlenmiþtir.

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CHAPTER 1

INTRODUCTION

Poly (vinyl chloride) (PVC) has large and broad uses in commerce. It has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds. PVC finds use in construction, packaging, appliances and machines, medical and safety, automotive etc. PVC is clear, colorable, nontoxic when fabricated and produced by free radical polymerization.

Most of PVC applications require the use of additives, which provide flexibility of processing and different properties to final products. One of the most common PVC compounds is plastisol (Jimenez et al., 2000). PVC plastisol is a suspension of small particles of PVC resin in a plasticizer (mainly some long chain phthalate). Plastigels in the form of coatings, films, sheets, foams, and rotational casting are obtained by heating the plastisol. As the plastisol is heated, diffusion of the plasticizer into the particles of PVC resin take place (Baltacýoðlu et al., 1999). Gelation of a PVC plastisol is the process whereby absorption of the plasticizer by PVC particles, which is the first major consequence of heat treatment, brings about the formation of a relatively weal gel. Fusion is the process whereby, as a result of heating PVC particles are permeated by the plasticizer which they have entirely absorbed become fully merged to form a physically homogeneous plasticized PVC material. In general, the higher the computability of the plasticizer with the polymer in a plastisol brings about the easier and faster gelation and fusion. Therefore phthalates are generally used for this purpose (Titow, 1985).

One of the most serious problems for PVC processing and handling is the rather low thermal stability. The dehydrochlorination of PVC starts at about 100 °C and is the reason for discoloration, owing to the formation of polyene sequences. It is catalyzed by HCl evolved (autocatalysis), and also be promoted by other strong acids. So a number of chemicals can be used as stabilizers against these very undesirable degradation processes. The basic principles of stabilization against heat and light were developed between 1930 and 1950, but the search for more effective, less toxic, and environmentally friendly systems has been one of the most important tasks of the PVC industry up to now. The compounds used as heat stabilizers for PVC are lead compounds, organotin compounds, organic stabilizers, compounds of other metals (calcium, zinc, barium, aluminum and their composites),and inorganic stabilizers (zeolite and hydrotalcite). Metal compounds are used to displace the labile chlorine atom in PVC polymer chain by more stable groups. Zeolite and hydrotalcite are used as acid absorbers in PVC in order to absorb evolved HCl and other strong acids which catalyzed the dehydrochlorination of PVC.

Thermal stabilization of PVC can be determined by PVC Thermomat equipment. When PVC plastigels are heated in PVC Thermomat in the presence of nitrogen gas, the conductivity of water, which nitrogen gas is passed, changes with respect to time. The period when the conductivity starts to increase is called as induction time, and the period when the conductivity value reaches to 50 μS/cm is called as stability time. This value is the maximum acceptable level of degradation.

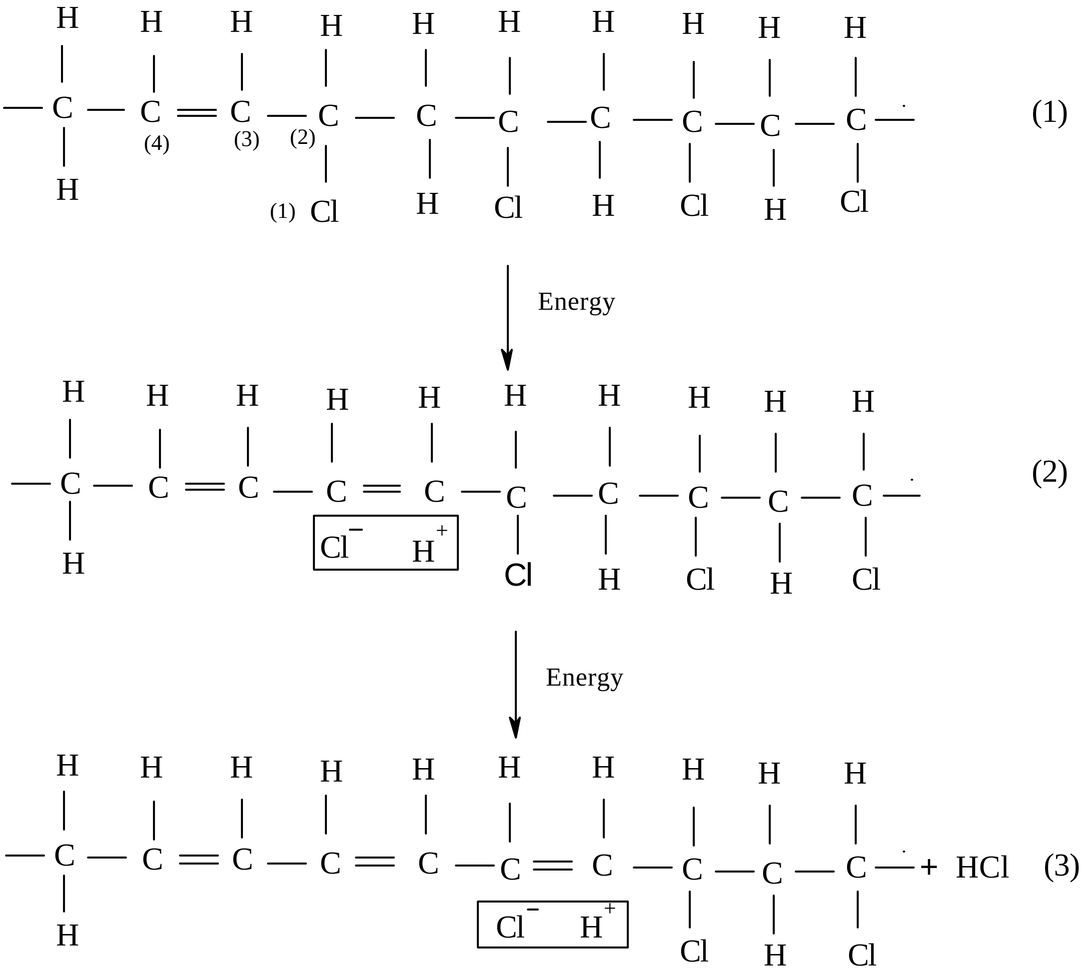
This study aims to investigate the synergistic effect of zinc stearate ($ZnSt_2$) and natural zeolite on PVC thermal stability. For this purpose, $ZnSt_2$ with high purity was produced by precipitation technique. Also clinoptilolite- rich natural zeolite from Gördes (Manisa) region was used as stabilizer for PVC.

CHAPTER 2

THERMAL DEGRADATION OF PVC

The main outward indicators of thermal degradation of PVC are the evolution of hydrogen chloride, development of color (from light yellow through reddish brown, to almost black in severe cases) and deterioration of physical, chemical and electrical properties.

It is widely accepted that dehydrochlorination (DHC) involves progressive unzipping of neighboring chlorine and hydrogen atoms along the polymer chain; a double bond is formed between the carbons to which the two atoms were originally attached. This constitutes an allyl chloride structure with (i.e. is in the 3,4 position) the next Cl down the chain, which is thereby strongly activated and so on (Titow,1985).



The development of color is attributed to the conjugated double bond systems formed in this process. The process starts with a chlorine atom activated by an adjacent allylic bond configuration where that is already present in mid-chain.

Dehydrochlorination can occur at only moderately elevated temperatures (about 100 °C). It is catalyzed by the HCl evolved (autocatalysis), and can also be promoted or initiated by other strong acids.

In addition to dehydrochlorination, thermal degradation of PVC polymer in the presence of oxygen also involves oxidation, with the formation of hydroperoxide, cylic peroxide, and keto groups, some of which can provide additional active sites for initiation of dehydrochlorination

Chain scission and cross-linking can also take place as degradation proceeds, both in air and in an inert atmosphere (although some investigators report no scission in nitrogen at 190 °C). These effects contribute to the general deterioration in properties.

If the thermal stability of PVC polymer or composition at a given temperature is defined in terms of time required for one of the main principles of degradation to reach a stated level and if the degradation is treated as a unified process, thermally activated in the classic manner, the appropriate Arrhenius-type relationship may be written in the form:

$$t = t_0 \; x \; exp(E/RT) \tag{4}$$

where ;
t is the duration of stability; t_0 is a constant; E is the activation energy for thermal degradation of PVC polymer in the conditions (and /or composition) concerned; R is the ideal gas constant; T is the absolute temperature.

Susceptibility to the thermal degradation varies with the process of manufacture of the PVC polymer and also with the source of supply. Other things being equal, the susceptibility increases (inherent stability decreases) in the sequence:

mass polymer $\longrightarrow$ suspension polymer $\longrightarrow$ emulsion polymer

Rate of dehydrochlorination can be determined by the conductivity of the solution where the evolved HCl gas is transferred. In ohmic material the resistance is proportional to the resistivity (ρ) measured in Ω.cm (in SI units Ω.m). Its inverse $K=\Omega.^{-1}$ is the conductivity. The unit of conductance is the Siemens ($S=\Omega.^{-1}$). The unit of conductivity is $S.m^{-1}$. Conductivity of an electrolyte solution depends on the number density of charge carriers (number of electrons z) and how fast they can move in the material (mobility U), concentration of the solution and the Faraday constant, so the conductivity can be found by the Equation 5.

$$K=F.\ \Sigma|Z_i|.\ C_i.\ U_i \qquad (5)$$

where ;

F=96485 (C/mol)

$|Z_i|$ = Total charge number

C_i.= Concentration of the solution (mol/m^3)

U_i= Mobility of ions. ($m^2/V.s$)

Mobility of ions (U_i) dissolved in water is the sum of electric mobilities of H^+ and Cl^- ions at 25 °C for HCl (Alberty,1987)

$$U_{H^+} = 36.25x10^{-8}(\frac{m^2}{V.s}) \qquad (6)$$

$$U_{Cl^-} = 7.913x10^{-8}(\frac{m^2}{V.s}) \qquad (7)$$

$$U_{HCl} = 44.163x10^{-8}(\frac{m^2}{V.s}) \qquad (8)$$

CHAPTER 3

THERMAL STABILIZATION OF PVC

3.1. Thermal Stabilization Theory

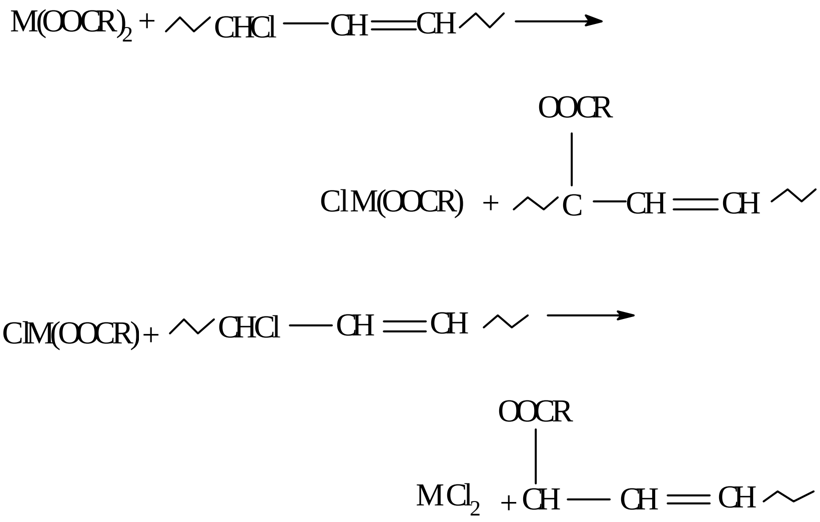
A stabilizer is used to increase of the chemical stabilization of PVC at the processing temperature of the material. An ideal stabilizer should ;

- have rapid binding of free HCl
- have high ability to replace labile Cl atoms with stable groups
- have saturation of double bonds
- have antioxidant action
- disrupt the chromophoric groups
- absorb the free radicals
- neutralize the impurities and degradation products
- have effective screening of UV radiation
- be readily dispersible in the PVC compound, and fully compatible with all its constituents even after prolonged service
- have no adverse effect on processing properties
- be equally effective in PVC resin of all types and from all sources
- be inexpensive and effective in small proportions.

The ideal stabilizer does not exist. However, many of the available stabilizers, and particularly composite stabilizer systems, can be highly effective in compositions and applications for which they are appropriate.

Commercial heat stabilizers in the market are actually synergistic mixtures of various compounds. The mixture has a better stabilizing effect than the pure substances. On the other hand, unknown composition of commercial heat stabilizers may cause drastic detrimental effect on degradation of PVC. The heat stabilizers and the PVC product having heat stabilizers should be handled with care considering their effect on human health (Gökçel et al.,1998).

According to Frye-Horst mechanism, the fatty acid salt of metal (II) ion M reacts with PVC by an esterifying displacement of chlorine. Stabilization arises from substitution of labile chlorine atoms with more stable carboxylate groups.



$$M(OOCR)_2 + \sim CHCl-CH=CH\sim \longrightarrow ClM(OOCR) + \sim \underset{}{\overset{OOCR}{\overset{|}{C}}}-CH=CH\sim$$

$$ClM(OOCR) + \sim CHCl-CH=CH\sim \longrightarrow MCl_2 + \overset{OOCR}{\overset{|}{CH}}-CH=CH\sim$$

3.2. Heat Stabilizers for PVC

3.2.1. Lead Compounds

These are either lead salts or lead soaps (salts with stearic acid). The main advantage of these old-established stabilizers is cost-effective good heat-stabilizing power, and particular suitability for use in electrical insulation. However, they are not suitable for clear compositions, where their toxicity presents a hazard, as, for example, in food-contact applications (e.g. packaging films, containers), products for medical use, or childrens’ toys (Titow et al.,1985).

The most important lead stabilizers are as follows;

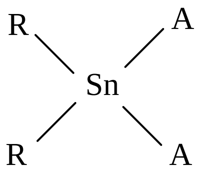
1. Basic lead carbonate (white lead)
2. Tribasic lead sulphate
3. Tetrabasic lead sulphate
4. Dibasic lead phophite
5. Lead silicate
6. Lead salicylate
7. Lead stearate
8. Dibasic lead stearate
9. Dibasic lead phthalate
10. Tribasic lead maleate
11. Tetrabasic lead fumarate

All lead compounds react with HCl and produce lead chloride. Also it is noted that bivalent lead possesses the chemical properties needed to replace labile chlorine atoms. Very important advantage of lead stabilizers is that the lead chloride produced from the stabilization reaction, does not influence the rate of PVC dehydrochlorination. (Göktepe et al.,1996)

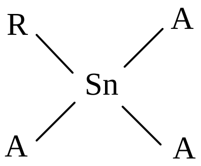
3.2.2. Organotin Compounds

All organotin stabilizers are derived from tetravalent tin. It is characteristic of them that at least one carbon atom is directly connected with a tin atom. Usually this is a straight-chain alkyl group.

Organotin stabilizers are mainly compounds of the general formula I, with some of those represented by formula II also in use.



I



II

Here R represents the ester or alkyl group and A represents the susbstituent group.

Alkyltin stabilizers in which the A substituents are mercapto compounds are usually reffered to as thiotin stabilizers, and those with A substituents of the sulphur-free carboxylic acid or ester type as tin carboxylates; the most numerous members of this latter group among commercial stabilizers are dibutylin carboxylates (Titow et al.,1985).

Organotin stabilizers can be used across a wide range of applications in vinyl chloride homo- and copolymers. But they set off a typical unpleasant odor during processing and in the finished product.

3.2.3. Organic Stabilizers

Organic stabilizers include compounds used in PVC stabilization that resemble each other neither in chemical structure nor in mechanism of the action. Only two common group features are shared by these stabilizers: they do not contain any metal atoms, and they are with some exceptions, secondary stabilizers. Most are not effective when used alone, indeed, they may even accelerate the rate of hydrochlorination: for this reason they are called secondary stabilizers, which enhance the performance of primary stabilizers.

The group includes the following chemicals:

1. Phospides
2. Epoxidized oil and fatty acid esters
3. Nitrogen-containing stabilizers
4. β-diketones
5. Polyols
6. Phenol derivatives

Benaniba et al., 2003 have studied the stabilization of PVC by epoxidized sunflower oil in the presence of zinc and calcium stearates. Table 3.1 gives the values of induction times and of initial rates of dehydrochlorination. These rates were computed from the slopes of kinetic curves in the first step of dehydrochlorination which were before the consumption of stabilizers. The addition of epoxidized sunflower oil to Ca/Zn increases the induction time and decreases the rate of dehydrochlorination. The effectiveness of epoxidized sunflower oil depends on the amount of epoxy groups in the molecule. The higher amount of epoxy groups the better is the effectiveness.

Table 3.1: Dehydrochlorination data at 170 °C for PVC films containing various ratios of Ca / Zn in the absence of and the presence of epoxidized sunflower oil (Benaniba et al.,2003).

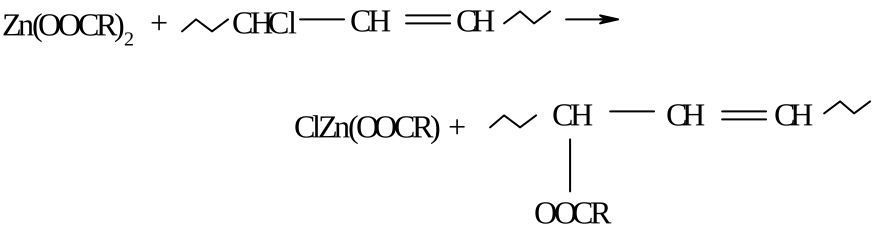
Stabilizer system	**Induction time (min)**	**Rate of DHC (mmolHCl/g PVC min)**
Ca/Zn(1/1)	23	0.12
Ca/Zn(1/2)	10	0.43
Ca/Zn(2/1)	12	0.38
Ca/Zn(1/1)-ESO	38	0.04
Ca/Zn(1/2)-ESO	13	0.13
Ca/Zn(2/1)-ESO	24	0.08

This stabilizing effect of epoxidized sunflower oil on the thermal degradation of PVC is a result of the facile reaction of HCl with epoxy groups to form chlorohydrins which is thought to reduce the autocatalytic effect of the HCl evolved at the initial stages of dehydrochlorination. Furthermore, the esterification and etherification reactions which occur with instable allylic chlorine groups in PVC provide an explanation for the very low values of the initial rates of dehydrochlorination observed when epoxidized sunflower oil is used in combination with Ca/Zn stearates.

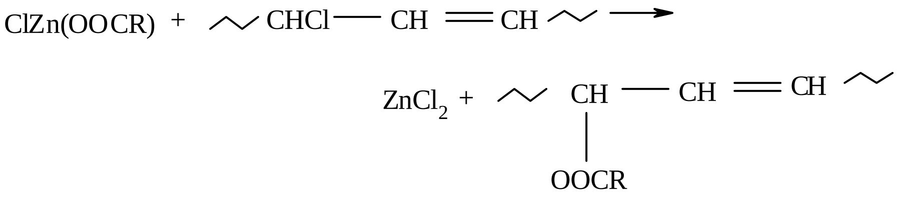
3.2.4. Metal Soaps

Apart from those of lead and thin, certain compounds of the following metals are of the practical interest as stabilizers for PVC: lithium, magnesium, aluminum, sodium, potassium, calcium, zinc, strontium, cadmium, antimony and barium (Titow et al., 1985).

Metal soaps are the most used heat stabilizers for PVC. The carboxylate group of the metal salt substitutes the tertiary or allylic chlorine atoms and stops the initiation of dehydrochlorination according to well known Frye and Horst mechanism. The parallel reactions that occur during dehydrochlorination of PVC in the presence of metal soaps are:



$$Zn(OOCR)_2 + \sim CHCl-CH=CH\sim \longrightarrow ClZn(OOCR) + \sim \underset{\displaystyle OOCR}{\underset{|}{CH}}-CH=CH\sim$$



$$ClZn(OOCR) + \sim CHCl-CH=CH\sim \longrightarrow ZnCl_2 + \sim \underset{\displaystyle OOCR}{\underset{|}{CH}}-CH=CH\sim$$

One group of commercially available PVC heat stabilizers are Ca/Zn stabilizers. Although these stabilizers are more expensive and less effective than many other stabilizer systems, they find use in food packaging materials, children’s toys and bottle seals.

According to the Frye-Horst mechanism the fatty acid salt of Zn reacts with PVC by an esterifying displacement of chlorine. Stabilization arises from substitution of labile chlorine atoms with more stable carboxylate groups.

The progressive dehydrochlorination reaction is prevented in this way, but the zinc chloride ($ZnCl_2$), produced as a result of the esterification reaction, will cause further rapid degradation. This problem is solved by the synergistic effect of combining alkaline earth (Ca) carboxylates with covalent metal carboxylates. Alkaline earth carboxylates undergo ester exchange reactions with covalent metal chlorides, thus regenerating the covalent metal carboxylates.

$$ZnCl_2 + Ca(OOCR)_2 \longrightarrow Zn(OOCR)_2 + CaCl_2$$

Unlike the covalent metal chloride, alkaline earth chlorides do not promote dehydrochlorination. Thus the alkaline earth carboxylates do not act as primary stabilizers of PVC resin but serve to regenerate the active stabilizer and remove the potentially destructive effect of the covalent metal chloride (Vrandeèiæ et al.,2000).

Benavides et al., 2001 studied the degradation of PVC and mixtures with $CaSt_2$ and $ZnSt_2$ at different temperatures (160,170,180 and 190 °C). When the degradation was followed by the curves of HCl evolution represented in Fig.3.1, a small induction time to degradation of PVC was observed as seen in Fig.3.1a, being longer for lower temperatures. The total amount of HCl evolved took the axis up to 0.2 V of potential in all cases, indicating that the temperature does not influence it, only the rate at which it was evolved. Fig.3.1b shows the traces obtained for the mixture of PVC and $CaSt_2$, where a long induction time to degradation is easily observed, especially for lower temperatures. The rate of fast dehydrochlorination, after the induction period, is also higher for high temperatures. The total amount of HCl evolved was about the same as in PVC alone. When PVC was mixed with $ZnSt_2$ (Figure 3.1c), the traces in the induction time were very stable, indicating the power of this soap to inhibit dehydrochlorination, but as soon as this was finished, HCl evolved instantaneously. The amount of HCl evolved was higher than previously since it reached to more than 0.25 V, for all temperatures.

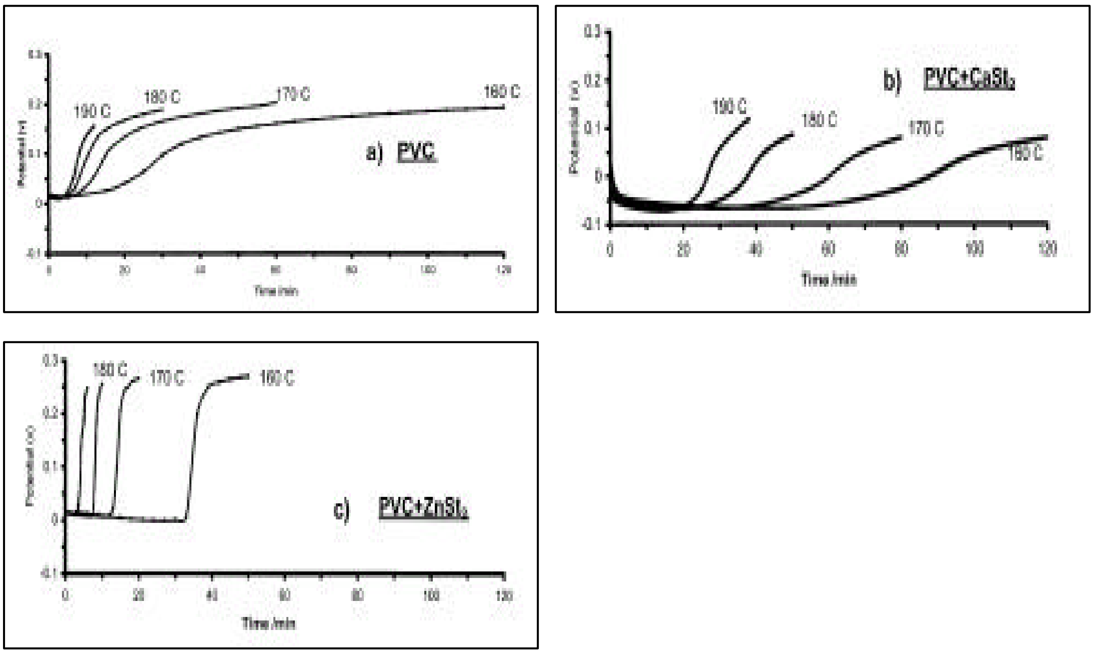


Figure 3.1. HCl evolution from mixtures with degradation time at different temperatures (Benavides et al., 2001)

Ulutan, 2003 studied the influence of additional thermal stabilizers on the reprocessing of postconsumer poly (vinyl chloride) bottles. According to this study, calcium and zinc stearates have worked well in combination with epoxy soy bean oil to prevent degradation and dioctyl phthalate was an adequate plasticizer for reformulating PVC resin that was cut out of label-free parts of water bottles. The effectiveness of the reformulating has been justified with spectroscopic, calorimetric, and weight-loss measurements after various heat treatments. It was observed that only after high-temperature treatments for long times had a small amount of decomposition been detected during UV and IR investigations.

3.2.5. Inorganic Stabilizers

Since heavy metal compounds such as cadmium stearate and lead stearate have some toxic effects, inorganic stabilizers such as hydrotalcite and zeolite are required for stabilization of PVC due to environmentally aspects. Therefore, the use of layered double hydroxide (LDH) with the general formula

$$\left[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2\right]_{layer}\left[A^{y-}_{x/y}(nH_2O)\right]_{interlayer} \tag{14}$$

has been proposed and tested by industrial manufacturers of stabilizers like Kyowa Chemical Industries (Miyata, 1981; Kyowa, 1986). The crystal structure of the hydrotalcite-like compounds is shown in Fig. 3.2. The stabilization activity results from the capacity of the layered double hydroxides (LDHs) to react with the HCl formed during degradation of PVC. There are at least three different possibilities to explain HCl absorption of hydrotalcite like substances, namely:

1. The HCl reacts just with the anion, e.g. CO_3^{2-} or OH^- located as counterion between the cationic LDH layers .
2. The HCl reacts with the LDH layers only
3. The HCl reacts with both the LDH and the counterions between the layers.

A linear relationship between HCl-capacity of LDHs with different counterions and their action as heat stabilizer in PVC were found (Ven et al., 2000).

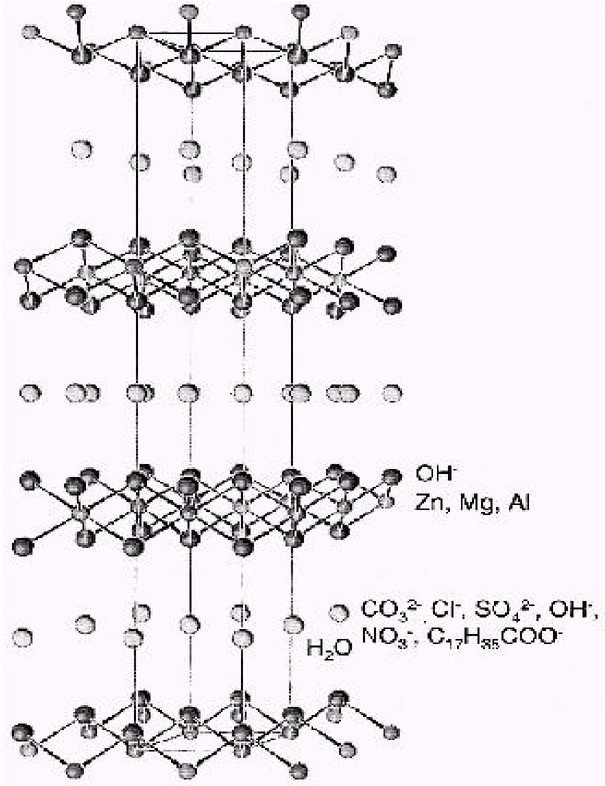


Figure 3.2: Crystal structure of the hydrotalcite-like compounds.
(Ven et al., 2000)

3.2.6. Synergism between Zinc Stearate and Natural Zeolite

The addition of heat stabilizers improves the thermal stability of polymers. One group of commercially available PVC heat stabilizers are metal soaps. Although these stabilizers are more expensive and less effective than other stabilizer systems, they find use in food packaging materials, children's toys and bottle seals (Vrandeèiæ et al., 2001).

When $ZnSt_2$ is used as a heat stabilizer for PVC, the effective rate constant of dehydrochlorination increased with increasing $ZnSt_2$ concentration. $ZnCl_2$ is produced at the end of dehydrochlorination reaction. $ZnCl_2$ and the evolved HCl increase the rate of the reaction since they have catalytic effects. Stabilizers that irreversibly bond HCl should be used to eliminate this auto-catalytic process. Heavy metal compounds or

metal soaps or salts are used for this purpose up to now. However, alternatives such as zeolite and hydrotalcite are required due to environmental aspects.
Zeolite is used as an acid absorber in PVC. It has been suggested that the acid absorbers that are effective as stabilizers form addition complexes at degrading sites, tending to deactivate such sites and capture catalytic, highly mobile HCl before elimination of further HCl occur. When zeolite is used as a primary stabilizer, the process stability is long, but color hold poor. This problem has been corrected in practice by combination with zinc carboxylates. Acid absorbers coated with zinc carboxylates are useful in flexible PVC compounds (Grossman, 2000).

Ertan et al., 2003 have investigated the chemical behaviour of natural zeolite from Gördes in aqueous medium. It was observed that pH values of the solution increased with time and this proved that depending on the amphoteric character of natural zeolite, it had a tendency to neutralize the acidic medium.

In this study, zeolite was used to neutralize of the evolved hydrogen chloride gas and metal soaps were used to replace the weakly bonded labile chlorine atoms by substituents which were of greater stability.

CHAPTER 4

PVC PLASTISOL AND PVC PLASTIGEL

4.1. Gelation and Fusion Behaviours of PVC Plastisol

PVC plastisols are suspensions of fine particles of PVC emulsion resins in a plasticizer. Plastisols are used in a growing number of applications (Beltran et al., 1997). Some of the application areas are:

-Construction (window seals, window screens, cable sheating, electrical wire insulation)
-Packaging (meat wrap, shrink wrap)
-Appliances and machines (refrigerator door seals, electrical wire insulation, telephone cords)
-Medical and safety (blood bags, goggles, gloves, aprons, tubing etc.)
-Automotive (dash boards, coated fabrics, handles, side panels etc.)
-Miscellaneous (room dividers, briefcases, table cloths, shower curtains etc.)

All the industrial processes for plastisols involve the heating of the platisol in an oven at about 180-200 °C, where the plastisol undergoes two processes known as gelation and fusion (Garcia et al., 1998). The stages of plasticization can be summarized as follows;

1. Irreversible uptake of plasticizer into the porous resin
2. Absorption of the plasticizer, during which the total resin-plasticizer volume may decrease although the resin particles swell slowly on the outside.
3. Diffusion of the plasticizer within the particles with little or no volume change, but involving high activation energies. At this stage the plasticizer is probably present as clusters of molecules between bundles of polymer segments or molecules.
4. The final step of plasticization when plasticizer molecules penetrate the bundles of polymer molecules so that they are no longer rigidly held together but behave as a polymer in its rubbery than glassy state (Titow, 1985).

Beltrán et al., 1997 have studied the FTIR spectrum of the PVC, DOP (di-2-ethylhexyl phthalate) and PVC plastisol which was prepared by 65 parts per hundred resin (phr) DOP. The spectra can be seen in Fig.4.1. The bands more characteristic of the spectrum of the resin are those in the region of 600-700 cm^{-1}, corresponding to C-Cl stretching vibrations. These bands are of complex origin and depend on the conformational structure of the polymer and on the spatial position of the atoms surrounding the C-Cl bonds. The rest of the bands of the spectrum correspond to different C-C and C-H vibrations, in some cases increased by the vicinity of chlorine atoms. The spectrum of the plasticizer shows the typical doublet of the phthalates at 1580-1600 cm^{-1}. The bands corresponding to the carbonyl and ester group, as well as those corresponding to the aromatic and aliphatic C-H bonds can also be observed. In the case of plastisols the spectra are almost identical to those of the plasticizer. The contribution of the resin to the spectrum of the plastisol is not very marked, although it can be clearly observed in the two bands at 1427 and 1435 cm^{-1}, corresponding to methylene groups, as well as in the 600-700 cm^{-1} zone, corresponding to the different vibration modes of the C-Cl bonds, all of them exclusively due to the resin. In other zones, the spectra of the resin and the plasticizer overlap, and the contribution of the resin is much less evident. This is the case of the zones between 3100-2800 and 1350-1150 cm^{-1}.

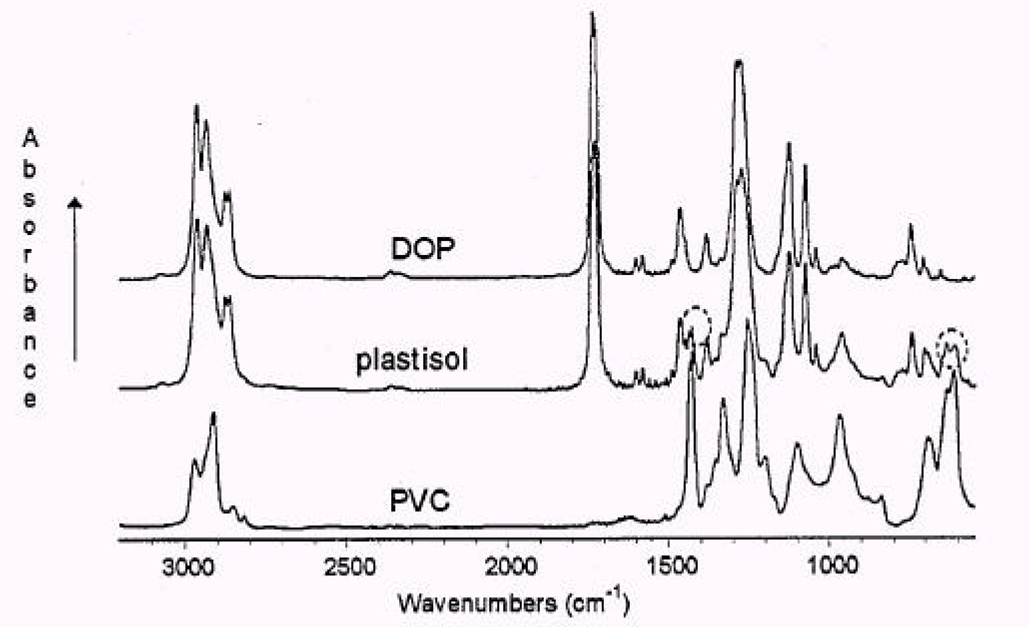


Figure 4.1. FTIR spectrum of PVC resin Etinox 450 (pressed disc), the DOP plasticizer and the plastisol with 65 phr of DOP (Beltran et al.,1997).

Beltrán and Marcilla (1997) found by TG that the evolution of the plasticizers from the plastisol samples took place at temperatures somewhat higher than from samples where the contact between the PVC and the plasticizer was avoided. The plasticizer is adsorbed by the resin in the plastisols during the gelation process, consequently delaying its evolution. On the other hand, the decomposition of the PVC from plastisol samples occurs at temperatures lower than those when the PVC and the DOP are separated in the sample holder. It was concluded that the presence of the DOP accelerates the process of decomposition of the PVC.

4.2. Kinetic Models for Degradation of PVC Plastisol

Phthalate plasticizers are thermally degraded from 200 °C on. However, when they are included in a polymer matrix, the evaporation of plasticizers is shifted to higher temperatures. It has been suggested that their thermal degradation lead first to the formation of monoester and olefins by a *cis*-elimination mechanism, and secondly to the cleaving of the monoester into phthalic anhydride and alcohol by a scission mechanism (Jiménez et al.,2000).

Jiménez et al. used thermogravimetric analysis (TG) to study the degradation kinetics of industrial PVC plastisol. The model parameters, such as activation energies and pseudo orders of reaction, were calculated using a non-linear regression analysis. A dynamic test in nitrogen at 10 °C/min of a PVC DEHP (di-(2-ethylhexyl)-phthalate) (70-30%) was reported in Fig.4.2.Two different processes of the degradation of plastisols could be observed. The peak with two maximums, the first at 270 °C and second at 300 °C represented the first degradation step, which includes dehydrochlorination reaction. The second step of the degradation corresponded to the peak having a maximum at 450 °C, which was related to the carbonization process. The models that were proposed in this study were related to the study area indicated in Fig.4.2.

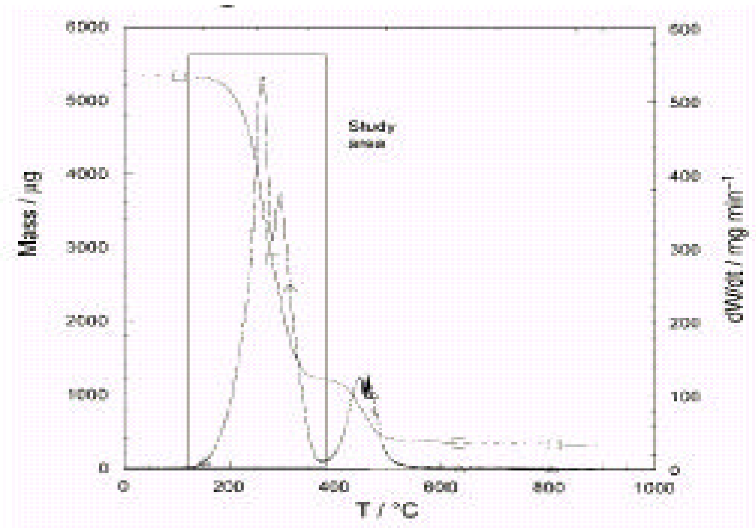


Figure 4.2. Dynamic TG and DTG curves at 10 °C/min of PVC:DEHP (100:70) plastisol (Jimenez et al.,2000)

The degree of reaction during both, the isothermal and the dynamic, tests was obtained applying the following equation, which assumes a linear relation between degree of reaction and mass loss:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \qquad (15)$$

Where;

α is the degree of reaction, W_0 is the initial mass, W is the actual mass, W_f is the residual mass obtained during each test.

A general kinetic model could be represented by the following expression:

$$\frac{\partial \alpha}{\partial t} = K(T)\, f(\alpha) \qquad (16)$$

The term K(T) is a function of the temperature, and its general form is an Arrhenius type expression:

$$K(T) = K_0 \exp\left(-\frac{E_A}{RT}\right) \qquad (17)$$

The shape of the reaction rate curves and the considerations about the maximum isothermal degree of reaction brought to a definition of the following models for the two indicated processes:

$$\frac{d\alpha}{dt} = K(T)(1-\alpha) \tag{18}$$

$$\frac{d\alpha}{dt} = K(T)\alpha^{m}(1-\alpha)^{n} \tag{19}$$

Equation (18) was related to the evaporation of the plasticizer, while Equation (17) was related to the dehydrochlorination reaction. The overall kinetic equation proposed for the degradation of plastisols has to take into account the fact that these two processes occurred simultaneously. Therefore a parallel kinetic model was proposed.

$$\alpha = y\alpha_1 + (1-y)\alpha_2 \tag{20}$$

where α_1 and α_2 referred to the degrees of reaction of the processes represented by Equations (15) and (16) respectively and y was a mass factor. An expression for the rate of reaction was obtained by the time derivative of Equation (20):

$$\frac{\partial\alpha}{\partial t} = y\frac{\partial\alpha_1}{\partial t} + (1-y)\frac{\partial\alpha_2}{\partial t} \tag{21}$$

Each α was calculated from TG data obtained by the integration of the peaks represented in Fig.4.3.

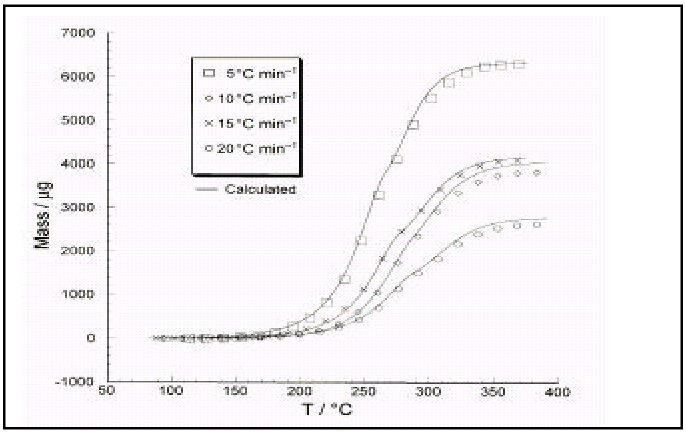


Figure 4.3. Integration of DTG curves for the calculated and experimental data.

The values of the activation energies and the order of reactions for Equations (18) and (19) were calculated using Friedman analysis. The order of reaction and the pre-exponential factor of both equations were obtained using a non-linear regression program and were reported in Table 4.1.

Table 4.1. Results of kinetic analysis (Jimenez et al., 2000)

	E_A/kj mol^{-1}	n	m	ln K
Evaporation	111±10	1.00	0	21.7
Degradation	145±2	1.73	0	25.8

The results of the kinetic analysis, in terms of degree of reaction vs. temperature were reported in Fig.4.4.

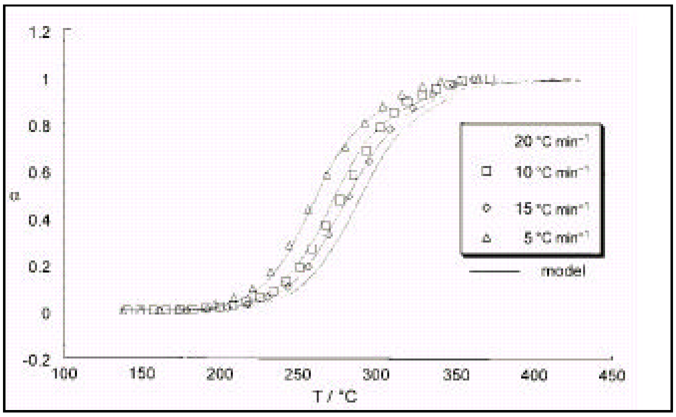


Figure 4.4. Comparison between the model and the experimental data on DEHP 30%.

Beltrán and Marcilla (1997) proposed two groups of kinetic models in order to explain the thermal decomposition of PVC plastisol. Both groups consider that the plasticizer volatilizes from the sample following a single reaction. One of the models considers that PVC decomposition takes place via two sets of parallel/consecutive reactions with an intermediate species that undergoes further decomposition. The other model considers that the interaction between the plasticizer and the resin leads two differentiated fractions in PVC with different levels of plasticization, both decomposing at well differentiated temperatures.

Baltacýoðlu and Balköse (1999) calculated the rate constant of dehydrochlorination reaction by using the concentration of the polyene sequences. 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 $\mathrm{H{-}({-}CH{=}CH{-})_n{-}H}$ or $\mathrm{CH_3{-}({-}CH{=}CH{-})_n{-}CH_3}$. Table 4.2 shows the number of produced conjugated double bonds, wavelength where the strongest absorption occurs and the related absorption coefficients.

Table 4.2: Molar absorption coefficient of H-(-CH=CH-)$_n$-H

(Shindo et al.,1972, Sondheimer at al.,1961)

Number of conjugated double bonds n	Wavelength where the strongest absorption occurs λ	Molar absorption coefficient ε_λx10^{-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

The distribution of values of n in the dehydrochlorinated PVC was determined from the absorption spectra of dehydrochlorinated PVC with the data given in Table 4.2. The concentration of polyene sequences, C_n (mol/l), is given by

$$C_n = A.(\boldsymbol{e}_l \ / \ d) \tag{22}$$

where A is the absorbance at wavelength λ, ε_λ is the molar absorption coefficient, and *d* is the thickness of the plastigel films (cm).

The mol fraction of polyene sequences containing *n* conjugated double bonds were determined from C_n as

$$N_n = C_n \ / \ C \tag{23}$$

where *C* is the concentration of vinyl chloride repeat units in PVC plastigel. The mol fractions of polyene sequences and of double bonds, N_T *and* N_D, are given by

$$N_T = \Sigma N_n \tag{24}$$

$$N_D = \Sigma n.N_n \tag{25}$$

The mol fractions of conjugated double bonds formed by dehydrochlorination were calculated using their UV spectra of the films for plastigels having different composition. The total number of double bonds of the polyene sequences was practically equal to the HCl molecules split off. Since thermal dehydrochlorination is a first order reaction, Equation (26) was obtained;

$$-\ln(1 - N_D) = k_1.t \tag{26}$$

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

$$N_D = k_1.t \tag{27}$$

Also N_D vs. t lines was plotted and the rate constant k_1 of each sample were determined the slopes of the first 45-min part of the lines. The rate constants (k_2) of the autoaccelerated reaction due to $ZnCl_2$ accumulation or HCl formation were 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 4.3.

Table 4.3. Determined rate constants for steps of the suggested reaction mechanism (Baltacýoðlu and Balköse, 1999)

Content of Plastigel	k_1x10^4 (min^{-1})	k_2 (min^{-1})
Control	1.62	6.60
2.5 phr $ZnSt_2$	0.77	
5 phr $ZnSt_2$	2.11	
5 phr ESO	0.47	0.47
5 phr ESO and 2.5 phr $ZnSt_2$	0.70	4.20
5 phr ESO and 5 phr $ZnSt_2$	can not be determined	

4.3. Yellowness Index of PVC Plastigels

Yellowness index is a measure of color change when compared with a white standard. Yellowness index of the plastigels were calculated by using their tristimulus (L, a, b) values. This index can be calculated by using Equation (28)

$$YI = \frac{(0.72xa + 1.79xb).100}{L} \tag{28}$$

The positive values of yellowness index point out the yellowness of the material and the minus values point out the blueness of the material. (Arý andÝçten., 1989)

Benavides et al. (2001) obtained the change of yellowing index for PVC and its mixtures at different temperatures as seen in Fig.4.5. Fig.4.5a shows the results for PVC alone, where the highest yellowing index (YI) obtained sees to depend on the temperature of degradation. For 160 °C maximum value of 80 was obtained, while for 180 and 190 °C it went to top (120 and 180). The rate is also higher for high temperatures. On the other hand, the mixture of PVC+ $CaSt_2$ (Fig.4.5b) gives the highest value of YI for the temperature of 160 °C. Fig.4.5c shows the YI traces for the mixture PVC+ $ZnSt_2$, where the highest value obtained is the same for the four temperatures. The rates of YI increments are higher for high temperatures.

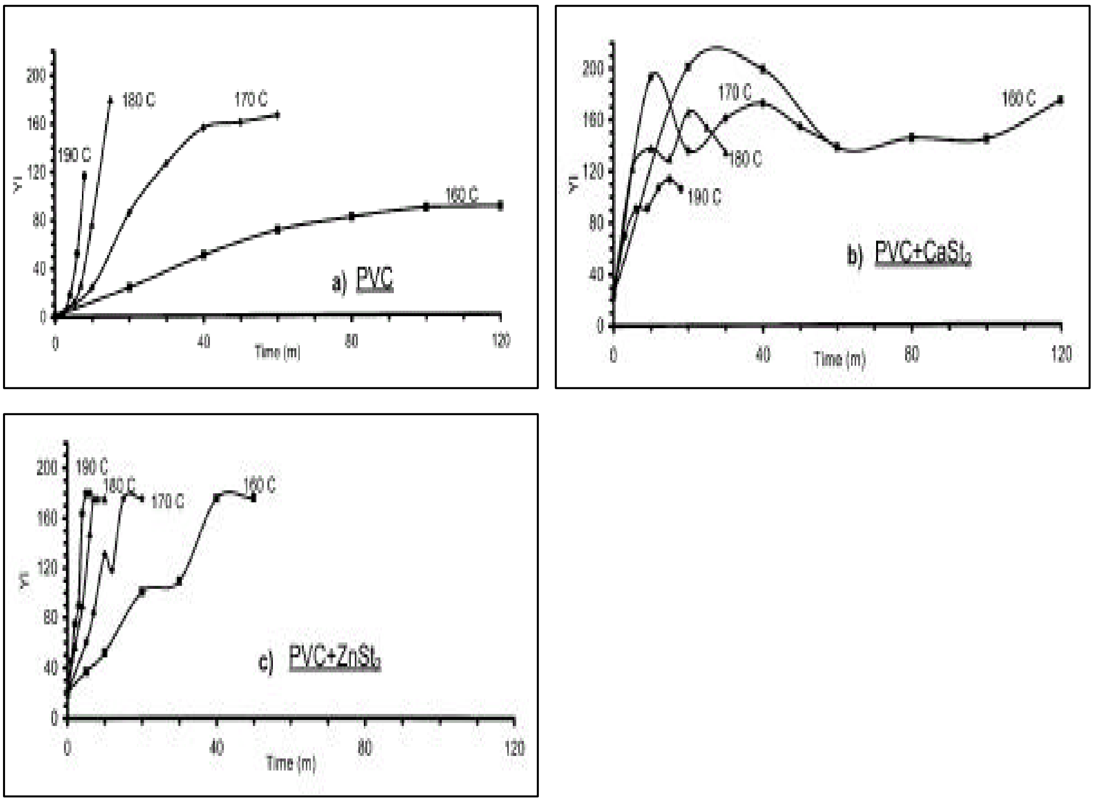


Figure 4.5. Yellowing index for mixtures with degradation time at different temperatures. (Benavides et al., 2001)

CHAPTER 5

MATERIALS AND METHOD

5.1. Materials

In this study, PVC plastisol films were prepared to determine the heat stabilization of PVC. Poly vinyl chloride, dioctylphthalate (DOP), viscobyk 5025, and different amounts of zinc stearate ($ZnSt_2$), calcium stearate ($CaSt_2$) and natural zeolite were used to produce PVC plastisol. Plastisol mixtures having composition given in Table 5.1 were obtained by mixing the additives and PVC plastisol.

The PVC used in this study was the product from Petkim (Petvinil P.38/74). It was emulsion type PVC.

Dioctylphthalate (DOP) was used as a plasticizer and the product of Merck. Its density is 0.98 g/ml and molecular weight is 390.54 g/mol. Its purity is greater than 98%. The structure of DOP is shown in Fig.5.1.

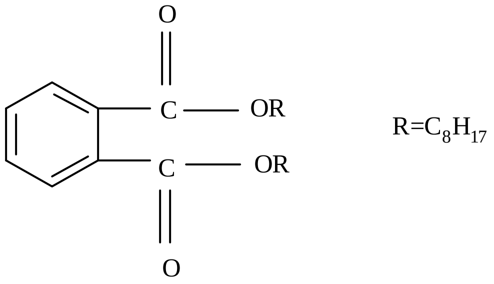


Figure 5.1: The structure of DOP.

Viscobyk 5025 was used as a wetting agent. It was produced by BYK Chemie and the mixture of aliphatic hydrocarbons or carboxylic acid derivatives. This material was used to reduce the viscosity of the liquid phase of the plastisol.

$ZnSt_2$, $CaSt_2$ and natural zeolite were used as heat stabilizers for PVC. $ZnSt_2$ and $CaSt_2$ were produced by precipitation technique, by Gönen (2003). Melting point of

$ZnSt_2$ was 120-121 °C. Melting point of $CaSt_2$ is 123.15 °C. Zeolitic tuff 1 rich in klinoptilolite mineral from Gördes in Western Anatolia was used. It was characterized in a previous study (Metin, 2002), used after grinding and using the fraction passing through 45 μm sieve.

5.2. Method

PVC plastisols having two different DOP concentrations were prepared. In the first part of the project, the plastisol was prepared by using 60 per hundred parts (phr) DOP (wt.33% DOP) for each 100 parts of PVC resin. PVC, DOP and the stabilizers were mixed in a mortar. The mixture was gelled in 10 cm diameter petri dishes in a static vacuum oven at 140 °C for 15 min. The gelled plastigels were used to test by PVC Thermomat. Because of the high viscosity of PVC plastisol and, the samples were not appropriate to characterize them by spectroscopic techniques.

The plastisol was prepared by using 80 per hundred parts (phr) DOP (wt.43% DOP) for each 100 parts of PVC resin. DOP, PVC and viscobyk 5025 were stirred by a mechanical mixer (IKA Labortechnik) at 20 °C for 30 minute. The additives were added to PVC plastisol samples and stirred by a glass rod.

Table 5.1. The weight %of additives used to stabilize the PVC plastisols

Plastisols contain 33 % DOP		Plastisols contain 43 % DOP			
Additive wt.%		Additive wt.%		Additive wt.%	
$ZnSt_2$	Zeolite	$ZnSt_2$	Zeolite	$CaSt_2$	Zeolite
-	-	-	-	-	-
2.44	-	2.11	-	2.11	-
-	1.84	-	2.11	-	2.11
-	2.44	0.53	0.53	0.53	0.53
0.62	0.62	1.05	1.05	1.05	1.05
1.22	1.22	1.56	1.56	1.56	1.56
2.44	2.44	2.07	2.07	2.07	2.07

Preparation of Plastisol Films

The PVC plastisol with 33% DOP was spread on microscope slides by a spatula.

The plastisol with 43% was spread onto a piece of cardboard then a film applicator (Sheen 113 N) was used to obtain plastisol films. The films were prepared by 90 ì-applicator (Fig.5.2)

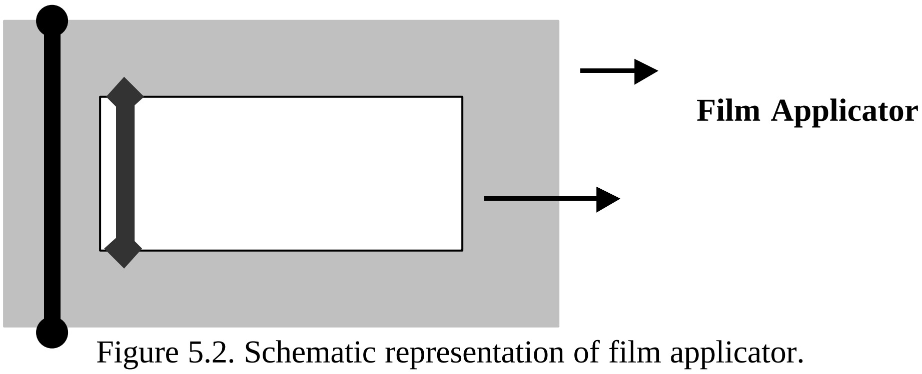


Figure 5.2. Schematic representation of film applicator.

Preparation of Plastigel Films

All of the prepared plastisol films were gelled for 15 min in an air-circulating oven (EV 018) at 140 °C ± 3 °C. Since the plasticizer diffused into the particles of PVC resin, the films were gelled and the plastigel sheets plastigel films were obtained. The thicknesses of the films were determined by using a micrometer (Mitutoya).

Static Oven Test

The prepared plastigel films were heated in an air-circulating oven at 140 and 160 °C for 15, 30, 45, 60, 75, 90 min in order to observe the change in the color of the films.

Thermal Stability Test

Thermal stability test was performed by 763 PVC Thermomat. It is equipped with two heating blocks each with four measuring positions. Each block can be individually heated, therefore two sets of four samples can be measured at two different temperatures or eight samples can be measured at the same temperature. Also the measurements at the individual measuring positions can be started individually. The films were cut into small squares having a side of 0.5 cm and 0.5 g. of samples were put into reaction vessel. The heating blocks of PVC Thermomat were heated to 140 and 160 °C. The reaction vessels that contained PVC plastigel films were placed into the heating blocks. As shown in Fig.5.3, HCl formed was taken up by a nitrogen gas stream and transferred into the measuring vessels. The deionized water absorbed HCl gas and the change in conductivity of the solution was determined with respect to time by the conductimeter. Therefore the decomposition process was monitored by measuring the conductivity of aqueous HCl solution.

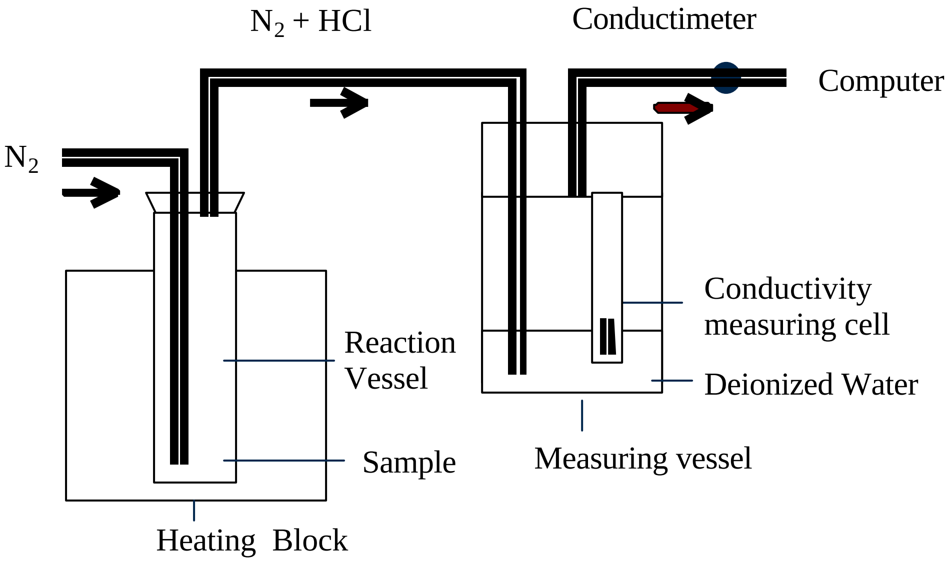


Figure 5.3. The measuring arrangement of 763 PVC Thermomat.

Study of the Films with FTIR, UV Spectroscopy and Spectrocam

FTIR spectra of PVC, viscobyk 5025 DOP, $ZnSt_2$, and $CaSt_2$ were obtained by KBr disc method.

The films having 43% DOP gelled at 140 °C for 15 min and heated at 160 °C for 90 min were studied by using FTIR spectroscopy (Shimadzu 8601 PC) and UV spectroscopy (Shimadzu UV-2450). Also the L, a, b values of these films were determined by Avantes Spectrocam.

Study of the Films with Scanning Electron Microscopy and Optical Microscopy

The cross section areas of the PVC films which were gelled at 140 °C for 15 min and heated at 160 °C for 90 min were studied by scanning electron microscopy (Philips, XL-30SFG). The elemental analysis of the particle and polymer phases was performed.

PVC plastisols were heated up to 200 °C in the hot stage controlled by a temperature controller (INSTEC STC 200) and the gelation of the plastisols were observed by optical microscopy (Olympus CH40) and the photographs were taken by a digital camera (Camedia C-4040).

TGA Study

TGA curves of PVC plastigels which were gelled at 140 °C for 15 min were obtained by heating the samples to 600 °C, with 10 °C/min heating rate under N_2 atmosphere. TGA studies were performed by Shimadzu TGA-51.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Characterization of the Materials

The FTIR spectrum of PVC produced by Petkim was shown in the Fig.6.1. The bands in the region of 600-700 cm^{-1} are corresponding to C-Cl stretching vibrations. These bands are of complex origin and depend on the conformational structure of the polymer and the spatial position of the atoms surrounding the C-Cl bonds. The band at 2920 cm^{-1} is corresponding to $–CH_2$- and –CH- stretching groups. The two bands at 1257 and 1321 are corresponding to –CH in –CHCl stretching groups. These characteristic peaks are consistent with the literature (Göktepe, 1996). The bands at 1540 cm^{-1} and 1740 cm^{-1} could be due to the presence of soaps and plasticizers present in emulsion type PVC.

TGA curve of PVC produced by Petkim is shown in Fig. 6.2. It was observed that the thermal degradation of PVC in the range of temperature was a two-step process. The first step (up to 350 °C) mainly involved dehydrochlorination of polymer resulting in the formation of conjugated double bonds. In the second step (up to 562 °C) the degradation of polymer which had already become the dehydrochlorinated product continued with cracking and pyrolysis to low hydrocarbons of linear or cyclic structure. The residual mass was found as 35.06% at 400 °C. Besides this no material remained at the end of 562 °C. This result is consistent with literature (Benaniba et al., 2001).

Figure 6.3 shows the FTIR spetrum of natural zeolite (Gördes1). The characteristic peaks of natural zeolite at 450 and 609 cm^{-1} were assigned to the internal and external Si (or Al)-O double ring respectively. H_2O bending vibration band was observed at 1627 cm^{-1}. At 3400 cm^{-1} hydrogen bonded OH stretching and 3700 cm^{-1} isolated OH stretching vibration bands are present.

The FTIR spectrum of viscobyk 5025 is shown in Fig.6.4. The peaks were assigned to the aliphatic hydrocarbons and carboxylic acid esters.

Fig. 6.5 shows the FTIR spectrum of $ZnSt_2$ which was produced by precipitation process. The characteristic peaks of $ZnSt_2$ at 1540 and 1398 cm^{-1} were observed. These bands are due to antisymmetric and symmetric carboxylate stretching bands ($\nu_a COO^-$ and $\nu_s COO^-$) respectively. Antisymmetric and symmetric methylene stretching, and methylene scissoring bands ($\nu_a CH_2$, $\nu_s CH_2$ and $\delta_s CH_2$) were observed at about 2914, 2850 and 1472 cm^{-1}. These bands are due to the alkyl chain in the zinc stearate structure. The FTIR spectrum of $CaSt_2$ is shown in Fig. 6.6. The existence of the peaks at 1540 and 1580 cm^{-1} indicates the chelating and ionic groups present in $CaSt_2$ (Göktepe, 1996).

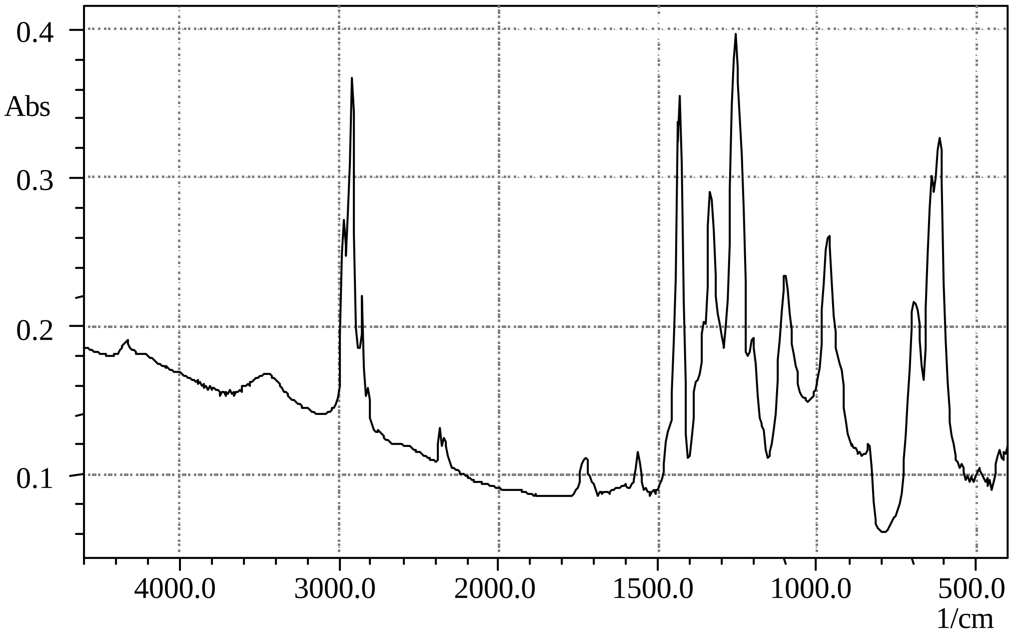


Figure 6.1. FTIR spectrum of PVC produced by Petkim

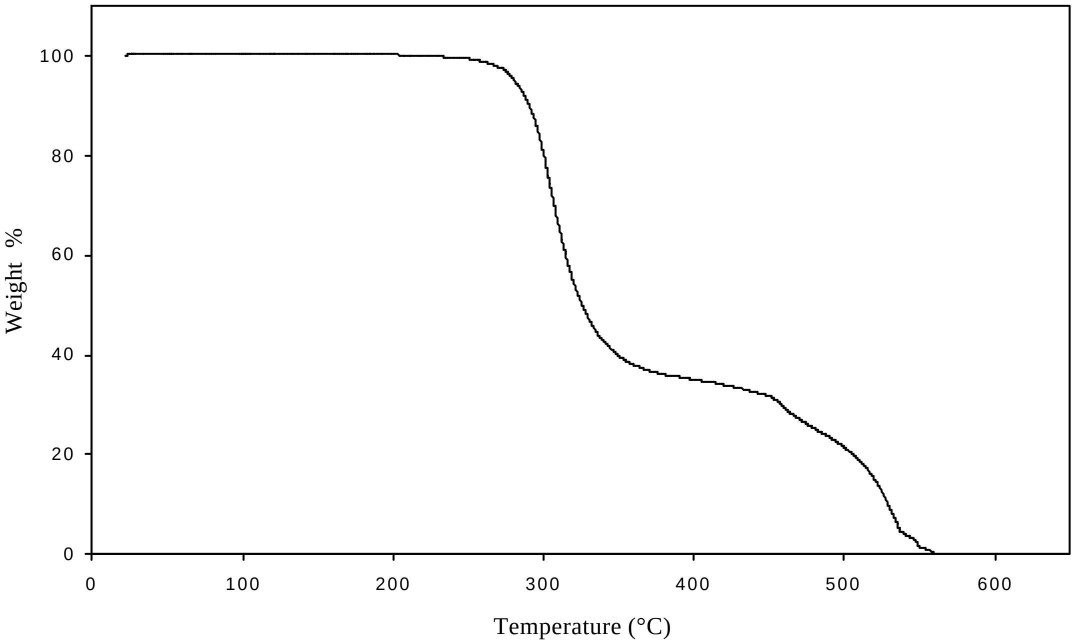


Figure 6.2. TGA curve of PVC.

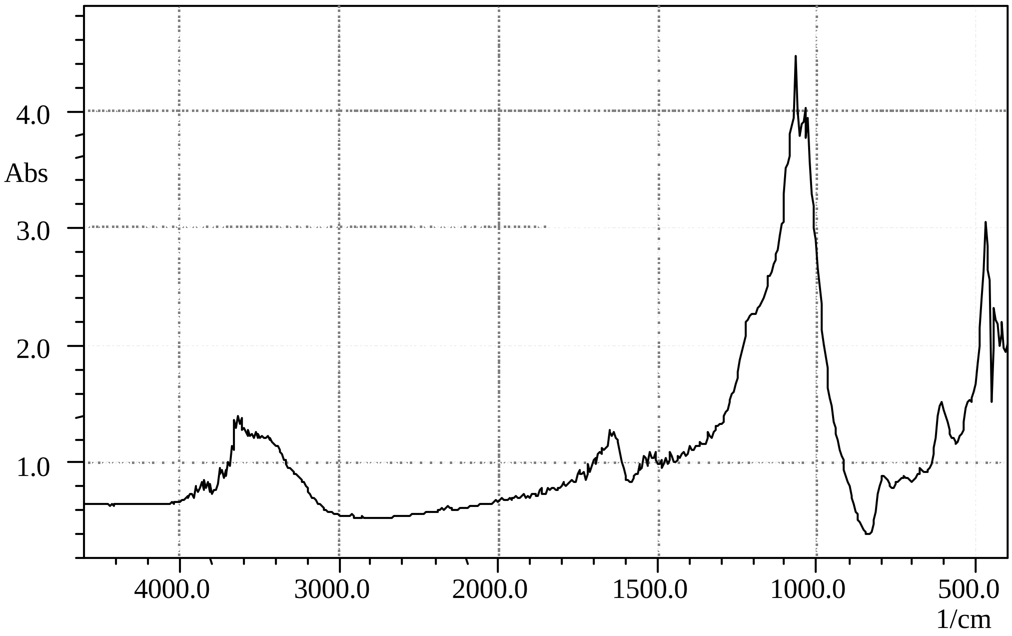


Figure 6.3. FTIR spectrum of natural zeolite.

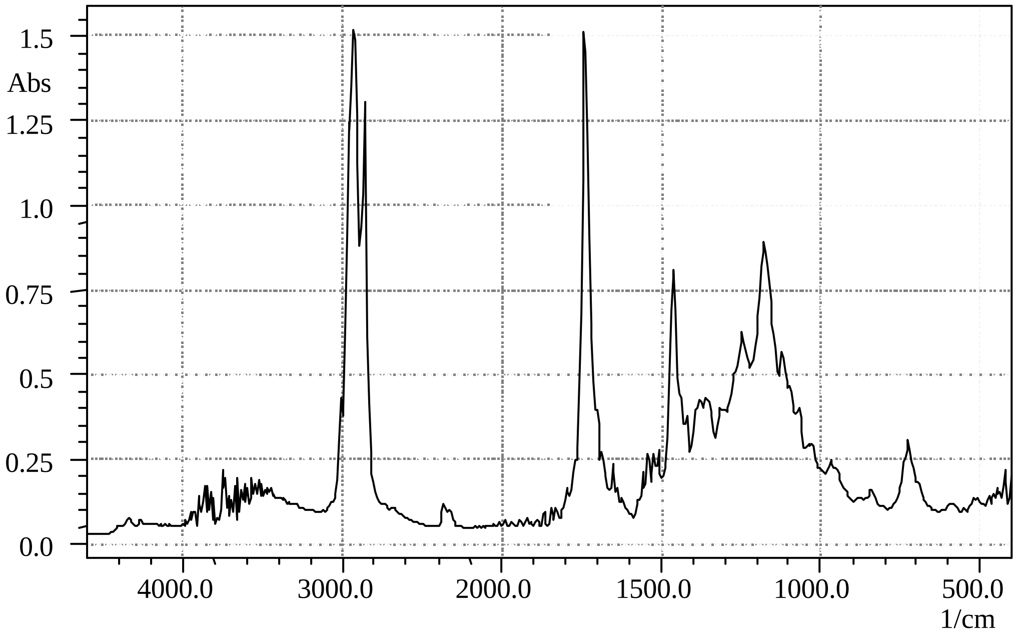


Figure 6.4. FTIR spectrum of viscobyk 5025

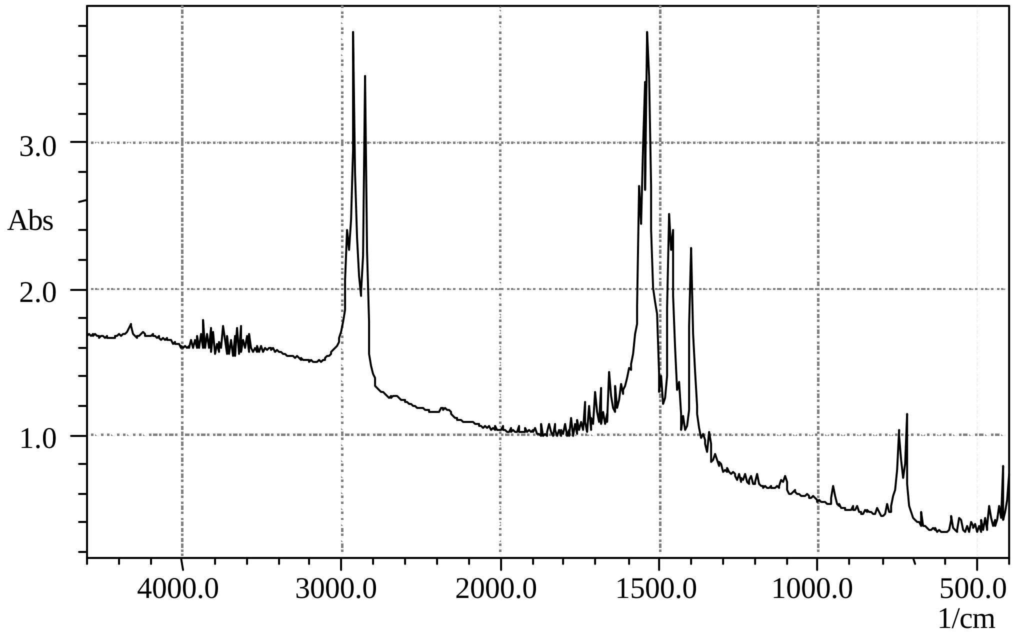


Figure 6.5. FTIR spectrum of $ZnSt_2$

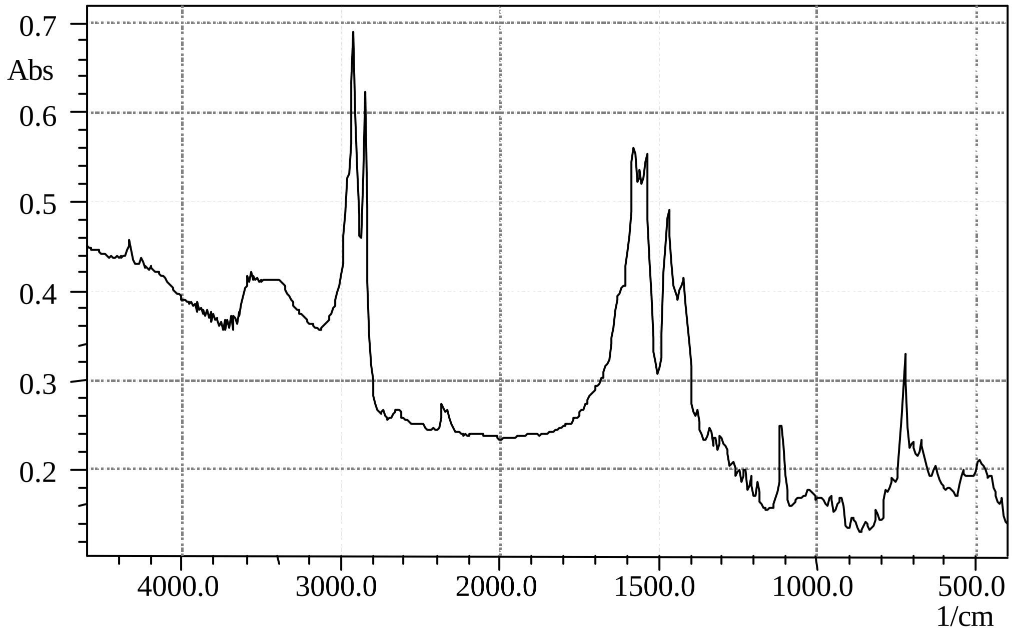
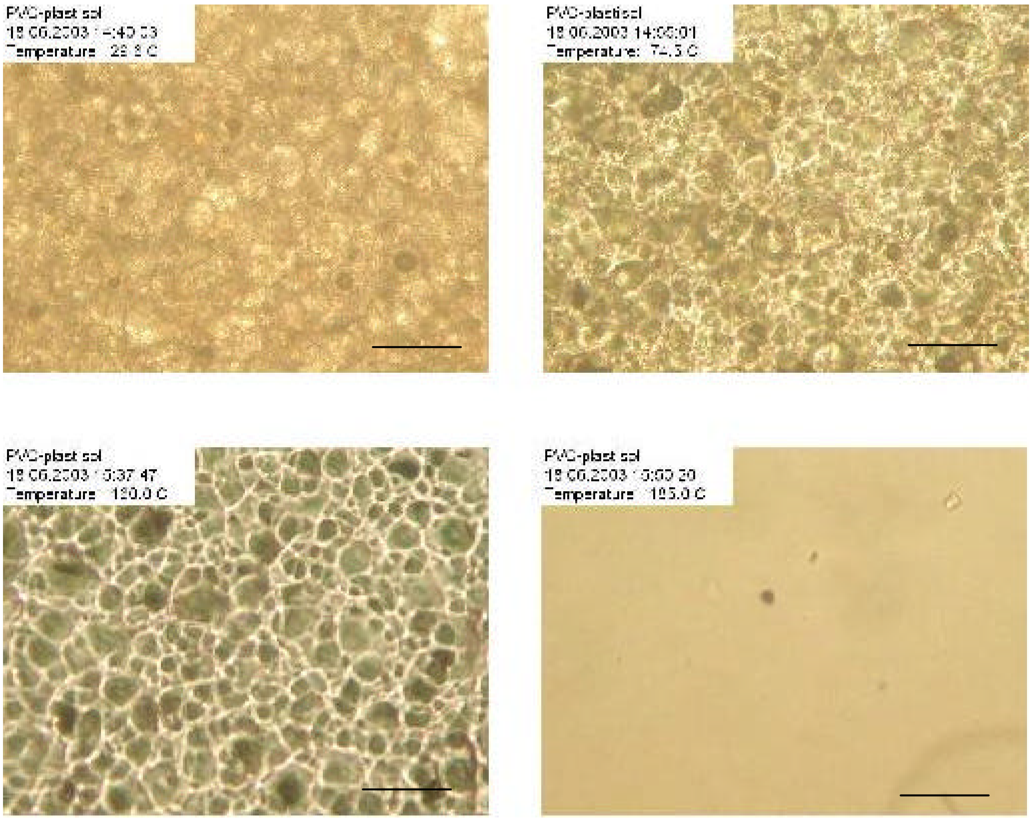


Figure 6.6. FTIR spectrum of $CaSt_2$

6.2. Characterization of PVC Plastisol and PVC Plastigel

6.2.1. Gelation and Fusion Behaviour of PVC Plastisol

All the industrial processes for plastisols involve the heating of the plastisol in an oven at about 180-200 °C. PVC plastisol samples were heated up to 200 °C in the hot stage controlled by a temperature controller. Optical micrographs of PVC plastisol stabilized with different amounts additives were taken at different temperatures to observe the penetration of plasticizer into PVC grains, and the fusion of PVC particles and plasticizer. The micrographs of PVC plastisol are shown in Fig.6.7.

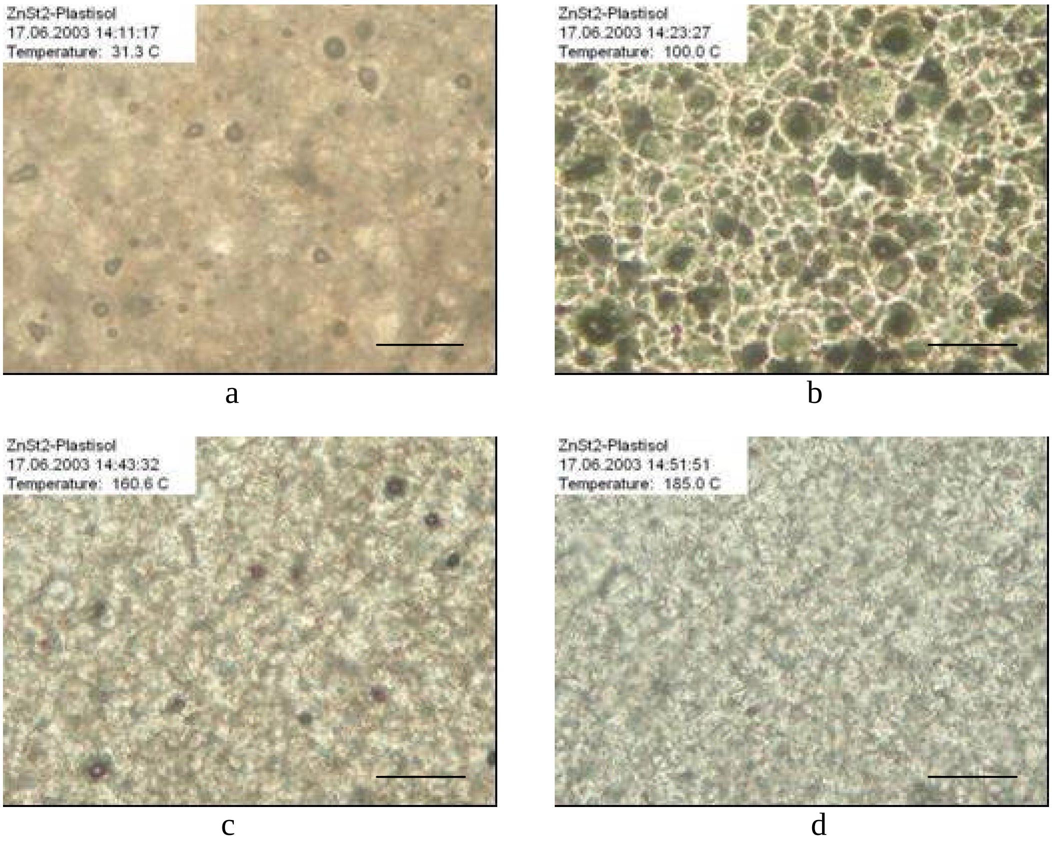


c d

Figure 6.7. Optical micrographs of PVC plastisol.
(a; 29.6 °C, b;74.5 °C, c;160.0 °C and d;185.0 °C)

It was observed that as the temperature was increased, plasticizer (DOP) swelled PVC particles and the particles touched each other. Since the parts where DOP diffuses into PVC particles are transparent, they are white in these micrographs (Baltacýoðlu, 1994). On the other hand the black parts indicate PVC as seen in Fig.6.7c. Finally a homogeneous material was formed called as plastigel. The gelation of PVC plastisol was completed at 185 °C.

Optical micrographs of PVC plastisol stabilized with 2.11%$ZnSt_2$ are shown in Fig.6.8.



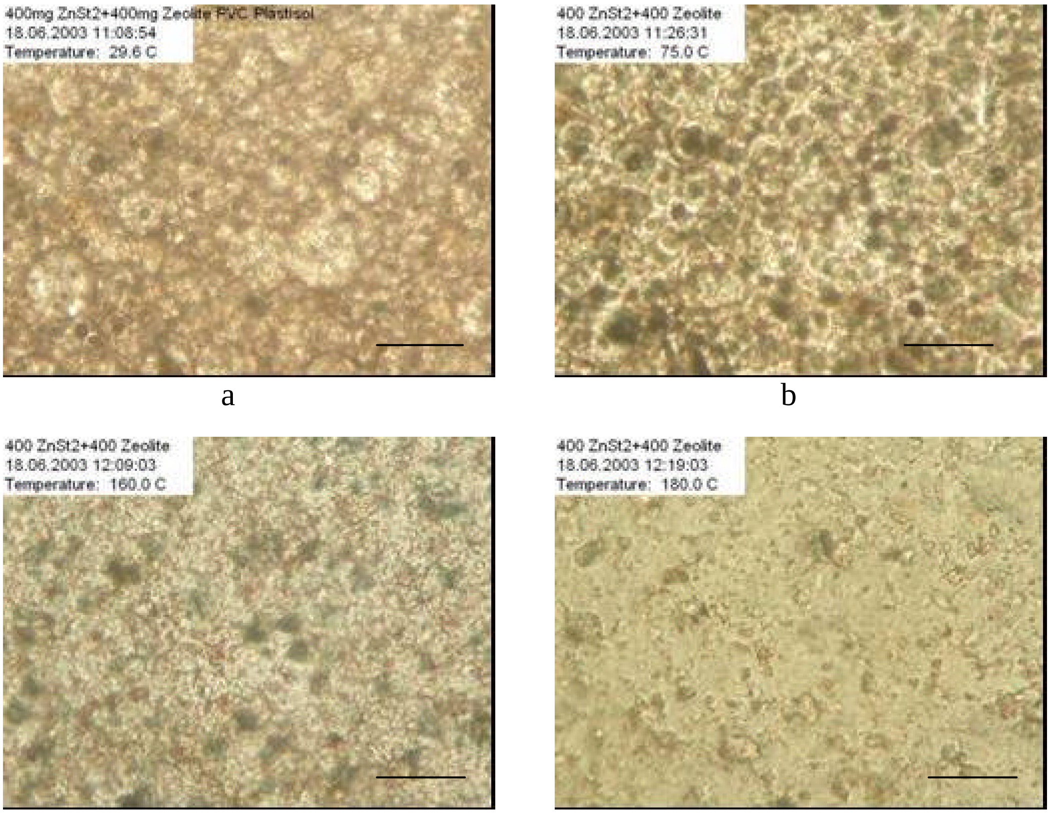
a b

c d

Figure 6.8. Optical micrographs of PVC plastisol stabilized with 2.11%$ZnSt_2$ (a; 31.3 °C, b;100.0 °C, c;160.6 °C and d;185.0 °C)

The black points in the PVC plastisol in Fig.6.8a are due to entrapped air during plastisol mixing. As the temperature is increased the holes due to entrapped air disappear. In spite of the melting of $ZnSt_2$ particles at 121 °C, the formed plastigel is not as homogeneous as the unstabilized one at 185 °C (Fig.6.8d).

The optical micrographs of PVC plastisol stabilized with 2.07 wt. % $ZnSt_2$ and 2.07 wt. % zeolite are shown in Fig.6.9.



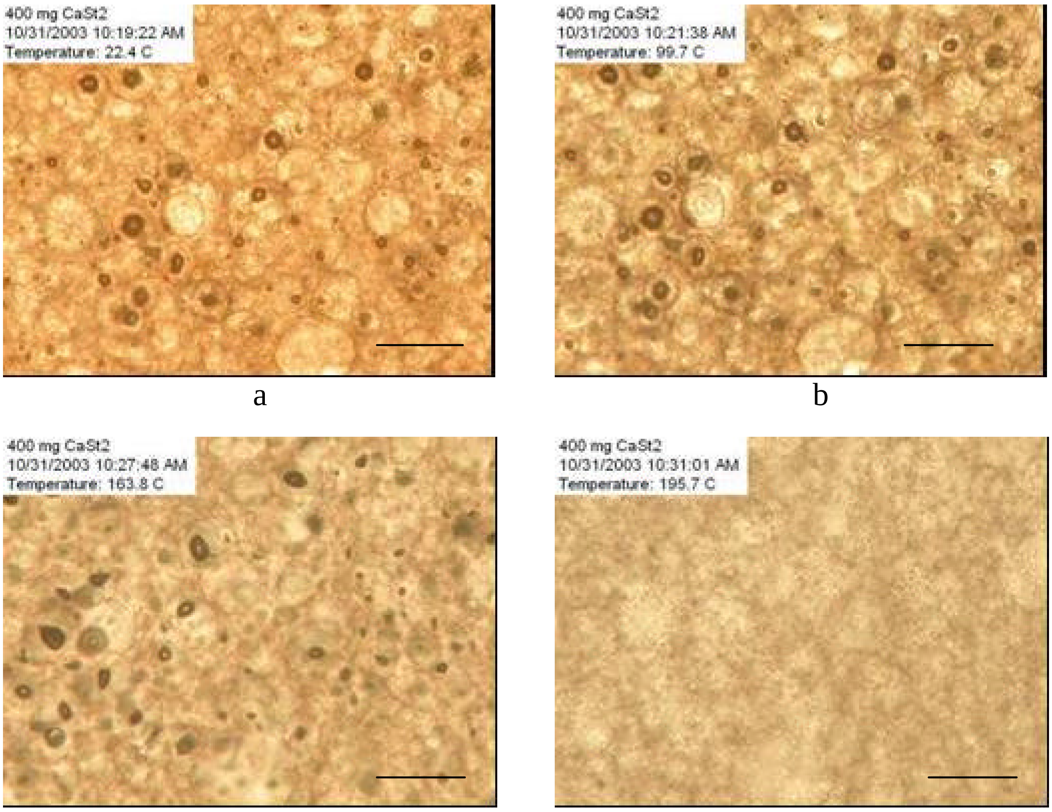
a b

c d

Figure 6.9. Optical micrographs PVC plastisol stabilized with 2.07% ZnSt$_2$ and 2.07% zeolite.
(a;29.6 °C, b;75 °C, c;160.0 °C, d;180 °C)

Gelation began to produce due to the swelling of the PVC particles (Fig.6.9b) and the interaction among themselves which developed a gel structure. The homogeneous material can not be observed in Fig.6.9d since PVC plastisol contains zeolite.

The homogeneous material was formed as shown in Fig.6.10, when the plastisol stabilized with 2.11 wt.%CaSt$_2$ since the melting temperature of CaSt$_2$ is 123.15 °C. At 163.8 °C, the size and number of ungelled particles were lower.

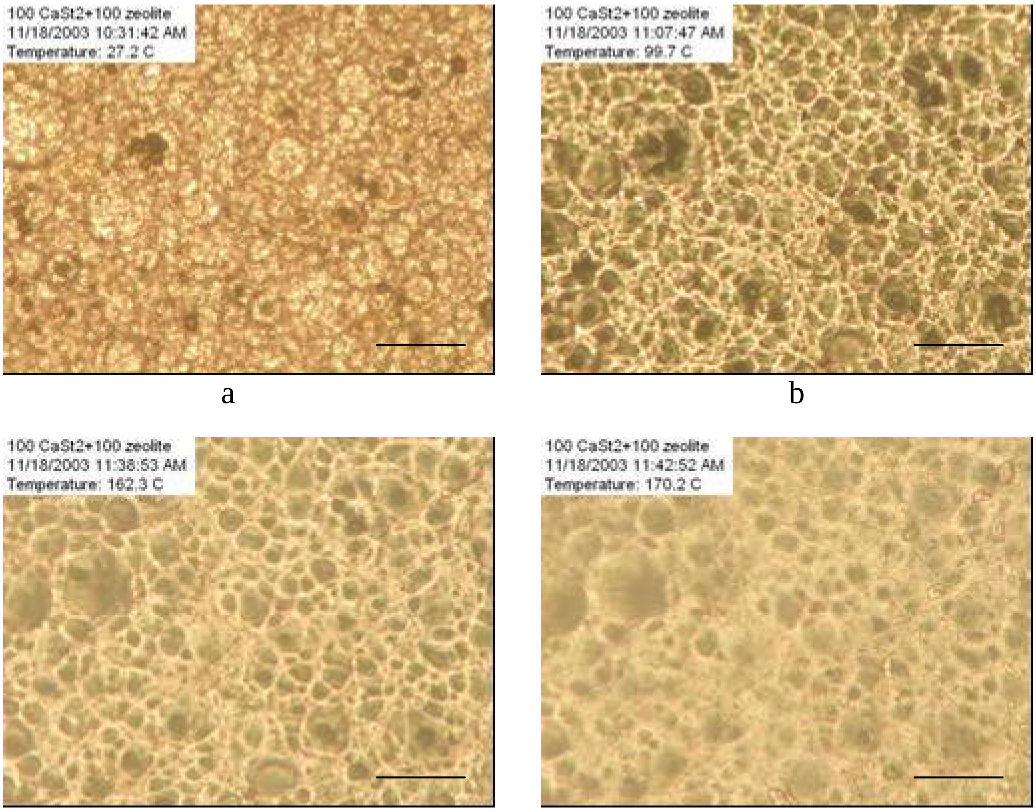


a b

c d

Figure 6.10. Optical micrographs PVC plastisols stabilized with 2.11% $CaSt_2$ (a;22.4 °C, b;99.7 °C, c;163.8 °C, d;195.7 °C)

The optical micrographs PVC plastisols stabilized with 0.53% $CaSt_2$ and 0.53% zeolite are shown in Fig.6.11. These micrographs clearly reveal that the diffusion of DOP into the PVC particles. It was observed that the homogeneous PVC plastisol was not formed at 170 °C.



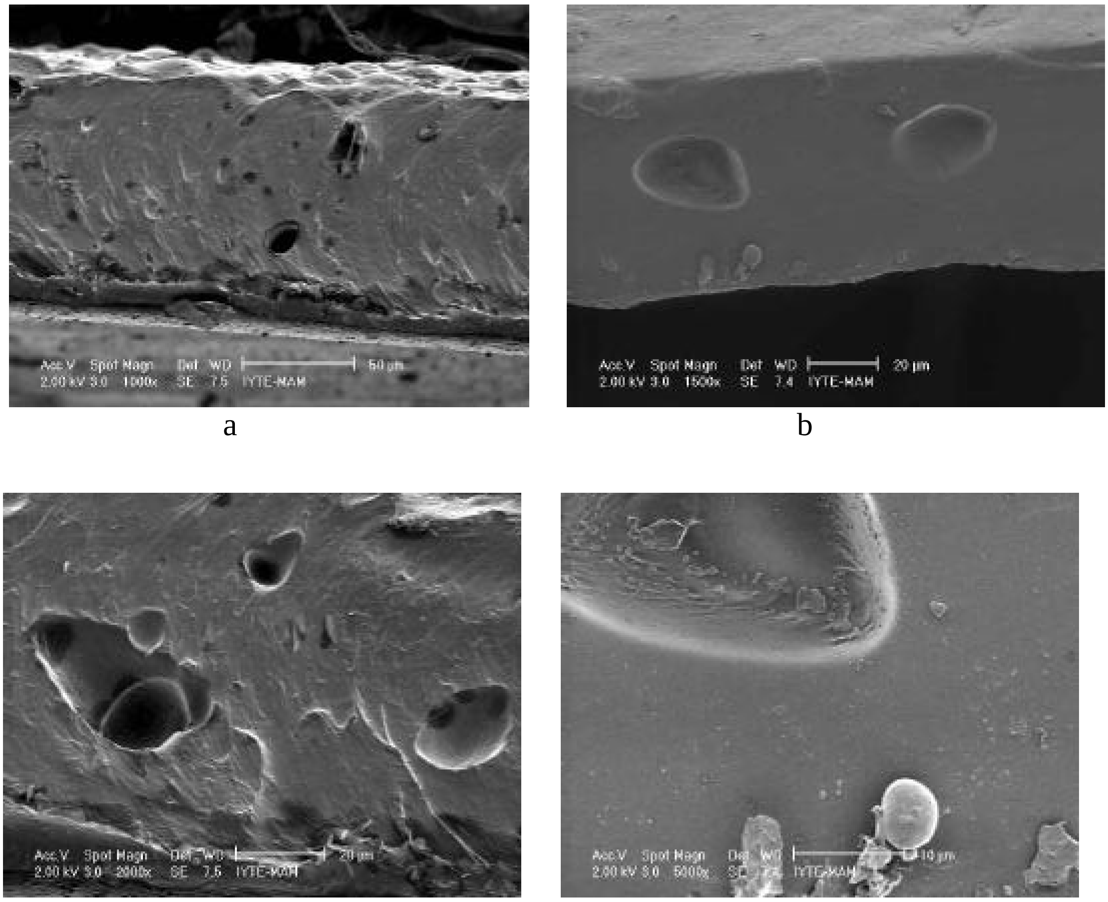
a b

c d

Figure 6.11. Optical micrographs PVC plastisols stabilized with 0.53% CaSt$_2$ and 0.53% zeolite (a;27.2°C, b;99.7 °C, c;162.3 °C, d;170.2°C)

6.2.2. Morphology of PVC Plastigels

SEM micrographs of cross section areas of PVC plastigel stabilized with different amounts of additives were investigated. It was observed that when the temperature and heating periods were increased the pores between PVC grains disappeared. SEM micrographs of PVC plastigel gelled at 140 °C for 15 min. and heated at 160 °C for 90 min are shown in Fig.6.12. At 160 °C a homogeneous plastigel was formed, but empty holes were still present.



a b

c d

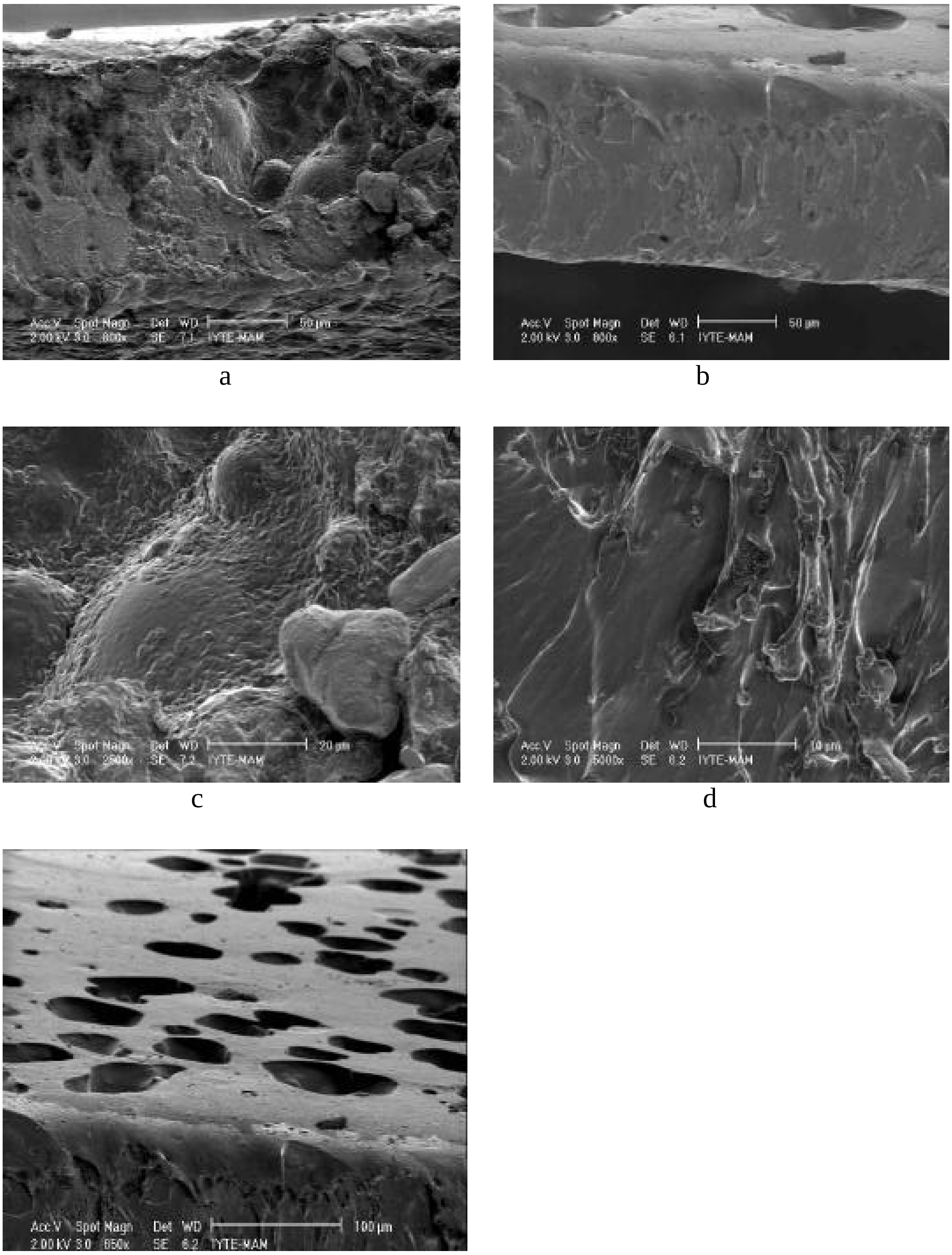
Figure 6.12. SEM micrographs of PVC plastigel
(a and c; gelled at 140 °C for 15 min. at 1000x, 2000x
b and d; heated at 160°C for 90 min. at 1500x and 5000x magnification)

SEM micrographs of the PVC plastigel films stabilized with different amount metal soap and zeolite are shown in Fig.6.13 to Fig.6.16. Additionally, the micrographs show the penetration and diffusion of the plasticizer into PVC particles (Fig.6.13c, Fig.6.13d, Fig.6.14c, Fig.6.14d, Fig.6.15c, Fig.6.15d, Fig.6.16c, and Fig.6.16d). Since the white parts represent both PVC and the plasticizer.

The micrographs of cross section and surface of the film stabilized with 2.11%$ZnSt_2$ are shown in Fig.6.13. Although the film had no pores on cross section, the pores with 50 μm diameter were observed on the surface of the film. A dense structure related with the sample stabilized with 2.11% $CaSt_2$ is shown in Fig.6.15a. When zeolite was added to PVC plastisol, porous structure was obtained. As shown in Fig.6.16a, the pore diameter is 30 μm approximately.

It was observed that a homogeneous material was not formed due to the zeolite content in PVC (Fig.6.14d and Fig.6.16d).

PVC film formed at 140 °C had more particulate structure when $ZnSt_2$, $CaSt_2$ or zeolite was present as seen in Fig.6.13a, 6.13c, Fig.6.14a, 6.14c, and Fig.6.16a, 6.16c. The particles were due to the agglomeration of PVC as well as additives. At long heating time, 90 min, PVC particles fused to each other, but zeolite particles appeared well dispersed in continuous polymer matrix as seen in Fig.6.12b, 6.12d, Fig.6.14b, 6.14d.

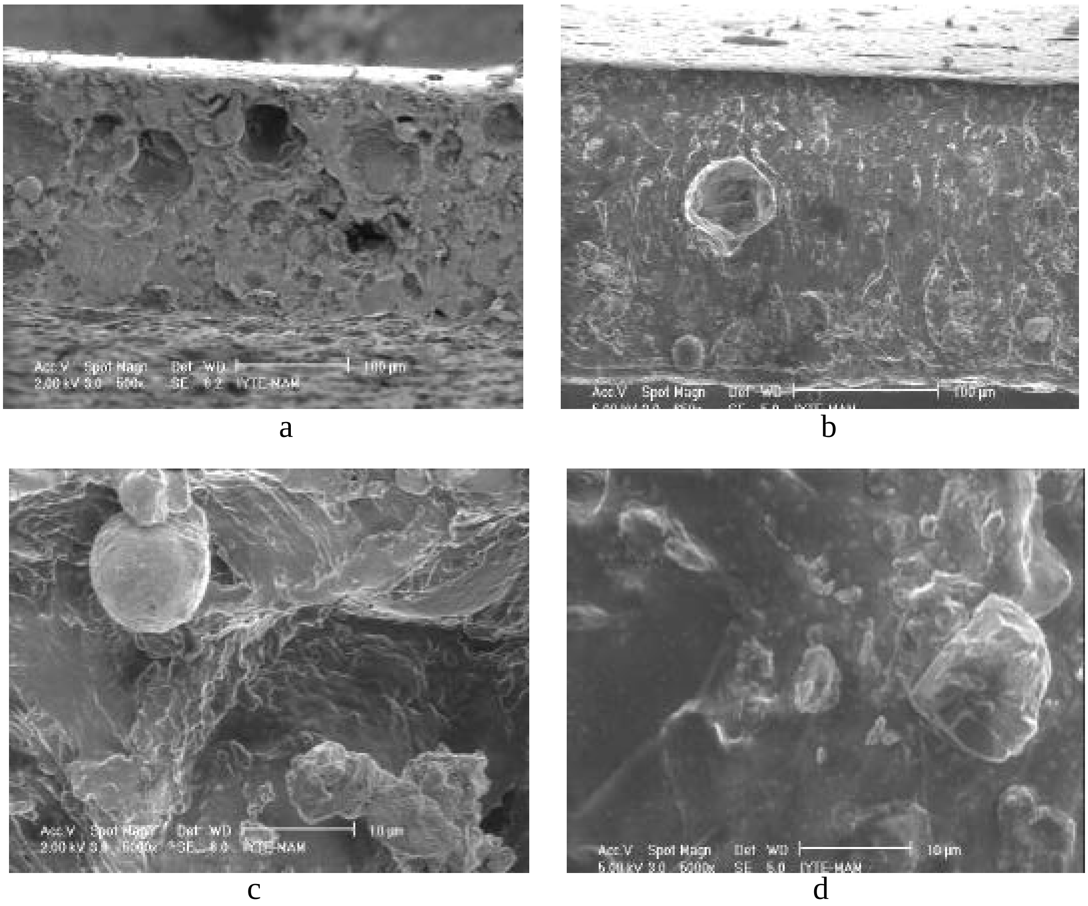


a b

c d

e

Figure 6.13. SEM micrographs of PVC plastigel stabilized with 2.11% $ZnSt_2$
(a and c; gelled at 140 °C for 15 min. at 800x, 2500x
b and d; heated at 160°C for 90 min. at 800x and 5000x magnification
e is the surface of PVC plastigel heated at 160 °C for 90 min.at 650x)



a b

c d

Figure 6.14. SEM micrographs of PVC plastigel stabilized with 2.07% ZnSt$_2$ and 2.07%zeolite

(a and c; gelled at 140 °C for 15 min. at 500x, 6000x

b and d; heated at 160°C for 90 min. at 650x and 5000x magnification)

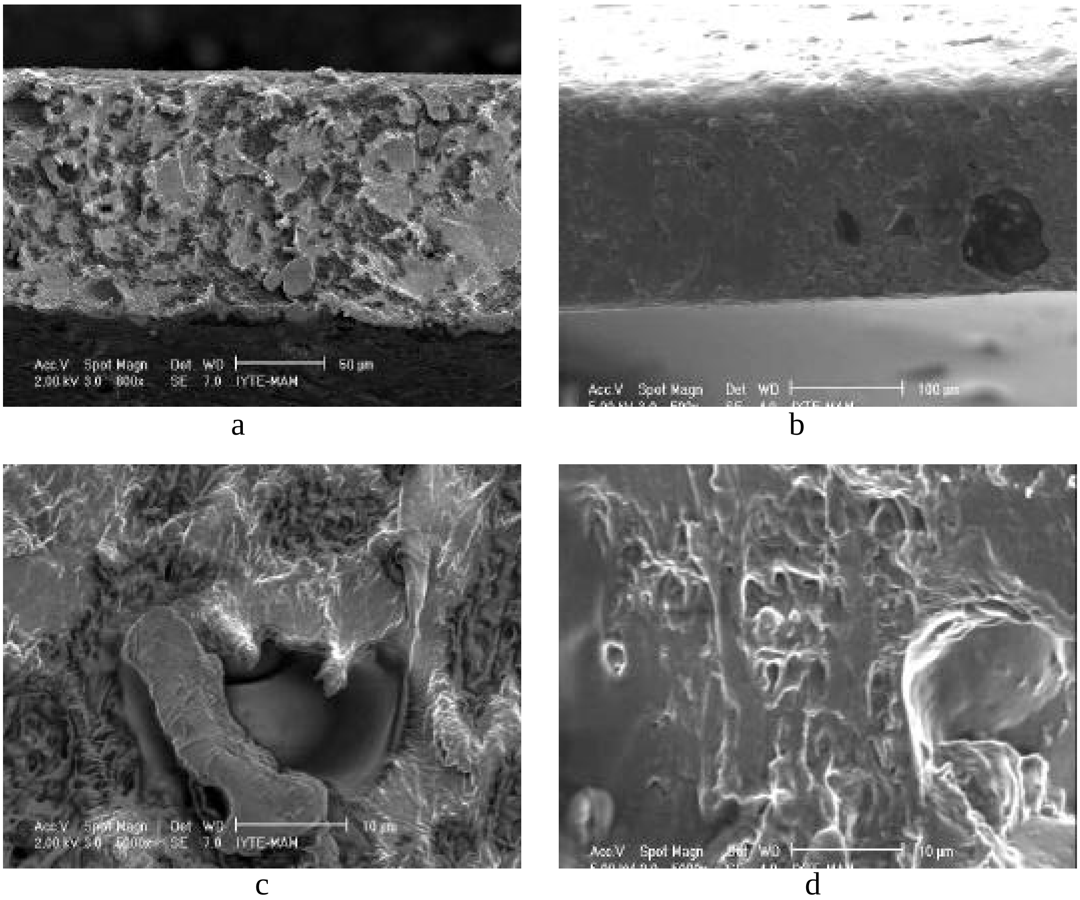
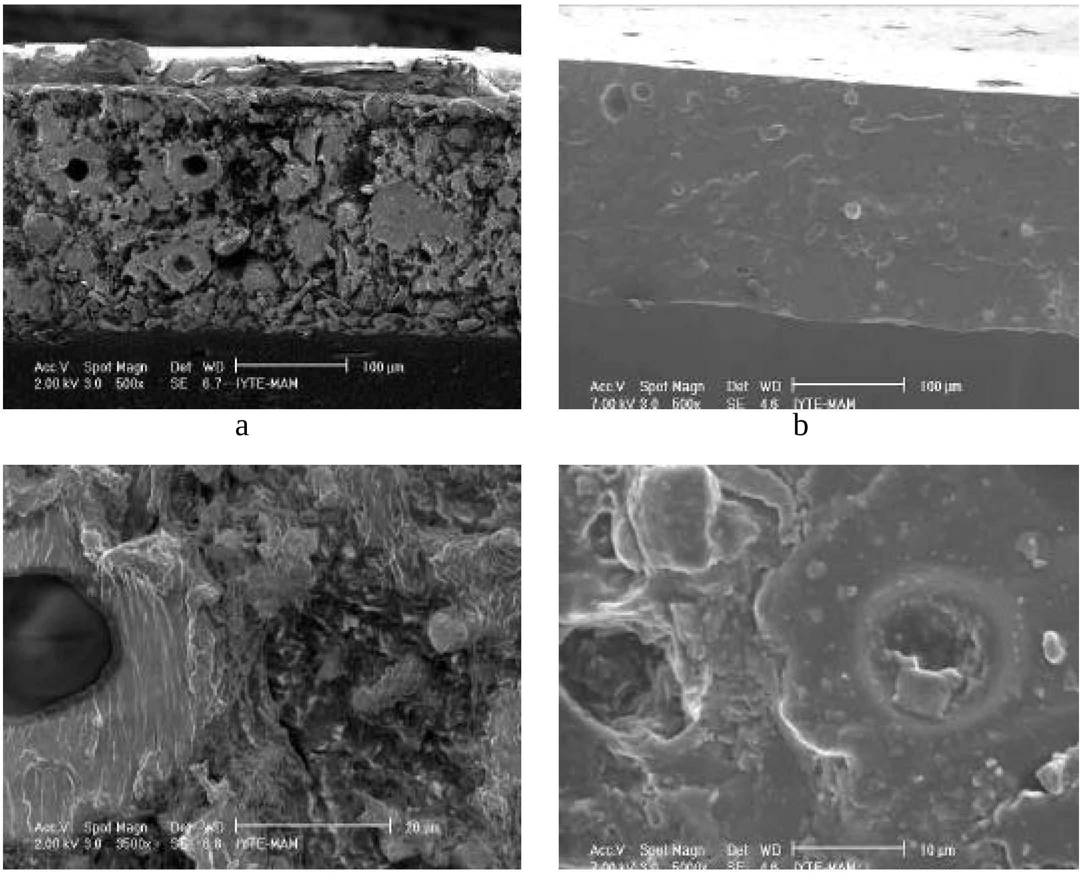


Figure 6.15. SEM micrographs of PVC plastigel stabilized with 2.11% $CaSt_2$
(a and c; gelled at 140 °C for 15 min. at 800x, 5000x
b and d; heated at 160°C for 90 min. at 500x and 5000x magnification)



a b

c d

Figure 6.16: SEM micrographs of PVC plastigel stabilized with 2.07% $CaSt_2$
and 2.07%zeolite
(a and c; gelled at 140 °C for 15 min. at 500x, 3500x
b and d; heated at 160°C for 90 min. at 500x and 5000x magnification)

The film thicknesses of the PVC plastigels measured by SEM and shown in Fig.6.12 to Fig.6.16 are reported in Table 6.1 at 140 and 160 °C. As the amount of additives was increased in PVC plastisol the film thicknesses of the films are increased although all the samples were prepared by 90 ì- applicator. The decrease in the film thicknesses at 160 °C might be due to the partially disappearing of the air holes and empty spaces after long heating period. Since the film thicknesses of the PVC plastigels were not identical on all sides of the films the increase in the thicknesses were observed at 160 °C.

Table 6.1. Film thickness of PVC plastigels at 140 and 160 °C.

Additive %			Film thickness at 140 °C (µm)	Film thickness at 160 °C (µm)
$ZnSt_2$	$CaSt_2$	Zeolite		
-	-	-	98.44	99.01
2.11	-	-	147.62	130.96
-	-	2.11	87.75	161.94
2.07	-	2.07	221.36	200.38
-	2.07	-	134.44	181.62
-	2.07	2.07	219.42	206.52

6.2.3. Elemental Analysis of PVC Plastigels

PVC plastigels were analyzed with EDX coupled to a scanning electron microscope (SEM) in order to investigate the composition of elements in polymer and particle phases and the dispersion of metal soap particles in PVC plastigel. Five different points were chosen to determine the weight % of each element in polymer and particle phases. The weight % of each element in particle phase was investigated for the samples stabilized with zeolite. The weight % values of each element were evaluated by taking the average of these five values. Additionally, the standard deviation values of each element were calculated. High standard deviations were evaluated since PVC plastigel was not a homogeneous material. An example for EDX analysis is shown in Fig.6.17 to Fig.6.19. As shown in these micrographs, the weight % of each element was investigated in polymer and particle phases. Fig.6.18 and Fig.6.19 show the distribution of elements in polymer and particle phases. The peaks corresponding to silicon (Si) and aluminum (Al) are not clear in polymer phase (Fig.6.18) but they become clear in particle phase since this particle belongs to natural zeolite (Fig.6.19). The theoretical values of composition of elements were calculated and they are reported in Table 6.2. The results of elemental analysis are shown in Table 6.3 to Table 6.6. Natural zeolite composition was previously reported by Özmýhçý et al., 2000.

It was observed that for all samples, the weight % values of carbon (C) in the range 70.06-81.20% at 140 °C were close to the weight % of carbon of the plasticizer (DOP) 73.81% (Table 6.2). Also the weight % of chlorine (Cl), 6.49-23.8%, at 140 °C was lower than the weight % in the range 14.01-64.12% at 160 °C. This indicated the incomplete gelation at low temperature. The high weight % of oxygen (O), 5.07-12.72% at 140 °C also justified this result, since DOP was not absorbed by PVC particles and it covered the surface where EDX analysis was performed. At 160 °C, the gelation was completed, DOP diffused into PVC particles. Accordingly, the weight % of oxygen decreased from 9.09 to 2.18, whereas the weight % of chlorine increased from 16.37 to 64.12 for PVC plastigel.

In particle phase, the weight % values of chlorine (Cl) were evaluated as 2.51 for the sample stabilized with 2.11% zeolite, 1.83 for the sample stabilized with 2.07% ZnSt$_2$ and 2.07% zeolite, 3.08 for the sample stabilized with 2.07% CaSt$_2$ and 2.07% zeolite at

140 °C. When these samples were heated at 160 °C for 90 min, these values were 13.71, 12.88 and 21.83 respectively. The increase in the percentage of chlorine were due to the covering the surface of particles by PVC plastisol or the adsorption of HCl that produced at the end of dehydrochlorination reaction by zeolite particles. Also $ZnCl_2$ and $CaCl_2$ produced from the reaction between HCl and the metal soaps might be the reason of this increase. It was observed that at 160 °C, the weight % values of Si and Al were lower than the compositions of Si and Al at 140 °C (Table 6.4 and Table 6.6). The decrease in weight % of Si and Al were due to the covering of surface of zeolite particles by PVC plastisol and the forming of homogeneous material when the temperature and heating period were increased. Therefore it became difficult to observe the particles in SEM photographs.

Particles of the films at 140 °C contained 12.58-16.53% Si and 4.45-5.67% Al and particles of the films heated at 160 °C contained 0.22-10.50% Si and 0.26-4.55%Al.

As shown in Table 6.3, 1.00-1.76 % Zn and 0.60-1.11 % Ca were present respectively in $ZnSt_2$ and $CaSt_2$ containing films in polymer phase. This indicated the dispersion of the metal soaps occurred on the films. At 140 °C 1.83% Zn and 2.72% Ca in the particle phase of $ZnSt_2$ and $CaSt_2$ containing films showed some of the particles could be $ZnSt_2$ or $CaSt_2$ (Table 6.4). Additionally, 6.86% Zn and 1.53% Ca for $ZnSt_2$ and $CaSt_2$ containing films in the particle phases indicated some of the particles could be $ZnSt_2$ and $CaSt_2$.

Table 6.2. Theoretical Compositions of Components

Elements	PVC	DOP	PVC plastigel	$ZnSt_2$	$CaSt_2$	Natural Zeolite
C	38.44	73.81	60.36	61.97	66.87	-
O	-	16.40	9.11	9.17	9.89	46.41
Cl	56.74	-	31.52	-	-	-
Zn	-	-	-	18.74	-	-
Ca	-	-	-	-	12.39	1.07
Al	-	-	-	-	-	5.29
Si	-	-	-	-	-	35.8
Others	-	-	-	-	-	11.43

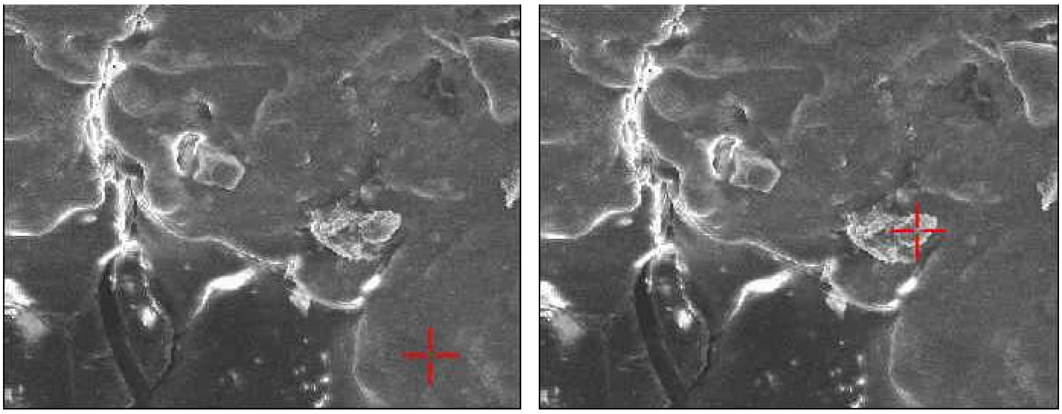


Figure 6.17. SEM micrographs of PVC plastigel stabilized with 2.07% $CaSt_2$ 2.07% zeolite and heated at 160 °C for 90 min.
(a; polymer phase, b; particle phase)

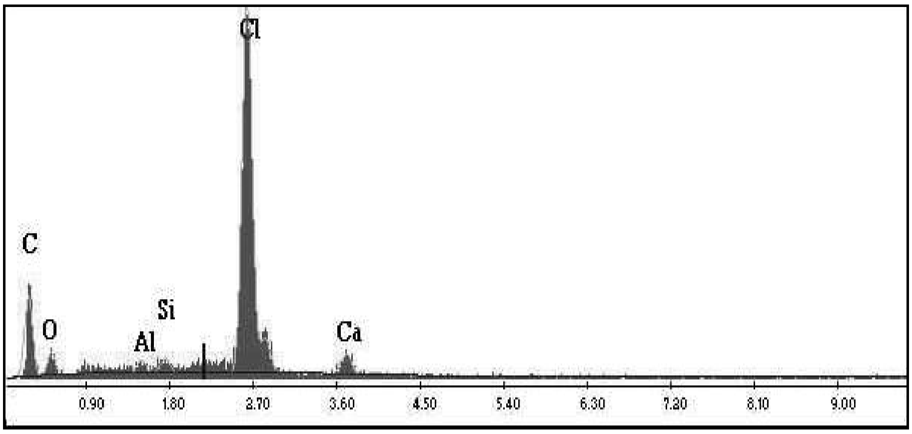


Figure 6.18. EDX analysis of elements of PVC plastigel stabilized with 2.07% $CaSt_2$ 2.07% zeolite and heated at 160 °C for 90 min (polymer phase)

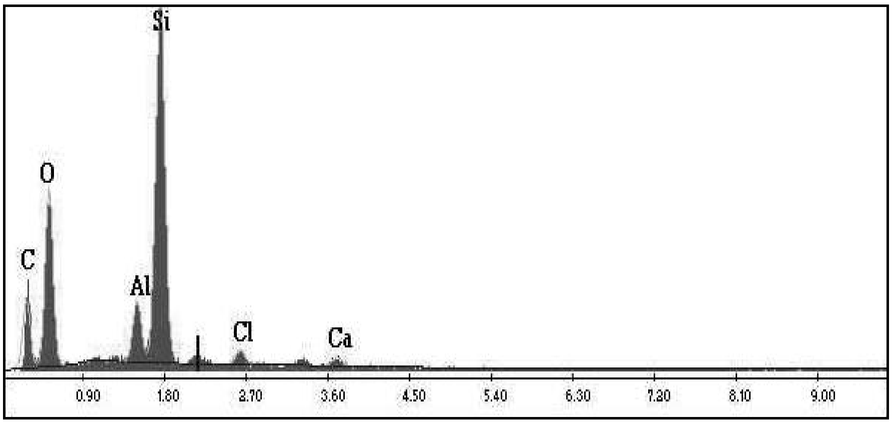


Figure 6.19. EDX analysis of elements of PVC plastigel stabilized with 2.07% $CaSt_2$ 2.07% zeolite and heated at 160 °C for 90 min (particle phase)

Table 6.3. Elemental analysis of polymer phase of PVC plastigel films gelled at 140 °C for 15 min.

% Additive			Polymer Phase									
$ZnSt_2$	$CaSt_2$	Zeolite	C%		O%		Cl%		Zn%		Ca%	
			Av.	Std.dev	Av.	Std.dev	Av	Std.dev	Av.	Std.dev	Av.	Std.dev
-	-	-	73.90	0.98	9.09	0.40	16.37	0.78	-	-	-	-
2.11	-	-	79.59	3.68	11.35	5.28	7.29	3.70	1.76	1.64	-	-
-	-	2.11	81.20	0.89	12.31	1.41	6.49	0.87	-	-	-	-
2.07	-	2.07	70.06	8.56	5.07	0.39	23.87	8.50	1.00	0.14	-	-
-	2.11	-	74.17	1.68	12.72	7.65	12.01	7.88	-	-	1.11	0.09
-	2.07	2.07	74.90	3.40	5.72	0.58	18.79	3.77	-	-	0.60	0.39

Table 6.4. Elemental analysis of particle phase of PVC plastigel films gelled at 140 °C for 15 min.

% Additive			Particle Phase													
ZnSt$_2$	CaSt$_2$	Zeolite	C%		O%		Cl%		Zn%		Ca%		Si%		Al%	
			Av.	Std.dev	Av.	Std.dev	Av.	Std.dev	Av.	Std.dev	Av.	Std.dev	Av.	Std.dev	Av.	Std.dev
-	-	2.11	53.58	24.28	21.22	6.80	2.51	10.37	-	-	-	-	12.58	10.37	5.67	7.07
2.07	-	2.07	27.79	3.39	34.90	4.90	1.83	0.50	1.83	0.50	-	-	25.30	2.90	4.87	1.29
-	2.07	2.07	46.86	11.90	42.70	9.04	3.08	1.10	-	-	2.72	3.77	16.53	8.84	4.45	2.45

Table 6.5. Elemental analysis of polymer phase of PVC plastigel films heated at 160 °C for 90 min.

% Additive			Polymer Phase									
$ZnSt_2$	$CaSt_2$	Zeolite	C%		O%		Cl%		Zn%		Ca%	
			Av.	Std.dev	Av.	Std.dev	Av	Std.dev	Av.	Std.dev	Av.	Std.dev
-	-	-	28.45	14.03	2.18	0.89	64.12	15.44	-	-	-	-
2.11	-	-	54.38	21.16	2.38	1.28	39.21	20.30	3.12	1.91	-	-
-	-	2.11	76.41	3.99	5.81	1.09	14.01	2.65	-	-	-	-
2.07	-	2.07	71.67	1.01	8.77	1.48	17.26	0.86	0.93	057	-	-
-	2.11	-	64.79	10.64	5.69	4.19	28.85	14.43	-	-	0.25	0.12
-	2.07	2.07	61.63	6.99	6.96	2.07	27.14	12.73	-	-	3.27	5.93

Table 6.6. Elemental analysis of particle phase of PVC plastigel films heated at 160 °C for 90 min.

% Additive			Particle Phase													
$ZnSt_2$	$CaSt_2$	Zeolite	C%		O%		Cl%		Zn%		Ca%		Si%		Al%	
			Av.	Std.dev	Av.	Std.dev	Av	Std.dev	Av	Std.dev	Av.	Std.dev	Av.	Std.dev	Av.	Std.dev
-	-	2.11	75.17	4.55	7.39	4.55	13.71	8.07	-	-	-	-	0.22	0.20	0.26	0.19
2.07	-	2.07	30.06	8.34	22.98	11.80	12.88	9.62	6.86	5.23	-	-	14.12	9.85	4.55	0.99
-	2.07	2.07	47.82	9.92	16.44	12.86	21.83	14.96	-	-	1.53	1.04	10.50	10.23	1.90	1.29

6.2.4. Color Test of PVC Plastigels

6.2.4.1. Static Oven Test

When PVC is exposed to heat, its color changes from white to black because of the formation of polyene sequences. The color of PVC is an indication of the presence of conjugated diens in it. The color changes from yellow-orange-brown as number of conjugated double bond sequences increases. Four conjugated double bonds indicate light yellow color whereas six conjugated double bonds indicate yellow color of PVC. Additionally, PVC which has eight and eleven conjugated double bonds in its polymer chain appears orange and red colors respectively (Braude and Nachod, 1955).

The prepared PVC plastigel films were heated in a static vacuum oven at 140 and 160 °C for different time periods. The observed colors are shown in Table 6.7 to 6.10. As seen from Table 6.9, while the control film without any additive appear white at 150 °C they become light yellow in 45 min. Thus yellow films were dehydrochlorinated with conjugated double bond formation. The color of the samples that were stabilized with $ZnSt_2$ became black at the end of 90 min in long heating periods. Because after consumption of $ZnSt_2$, the conjugated polyenes reinitiated the unzipping process to yield free HCl, and long polyenes were formed and the films discolored, known as blackening. The samples stabilized with $CaSt_2$ were still white or light yellow at the end of 90 min. since $CaCl_2$ produced from dehydrochlorination does not accelerate the decomposition process as $ZnCl_2$ did. Table 6.11 and 6.12 show the change of the color of PVC plastigel films with respect to time. The films demonstrated how the extent of discoloration was strongly affected by the time of degradation. Discoloration of the films was observed even in the presence of large amounts of stabilizers. In other words, the initiation of dehydrochlorination could not be prevented by stabilizers, at least not efficiently. When zeolite was used as a primary stabilizer for PVC it prevented the early blackening of the samples.

Table 6.7. The color change of PVC plastigel having $ZnSt_2$ and zeolite films with respect to time at 140 °C

Additive wt. %		Color					
$ZnSt_2$	Zeolite	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
-	-	white	white	white	white	white	white
2.11	-	white	white	white	white	light yellow	light yellow
-	2.11	white	white	white	light yellow	light yellow	light yellow
0.53	0.53	white	white	white	white	white	white
1.05	1.05	white	white	white	light yellow	light yellow	light yellow
1.56	1.56	white	white	white	white	light yellow	light yellow
2.07	2.07	white	white	white	white	light yellow	light yellow

Table 6.8. The color change of PVC plastigel films having $CaSt_2$ and zeolite with respect to time at 140 °C

Additive wt. %		Color					
$CaSt_2$	Zeolite	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
-	-	white	white	white	white	white	white
2.11	-	white	white	white	white	white	white
-	2.11	white	white	white	white	white	white
0.53	0.53	white	white	white	white	white	white
1.05	1.05	white	white	white	white	white	white
1.56	1.56	white	white	white	white	white	white
2.07	2.07	white	white	white	white	white	white

Table 6.9. The color change of PVC plastigel films having $ZnSt_2$ and zeolite with respect to time at 160 °C

Additive wt. %		Color					
$ZnSt_2$	Zeolite	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
-	-	white	white	light yellow	light yellow	light yellow	light yellow
2.11	-	white	white	light yellow	light yellow	light yellow	brown
-	2.11	white	white	light yellow	yellow	dark yellow	yellow
0.53	0.53	white	white	white	light yellow	dark yellow	dark yellow
1.05	1.05	white	white	light yellow	dark yellow	brown	black
1.56	1.56	white	light yellow	black	black	black	black
2.07	2.07	white	white	white	light yellow	black	black

Table 6.10. The color change of PVC plastigel films having $CaSt_2$and zeolite with respect to time at 160 °C

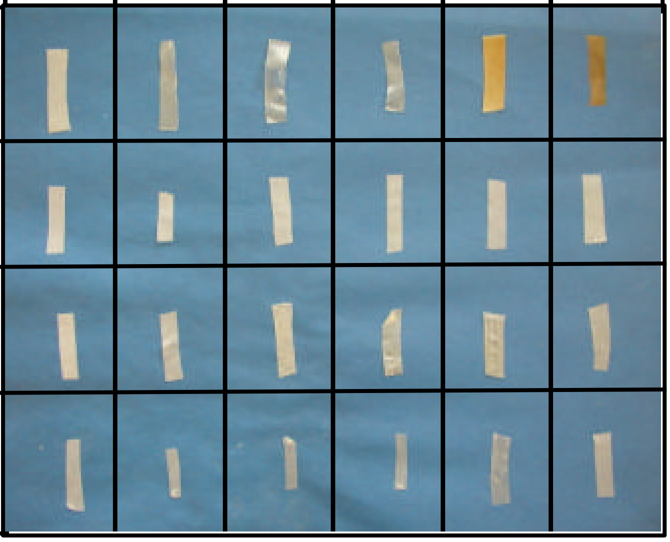
Additive wt. %		Color					
$CaSt_2$	Zeolite	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
-	-	white	white	light yellow	light yellow	light yellow	light yellow
2.11	-	white	white	white	white	light yellow	light yellow
-	2.11	white	white	white	light yellow	light yellow	light yellow
0.53	0.53	white	light yellow	light yellow	light yellow	light yellow	light yellow
1.05	1.05	white	white	white	white	light yellow	light yellow
1.56	1.56	white	white	light yellow	light yellow	light yellow	light yellow
2.07	2.07	white	white	white	white	white	white

Table 6.11. The change of the color of PVC plastigels having ZnSt$_2$ and zeolite with respect to time

Heating Period of PVC Plastigel Films in an Air-Circulating Oven at 160 °C (min)						
Samples	15	30	45	60	75	90
PVC plastigel						
2.11% Zeolite						
2.11% ZnSt$_2$						
2.07% ZnSt$_2$+ 2.07% Zeolite						

Table 6.12. The change of the color of PVC plastigels having CaSt$_2$ and zeolite with respect to time

Heating Period of PVC Plastigel Films in an Air-Circulating Oven at 160 °C						
Samples	15	30	45	60	75	90
PVC plastigel						
2.11% CaSt$_2$						
2.11% zeolite						
2.07% CaSt$_2$ + 2.07% zeolite						



6.2.4.2. Yellowness Index of PVC Plastigels

Yellowness index of the plastigels were calculated by using their tristimulus (L, a, b) values. Equation 8 was used for these calculations. The yellowness index values and the observed colors by naked eye were presented in Table 6.13to Table 6.16. As the yellowness index increases, the color of the plastigels changes from white to black.

Table 6.13. PVC Plastigels stabilized with $ZnSt_2$ and zeolite gelled for 15 min at 140 °C

% Additive $ZnSt_2$	 Zeolite	L	a	b	YI	Color
-	-	84.66	-1.60	-4.08824	1.37	white
2.11	-	90.71	-1.14	-3.03605	1.23	white
-	2.11	90.54	-1.36	-5.945	3.78	white
0.53	0.53	80.75	-1.30	-5.23789	2.92	white
1.05	1.05	88.40	-1.45	-5.71674	3.35	white
1.56	1.56	86.13	-1.60	-6.38767	3.71	white
2.07	2.07	90.76	-1.68	-7.24945	4.58	white

Table 6.14. PVC Plastigels stabilized with $CaSt_2$ and zeolite gelled for 15 min at 140 °C

% Additive $CaSt_2$	 Zeolite	L	a	b	YI	Color
-	-	84.66	-1.60	1.29	1.37	white
2.11	-	90.71	-1.14	1.03	1.13	white
-	2.11	90.54	-1.36	2.46	3.78	white
0.53	0.53	80.75	-1.30	0.93	0.90	white
1.05	1.05	88.40	-1.45	2.00	2.87	white
1.56	1.56	86.13	-1.60	1.69	2.17	white
2.07	2.07	90.76	-1.68	2.03	2.67	white

Table 6.15. PVC Plastigels stabilized with $ZnSt_2$ and zeolite heated for 90 min at 160 °C

% Additive $ZnSt_2$	 Zeolite	L	a	b	YI	Color
-	-	93.72	-1.31	7.15	12.65	Light yellow
2.11	-	99.77	-0.51	4.62	7.92	Light yellow
-	2.11	93.17	-1.32	9.33	16.90	Yellow
0.53	0.53	94.56	-1.80	16.64	30.13	Dark yellow
1.05	1.05	74.45	6.57	47.77	121.21	Black
1.56	1.56	72.60	6.29	47.00	122.12	Black
2.07	2.07	28.30	12.77	12.45	111.24	Black

Table 6.16. PVC Plastigels stabilized with $CaSt_2$ and zeolite heated for 90 min at 160 °C

% Additive $CaSt_2$	 Zeolite	L	a	b	YI	Color
-	-	93.72	-1.31	7.15	12.65	Light yellow
2.11	-	91.49	-1.62	7.33	13.07	Light yellow
-	2.11	93.17	-1.32	9.33	16.90	Yellow
0.53	0.53	92.55	-1.27	7.73	13.96	Light yellow
1.05	1.05	91.46	-1.38	7.33	13.26	Light yellow
1.56	1.56	92.04	-1.01	11.63	21.83	Light yellow
2.07	2.07	90.67	-0.97	7.41	13.86	Light yellow

Benavides et al., (2000) determined yellowness index of the PVC samples degraded at 160 °C. The yellowness index for PVC was found as 80 whereas the values for mixtures PVC+$CaSt_2$ and PVC+$ZnSt_2$ were determined as 160 and 170 respectively. The measured yellowness index values were not consistent with the literature (Benavides et al., 2000) since they have prepared the mixtures without a plasticizer in a dry blender and measured the yellowness index values in a Hunter Lab D25-2 instrument.

6.2.5. UV Study of PVC Plastigels

The transparency of PVC plastigels films stabilized with different amount of $ZnSt_2$/ $CaSt_2$ and zeolite were investigated by UV spectroscopy. Fig.6.20 to Fig.6.23 show the results of UV study. The maximum absorbance values compared with the samples gelled at 140 °C are higher than the absorbance values of the samples heated at 160 °C for 90 min. because of the complete gelation at high temperature. DOP diffused into PVC particles and the films became transparent having low absorbance values. Since the thicknesses of the films are different, the absorbance values of the samples are different. When samples stabilized $ZnSt_2$ were heated at 160 °C for 90 min. the absorbance values increase between 350-600 nm due to the discoloration of the films. The peaks between 200-300 nm are the specific peaks of DOP. So the spectra of the samples between 200-300nm are masked by that of the peaks of DOP as seen Fig.6.20 to Fig. 6.23.

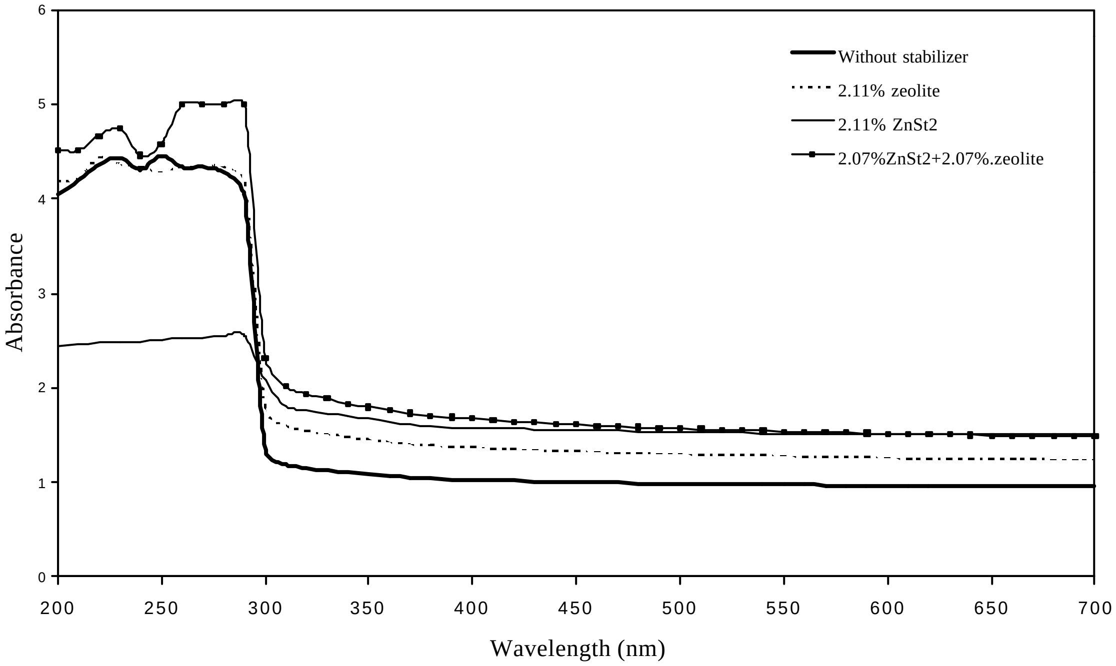


Figure 6.20. UV spectra of PVC plastigels having $ZnSt_2$ and zeolite gelled. at 140 °C for 15 min..

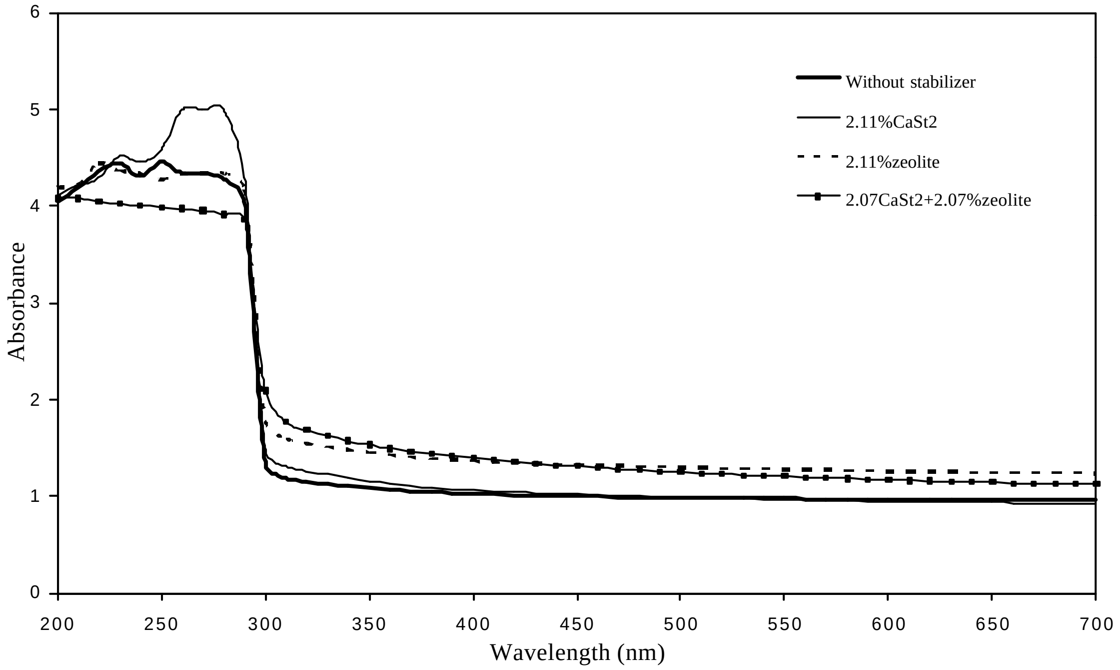


Figure 6.21. UV spectra of PVC plastigels having $CaSt_2$ and zeolite gelled at 140 °C for 15 min.

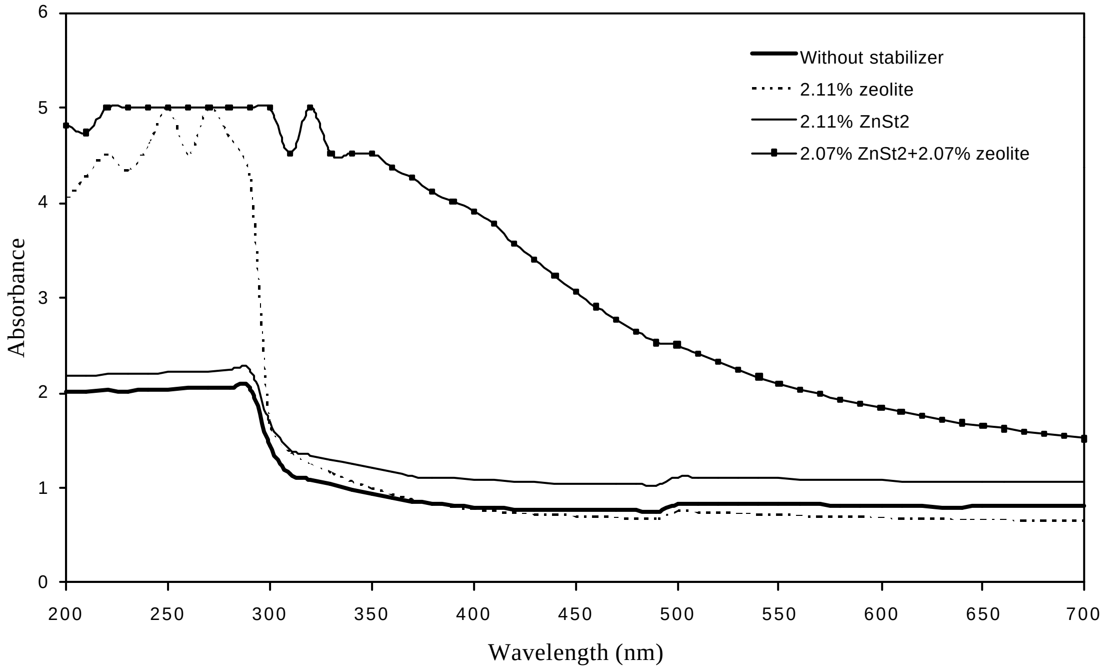


Figure 6.22. UV spectra of PVC plastigels having $ZnSt_2$ and zeolite heated at 160 °C for 90 min.

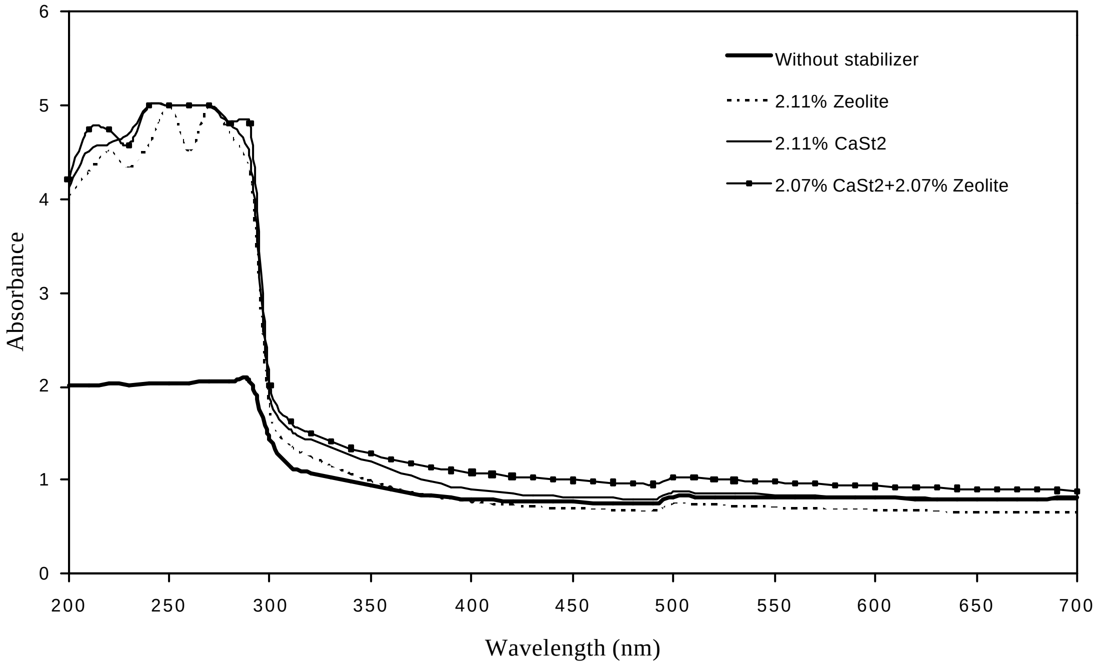


Figure 6.23. UV spectra of PVC plastigels having $CaSt_2$ and zeolite heated at 160 °C for 90 min.

When PVC plastigels were heated at 160°C for 90 min. conjugated double bonds were formed since the films were discolored. The concentrations of conjugated double bonds were calculated by using Equation (22) to observe amount of HCl evolved. 364 nm, peak which belongs to 6-n conjugated double bonds was taken as a reference of degradation The absorbance value at 364 nm, film thickness and the concentration of conjugated polyenes are shown in Table 6.17 and Table 6.18. The concentrations were found from absorbance, A at 364 nm and ε_A was taken as $1.38x10^{-3}$ dm^3. mol^{-1}. cm^{-1}. When the amount of zinc stearate in the samples increased the absorbance and the concentration of 6-n conjugated double bonds increased since $ZnCl_2$ formed from $ZnSt_2$ had an acceleration effect on dehydrochlorination of PVC. The concentration of 6-n's had highest value when the samples were stabilized with 2.07 wt. %$ZnSt_2$ and 2.07 wt. %zeolite.

Table 6.17. The absorbance (A), film thickness and the concentration of 6-n conjugated double bonds of PVC plastigels stabilized with $ZnSt_2$ and zeolite at λ=364 nm.

% Additive		A (λ364)	Film Thickness(μ)	C x 10^4 (mol/l)
$ZnSt_2$	Zeolite			
-	-	0.88	99.01	6.40
2.11	-	0.90	161.94	4.01
-	2.11	1.14	130.96	6.30
0.53	0.53	0.79	150.00	3.80
1.05	1.05	2.11	200.00	7.65
1.56	1.56	2.26	220.00	7.43
2.07	2.07	4.31	200.38	15.57

Table 6.18. The absorbance (A), film thickness and the concentration of 6-n conjugated double bonds of PVC plastigels stabilized with $CaSt_2$ and zeolite at λ=364 nm.

% Additive		A (λ364)	Film Thickness(μ)	C x 10^4 (mol/l)
$CaSt_2$	Zeolite			
-	-	0.88	99.01	6.40
2.11	-	1.08	181.62	4.29
-	2.11	1.14	130.96	6.30
0.53	0.53	0.68	173.00	2.84
1.05	1.05	1.03	213.00	3.52
1.56	1.56	1.138	183.00	5.46
2.07	2.07	1.19	206.52	4.19

The concentration of 6-n conjugated double bonds of the samples shown in Table 6.17 and 6.18, were plotted in Fig. 6.24 to Fig. 6.27.

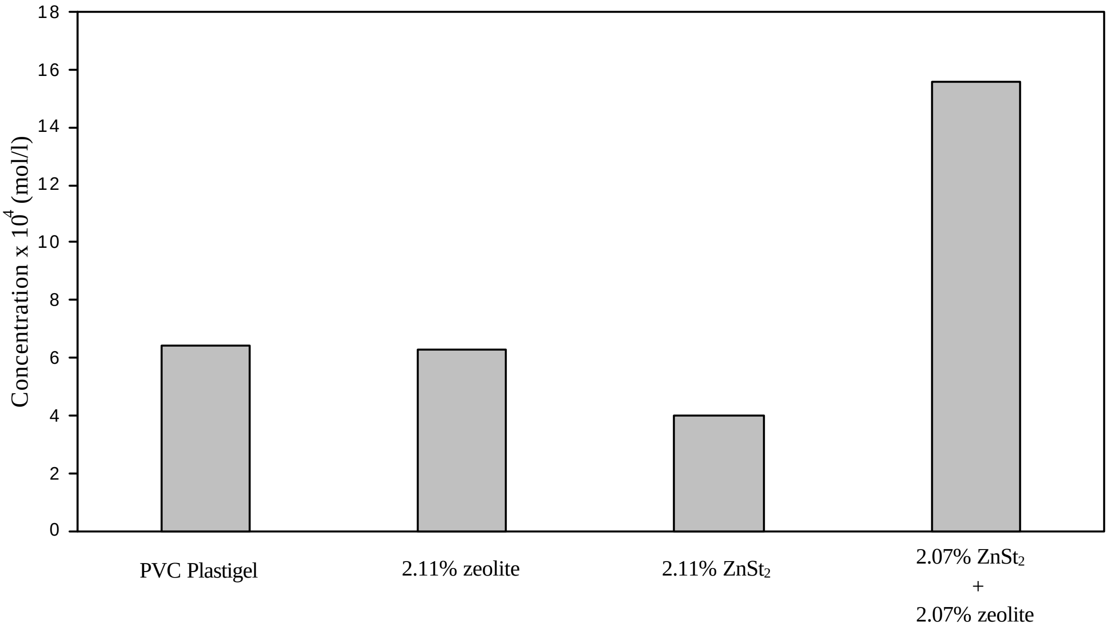


Figure 6.24. The concentration of 6-n conjugated double bonds of PVC plastigel having $ZnSt_2$ and/or zeolite heated at 160 °C for 90 min.

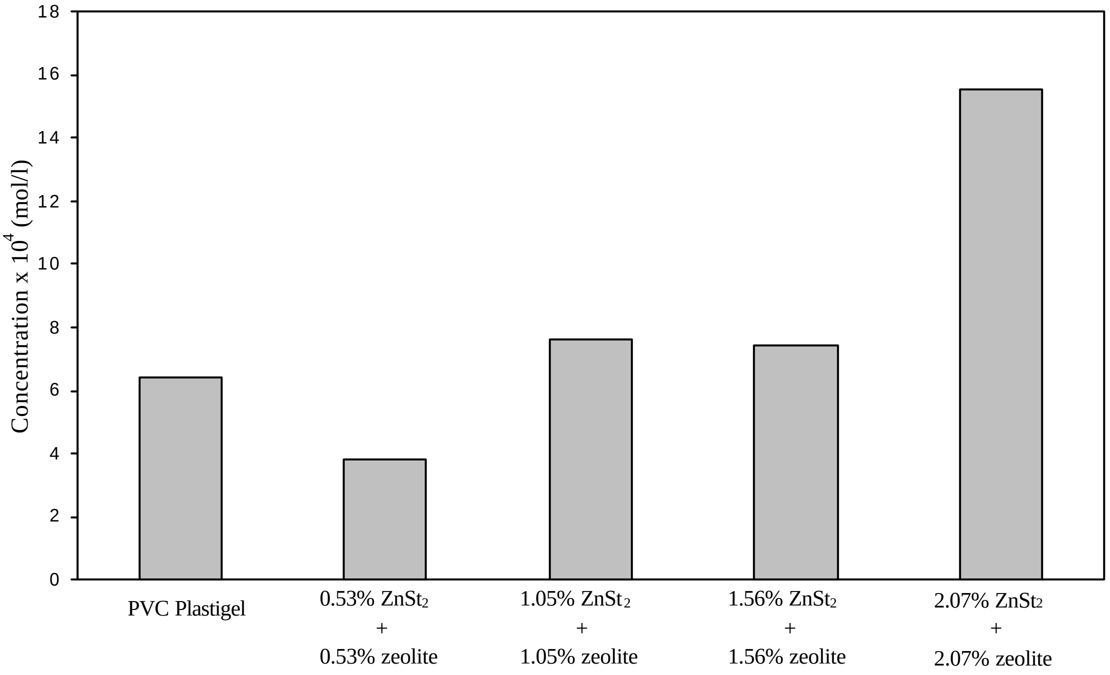


Figure 6.25. The concentration of 6-n conjugated double bonds of PVC plastigel films having $ZnSt_2$ and zeolite heated at 160°C for 90 min.

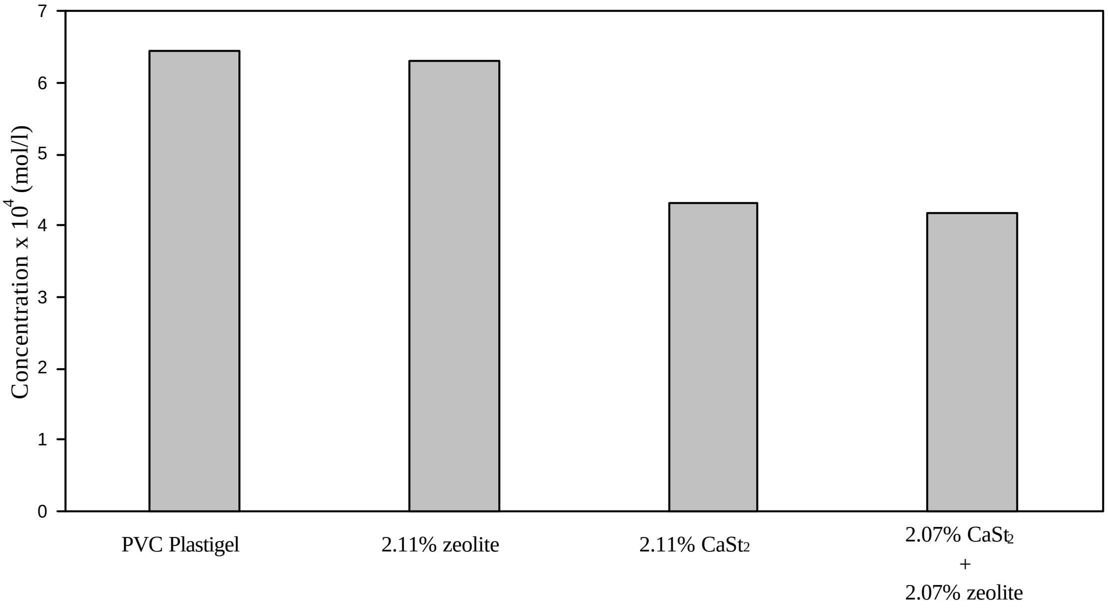


Figure 6.26. The concentration of 6-n conjugated double bonds of PVC plastigel films having CaSt$_2$ and/or zeolite heated at 160 °C for 90 min.

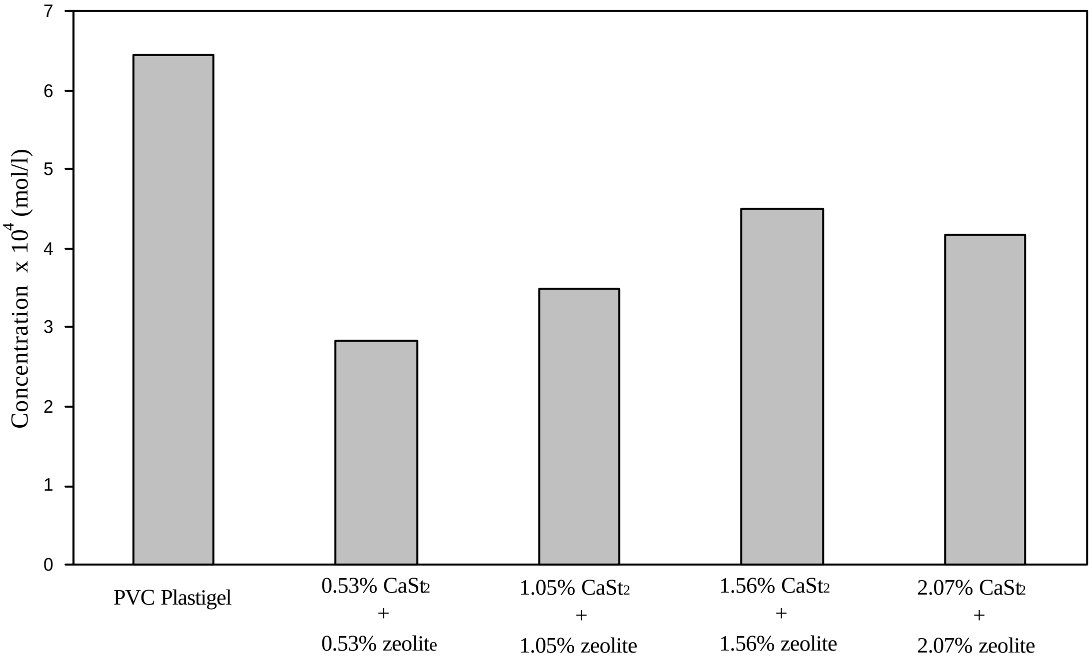


Figure 6.27. The concentration of 6-n conjugated double bonds of PVC plastigel films stabilized with CaSt$_2$ and zeolite and heated at 160 °C for 90 min.

In the theory of dehydrochlorination, discoloration of PVC is the result of the produced conjugated double bonds. As seen in Table 6.11 the sample stabilized with 2.07%$ZnSt_2$ and 2.07% zeolite is black at the end of 90 min and this film has highest concentration of 6-n's as shown in Fig.6.24 and Fig.6.25. Therefore these results are consistent with the theory in literature. When the sample stabilized with 0.53%$ZnSt_2$ and 0.53%zeolite was compared with PVC plastigel that did not contain any additive, the synergism was observed because the concentration of 6-n conjugated double bonds of this film was found as $3.80x10^{-4}$ mol/l and lower than the concentration of 6-n's of PVC plastigel. So if the amount of $ZnSt_2$ was low in PVC, it prevented the degradation process.

On the other hand the films stabilized with $CaSt_2$ were not discolored after 90 min. The concentrations of 6-n's of the samples stabilized with 2.11% Zeolite and 2.11% $CaSt_2$ were evaluated as $4.01x10^{-4}$ and $4.29x10^{-4}$. But the concentration of 6-n's of the sample stabilized with 0.53% $CaSt_2$ and 0.53%zeolite was found as $2.84x10^{-4}$ mol/l. The observed decrease in the 6-n's concentration when they were used at low level indicated the synergism between $CaSt_2$ and zeolite. Additionally the concentration of 6-n double conjugated bonds of all samples stabilized with different amount of $CaSt_2$ and zeolite are lower than the concentration of 6-n conjugated double bonds of PVC plastigel as shown in Fig.6.26 and Fig.6.27.

6.2.6. FTIR Study of PVC Plastigels

FTIR spectra of PVC produced by Petkim and PVC plastigel which was prepared by 43% DOP and gelled at 140 °C for 15 min. are shown in Fig.6.28. The spectrum of PVC plastigel prepared by 43% DOP shows the typical doublet of the phthalates at 1580-1600 cm^{-1} corresponding to the aromatic ring of the plasticizer. These bands are consistent with the literature (Beltrán, 1997). Fig.6.30 to Fig.6.35 show the FTIR spectrum of PVC plastigels stabilized with $ZnSt_2$ and zeolite. The peak at 1540 cm^{-1} is characteristic vibration of COO^- group of $ZnSt_2$ and the peak at 1640 cm^{-1} and 3400 cm^{-1} are due to the vibration of H_2O absorbed by zeolite. The band at 3700 cm^{-1} is the characteristic peak of natural zeolite. Fig.6.36 to Fig 6.39 show the FTIR spectrum of PVC plastigels stabilized with $CaSt_2$ and zeolite. The peak at 1540 cm^{-1} is corresponding to the antisymmetrical stretching vibration of carboxylate group of $CaSt_2$.

When PVC with metal soaps was heated labile chlorine atoms undergo ester interchange reaction with COO^- groups according to Frye and Horst Mechanism shown in Eq.9 and 10. The ester groups substituted with labile Cl atoms had also limited thermal stability and they were broken at long heating periods and the dehydrochlorination of PVC was initiated.

When PVC was dehydrochlorinated at high temperature, HCl formed with the dehydrochlorination reacted with zinc or calcium carboxylate and carboxylate anion was transferred into organic acid. The reactions can be shown as;

$$ZnSt_2 + 2HCl \longrightarrow ZnCl_2 + 2HSt \qquad (29)$$

$$CaSt_2 + 2HCl \longrightarrow CaCl_2 + 2HSt \qquad (30)$$

Reaction stoichiometry with zinc stearate and calcium stearate with HCl showed that 5.0 g metal soap in 100 g PVC could react with 0.6 g of HCl (Balköse et al., 2001). This was also indicated by the decrease of COO^- band of metal soap in FTIR spectrum. So the decrease in the amount of metal soap was observed by the decrease in the intensity of the band at 1540 cm^{-1}. The bands corresponding to the plasticizer (DOP) gradually disappeared when the samples were heated at 160 °C as a result of partially evaporation of DOP. The absorbance difference of the peaks at 1540, 1580 and 1600 cm^{-1} were measured using base line method. These results were divided to film thickness of each PVC plastigel since all the thicknesses of the films were not identical. Table 6.19 and 6.20 show these results for the samples stabilized with $ZnSt_2$ and zeolite. Their graph is given as a function of $ZnSt_2$ content of the gelled (at 140 °C) and heated (at 160 °C) films and shown in Fig.6.40. Table 6.21 and 6.22 show absorbance difference at 1540 and 1600 cm^{-1}/film thickness values of the films stabilized with $CaSt_2$ and zeolite. Their graph is given as a function of $CaSt_2$ content of the gelled (at 140 °C) and heated (at 160 °C) films and shown in Fig.6.41. As shown in Table 6.23 and 6.24, the absorbance difference values at 1580 cm^{-1} were not evaluated because they overlapped with the peak at 1580 cm^{-1} which was attributed to the vibration of aromatic ring of the plasticizer.

The absorbance difference at 1540 cm^{-1} / film thickness ratios increase with increasing the amount of $ZnSt_2$ in PVC plastisol except the samples having 2.07% and 2.11% $ZnSt_2$ as shown in Fig.6.40. This confirmed that dehydrochlorination (Eq.3) was occurred although the temperature was 140 °C. The produced HCl reacted with $ZnSt_2$ (Eq.29), then the formed $ZnCl_2$ promoted the degradation of the samples because of the accelerator effect of $ZnCl_2$ on the dehydrochlorination. At 160 °C, the dehydrochlorination of PVC was observed for all the samples since the absorbance difference at 1540 cm^{-1} / film thickness ratios were lower than the ratios at 140 °C. On the other hand, Equation 30 occurred efficiently when the samples were heated at 160 °C. The absorbance difference at 1540 cm^{-1} / film thickness ratio of the sample having 2.11% $CaSt_2$ did not decrease with increasing the amount of $CaSt_2$ in PVC plastisol. This indicated that the produced $CaCl_2$ (Eq.30) did not promote the dehydrochlorination as $ZnCl_2$ did.

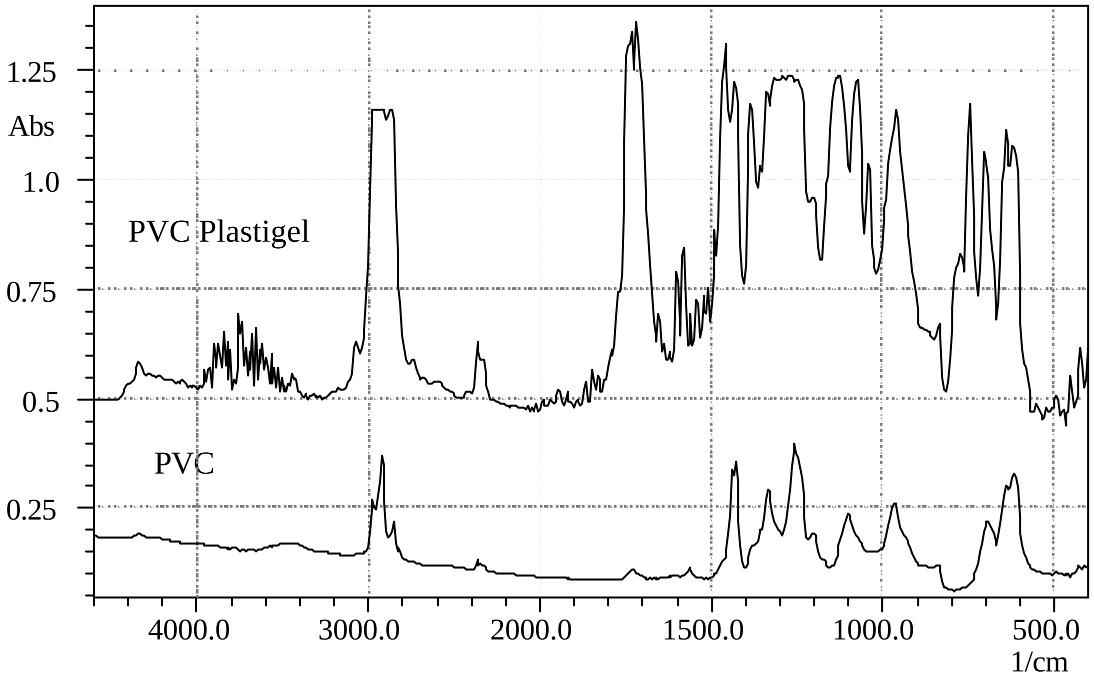


Figure 6.28. FTIR spectra of PVC and PVC plastigel gelled at 140 °C for 15 min.

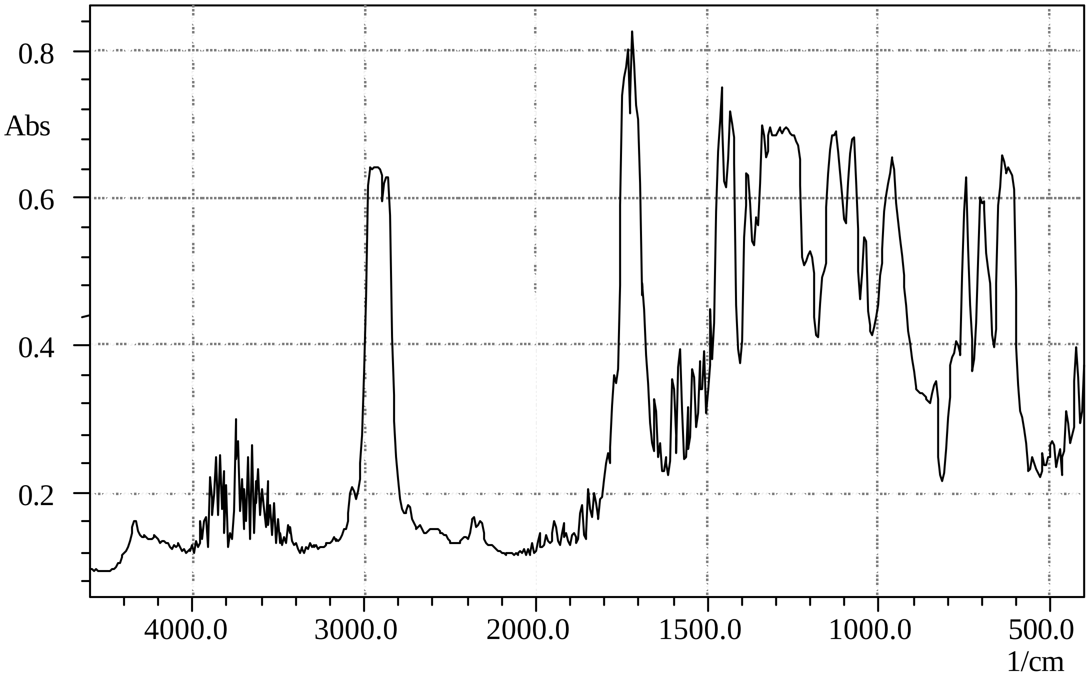


Figure 6.29. FTIR spectrum of PVC plastigel gelled at 160 °C for 90 min.

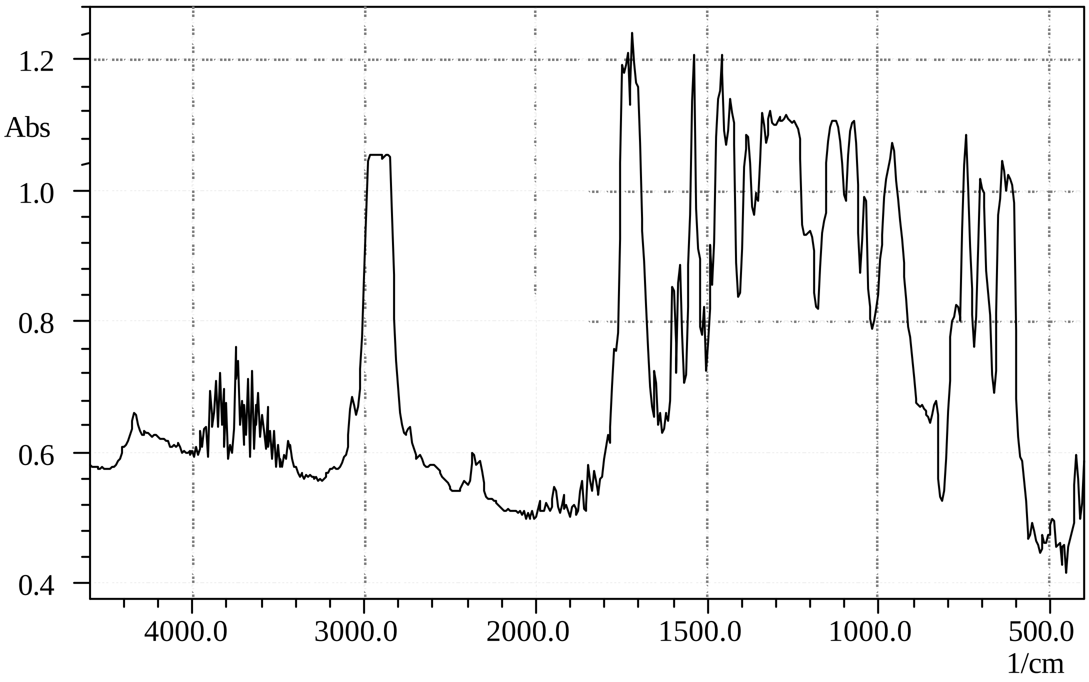


Figure 6.30. FTIR spectra of PVC and PVC plastigel stabilized with 2.11%$ZnSt_2$ and gelled at 140 °C for 15 min.

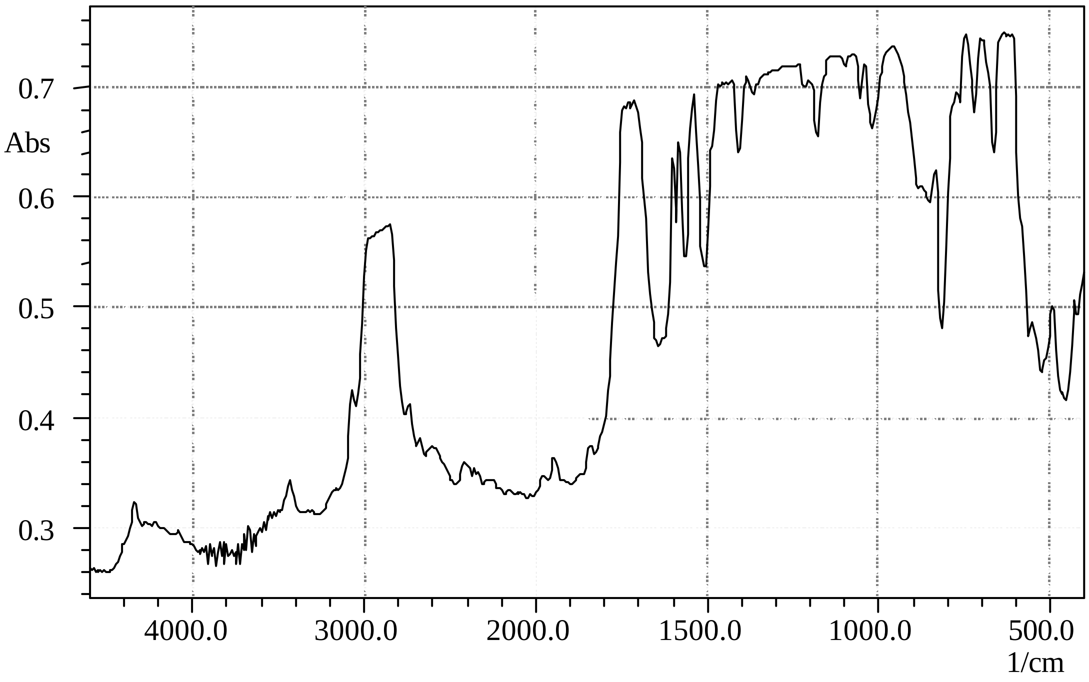


Figure 6.31. FTIR spectra of PVC and PVC plastigel stabilized with 2.11%$ZnSt_2$ and heated at 160 °C for 90 min.

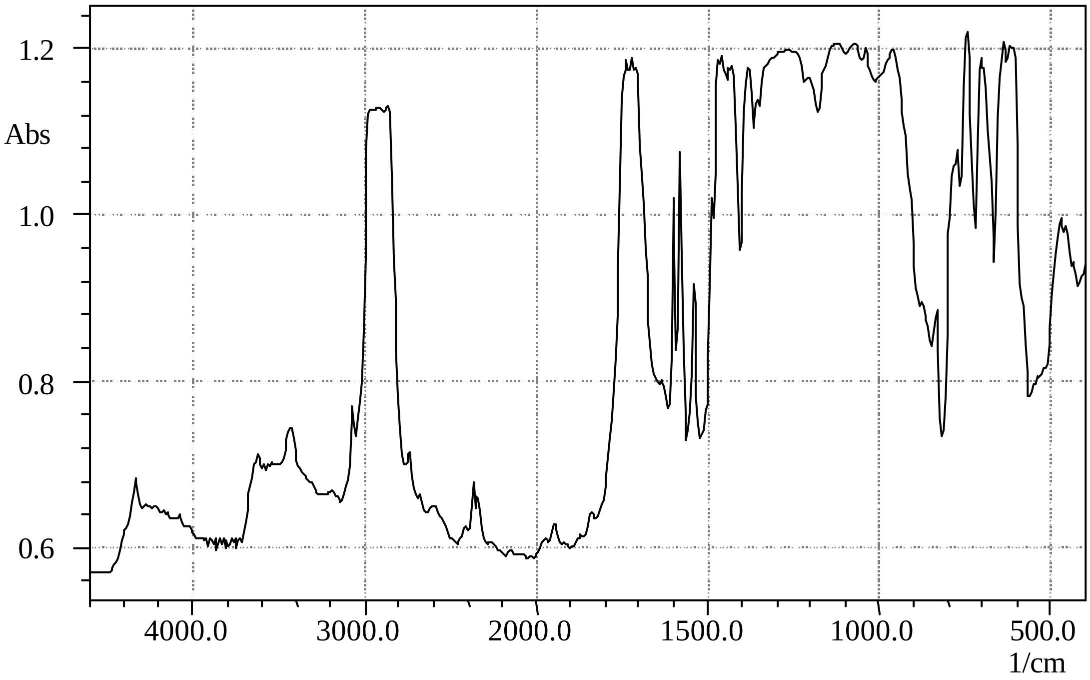


Figure 6.32. FTIR spectra of PVC and PVC plastigel stabilized with 2.11% zeolite and gelled at 140 °C for 15 min.

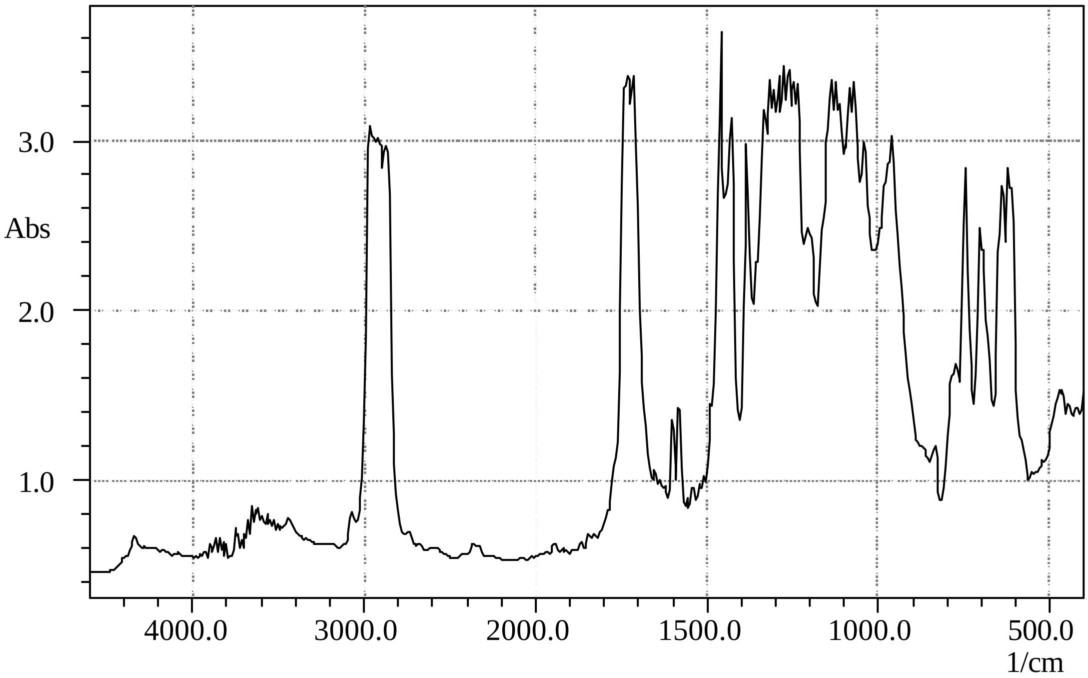


Figure 6.33. FTIR spectra of PVC and PVC plastigel stabilized with 2.11%zeolite and heated at 160 °C for 90 min.

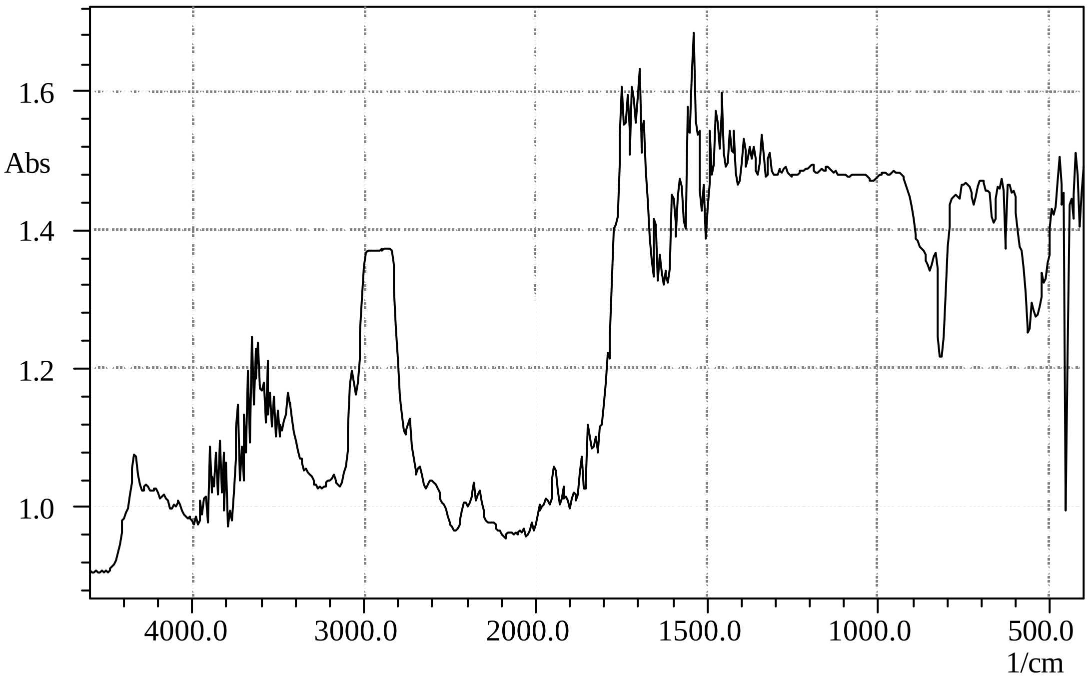


Figure 6.34. FTIR spectra of PVC and PVC plastigel stabilized with 2.07%$ZnSt_2$ and 2.07% zeolite gelled at 140 °C for 15 min.

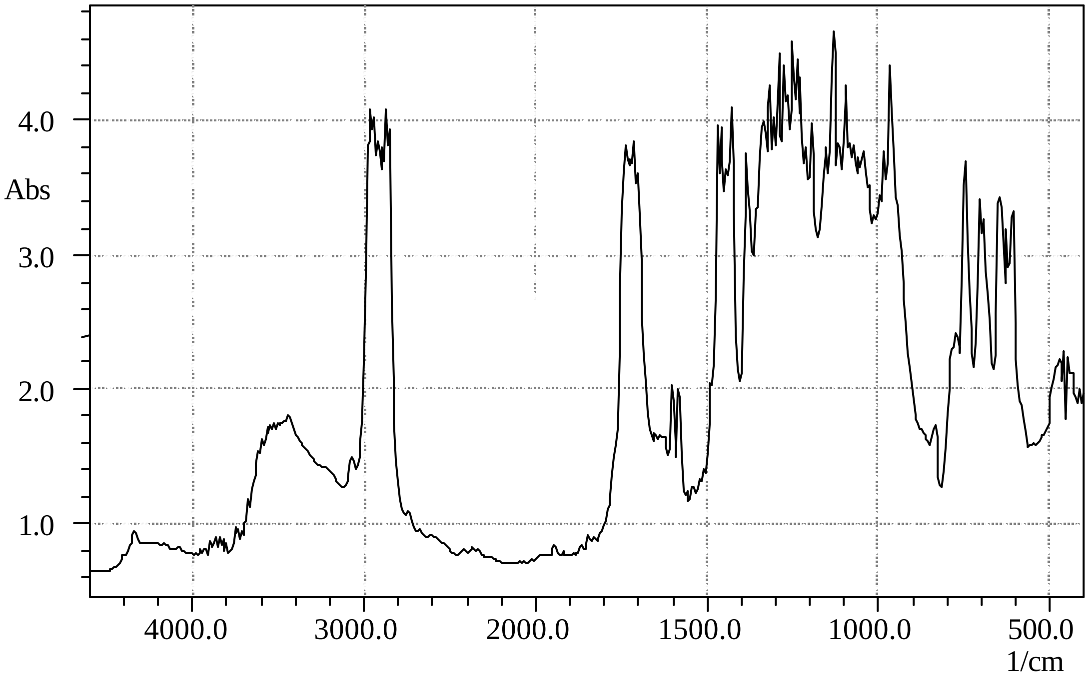


Figure 6.35. FTIR spectra of PVC and PVC plastigel stabilized with 2.07%$ZnSt_2$ and 2.07% zeolite heated at 160 °C for 90 min.

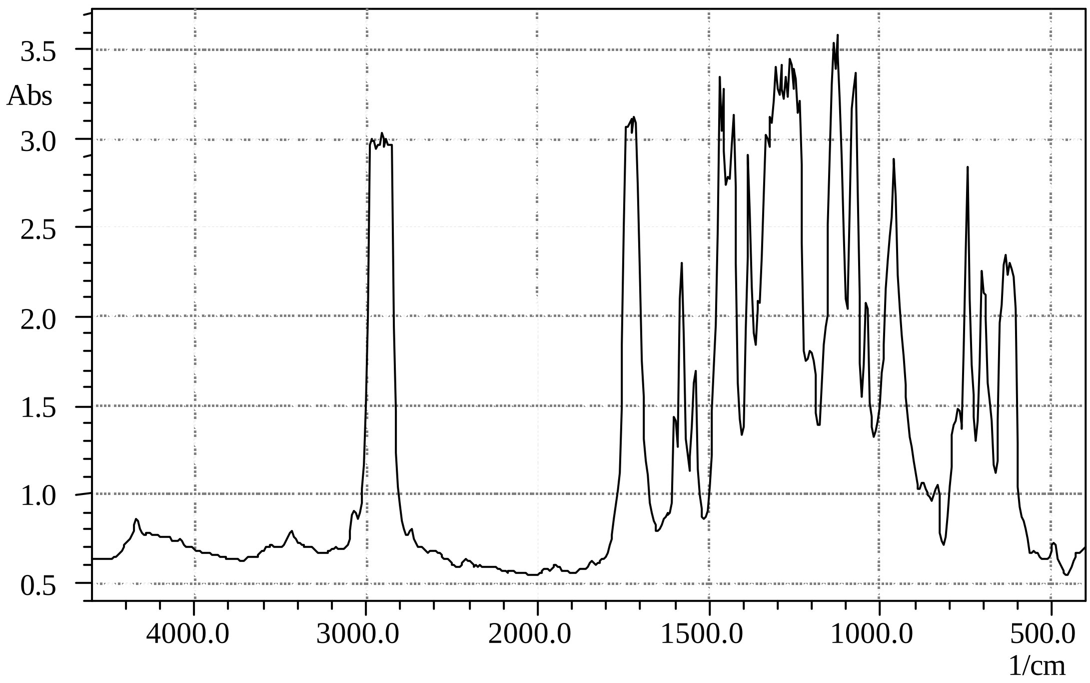


Figure 6.36. FTIR spectra of PVC and PVC plastigel stabilized with 2.11%$CaSt_2$ and gelled at 140 °C for 15 min.

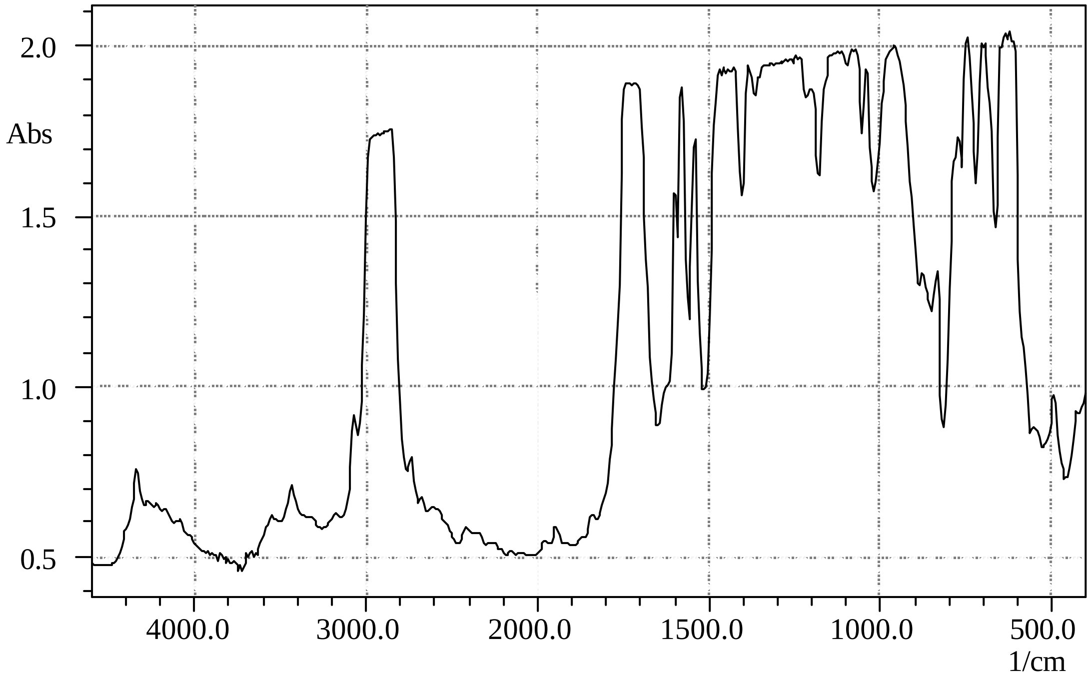


Figure 6.37. FTIR spectra of PVC and PVC plastigel stabilized with 2.11%$CaSt_2$ and heated at 160 °C for 90 min.

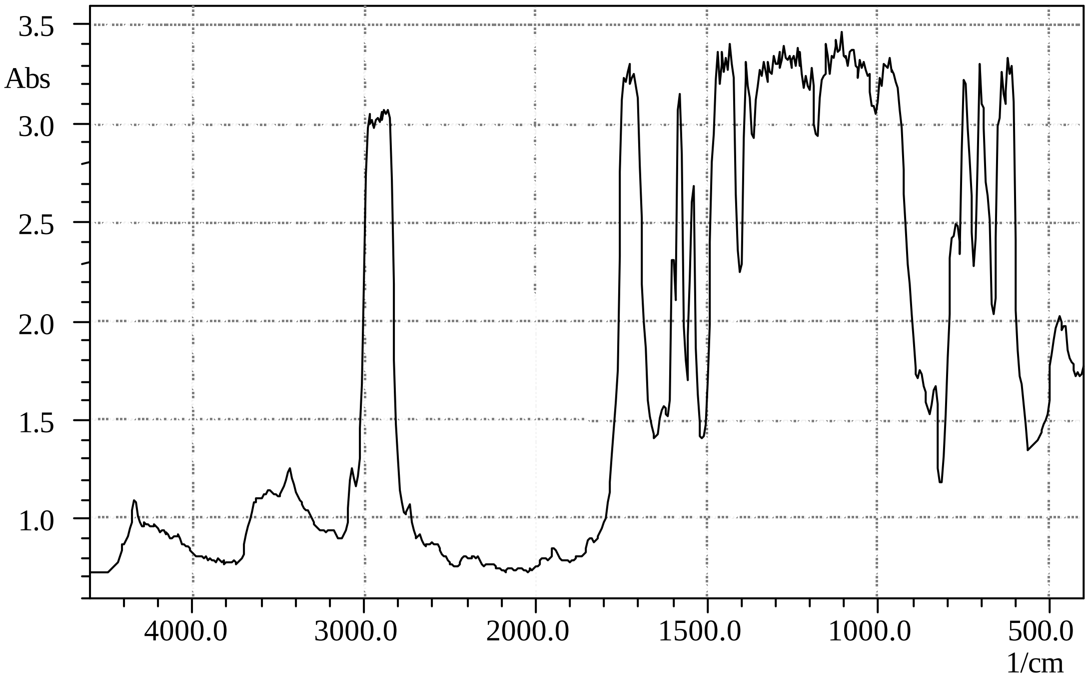


Figure 6.38. FTIR spectra of PVC and PVC plastigel stabilized with 2.07%CaSt$_2$ and 2.07% zeolite gelled at 140 °C for 15 min.

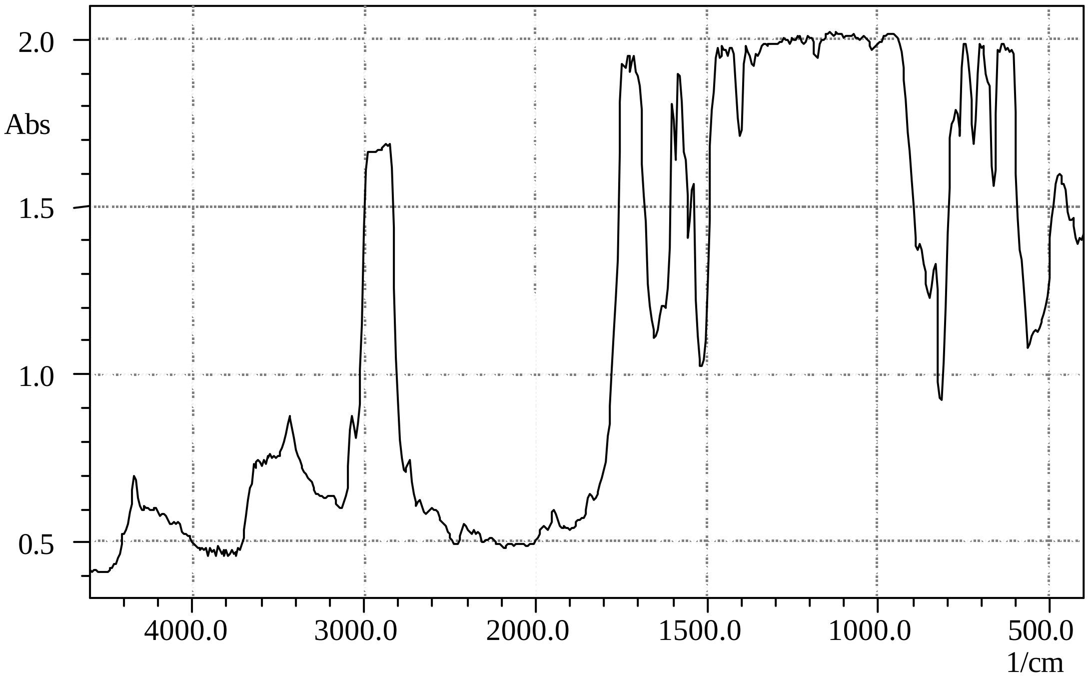


Figure 6.39. FTIR spectra of PVC and PVC plastigel stabilized with 2.07%CaSt$_2$ and 2.07% zeolite heated at 160 °C for 90 min.

Table 6.19. Absorbance difference / film thickness (cm) values of PVC Plastisol stabilized with $ZnSt_2$ and zeolite gelled 15 min at 140 °C.

% Addtive		Absorbance at 1540 cm^{-1}	Absorbance at 1580 cm^{-1}	Absorbance at 1600 cm^{-1}
$ZnSt_2$	Zeolite			
-	-	-	19.60	16.23
2.11	-	12.19	1.55	2.13
-	2.11	-	8.72	9.33
0.53	0.53	12.00	13.65	13.97
1.05	1.05	40.00	20.33	20.31
1.56	1.56	61.36	24.80	22.93
2.07	2.07	15.09	2.25	2.92

Table 6.20. Absorbance difference / film thickness (cm) values of PVC plastisol stabilized with $ZnSt_2$ and zeolite and heated 90 min at 160 °C

% Addtive		Absorbance at 1540 cm^{-1}	Absorbance at 1580 cm^{-1}	Absorbance at 1600 cm^{-1}
$ZnSt_2$	Zeolite			
-	-	-	17.50	14.36
2.11	-	10.83	5.31	3.75
-	2.11	-	31.36	27.84
0.53	0.53	13.80	37.50	27.02
1.05	1.05	6.29	35.62	27.58
1.56	1.56	9.78	33.08	28.66
2.07	2.07	6.07	27.41	24.39

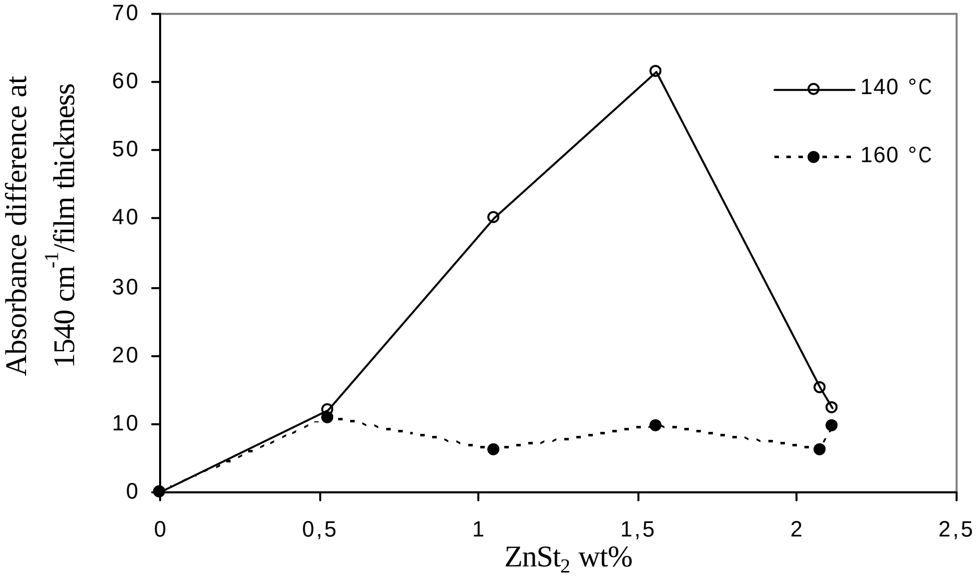


Figure 6.40. Absorbance difference at 1540 cm^{-1}/film thickness of PVC plastigel films stabilized with $ZnSt_2$ and zeolite.

Table 6.21. Absorbance difference / film thickness (cm) values of PVC Plastisol stabilized with $CaSt_2$ and zeolite and gelled 15 min at 140 °C.

Additive wt.%		Absorbance at 1540 cm^{-1}	Absorbance at 1600 cm^{-1}
$CaSt_2$	Zeolite		
-	-	-	16.20
2.11	-	52.10	20.60
-	2.11	-	9.30
0.53	0.53	33.06	17.20
1.05	1.05	31.08	21.11
1.56	1.56	44.12	18.72
2.07	2.07	49.43	21.20

Table 6.22. Absorbance difference / film thickness (cm) values of PVC plastisol stabilized with $CaSt_2$and zeolite heated 90 min at 160 °C

Additive wt.% $ZnSt_2$	Zeolite	Absorbance at 1540 cm^{-1}	Absorbance at 1600 cm^{-1}
-	-	-	1.44
2.11	-	30.40	1.79
-	2.11	-	2.68
0.53	0.53	8.82	1.70
1.05	1.05	3.59	3.60
1.56	1.56	12.80	3.64
2.07	2.07	20.10	1.97

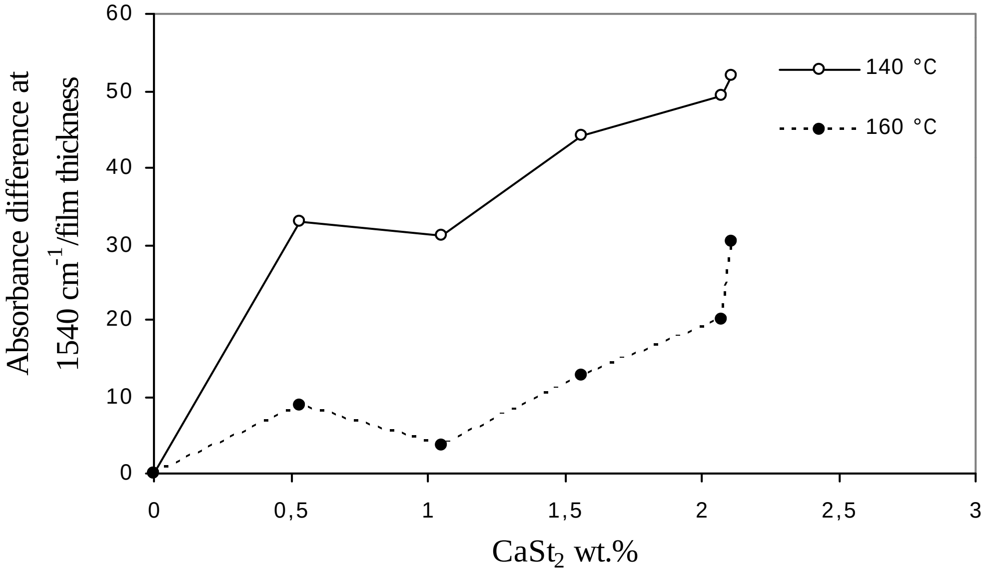


Figure 6.41. Absorbance difference at 1540 cm^{-1} /film thickness of PVC plastigel films stabilized with $CaSt_2$ and zeolite.

6.2.7. TGA Study of PVC Plastigel Films

Thermogravimetric analysis is one of the most known techniques to observe the loss of mass caused by elimination of HCl and the evaporation of plasticizer from plastisols. Elimination of HCl is the first step of the thermal degradation of PVC plastisol and simultaneously conjugated double bond are formed in the polymer chain. At higher temperatures the material undergoes a partial carbonization with the release of benzene and other aromatics. Phthalate plasticizers are thermally degraded from 200 °C and the boiling point of DOP is 231 °C. Therefore, the weight loss before 231 °C is mainly due to the elimination of HCl gas and partially to evaporation of DOP. TGA curves of PVC plastigel films gelled at 140 °C for 15 min. were obtained by heating them from 25 °C to 600 °C at a rate of 10 °C/min. The weight losses of the samples by heating are shown in Fig.6.42 to Fig.6.45. To determine the thermal stability of the PVC plastigels the following characteristics of the first and the second degradation step were evaluated from the TGA curves: the residual mass % at, 400 and 600 °C. These results were reported in Table 6.23 and 6.24. Unstabilized PVC plastigel had the lowest residual mass loss at 400 and 600 °C due to the catalytic effect of HCl on dehydrochlorination of PVC at a low level of degradation. The residual mass loss % values of stabilized PVC plastigels were somewhat different depending on the zeolite content. Onset temperatures (the intersection of the extrapolated base line with inflection tangent) of mass loss are shown in Table 6.25 and 6.26 for both stabilized and unstabilized samples. The sample stabilized with 1.05%$Znst_2$ and 1.05%zeolite presented the highest onset temperature (204.4 °C). So these stabilizers prevented early dehydrochlorination when they were used at low levels. It was observed that when $ZnSt_2$ or zeolite was used individually the onset temperature has never reached to 204.4 °C This might be the synergistic effect between these stabilizers on PVC thermal degradation at low levels. On the other hand, the samples stabilized with $CaSt_2$ and zeolite presents lower onset temperature than the unstabilized PVC plastigel.

Since PVC is unstable and rapidly degrades at processing temperature, the residual mass% of the samples at 225 °C are reported in Table 6.25 and 6.26 and shown in Fig.6.46 to 6.49. Although the sample stabilized with 1.05% $ZnSt_2$ and 1.05% zeolite increased the onset temperature up to 204.4 °C, it could not reduce the mass loss % at the processing temperature. As shown in Fig.6.46 and 6.47, the addition of $ZnSt_2$ and/or zeolite does not have any effect on stabilization of PVC at the processing temperature. The PVC plastigels having $CaSt_2$ present lower mass loss % at 225 °C.

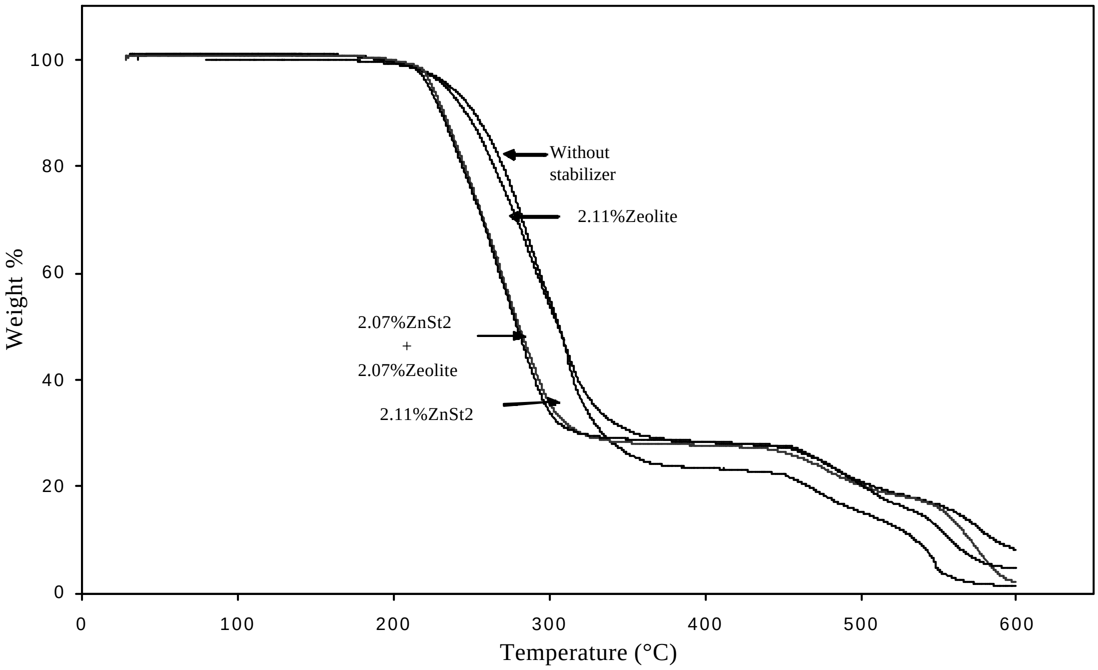


Figure 6.42. TGA curves of unstabilized plastigel and the plastigels stabilized with $ZnSt_2$ or zeolite

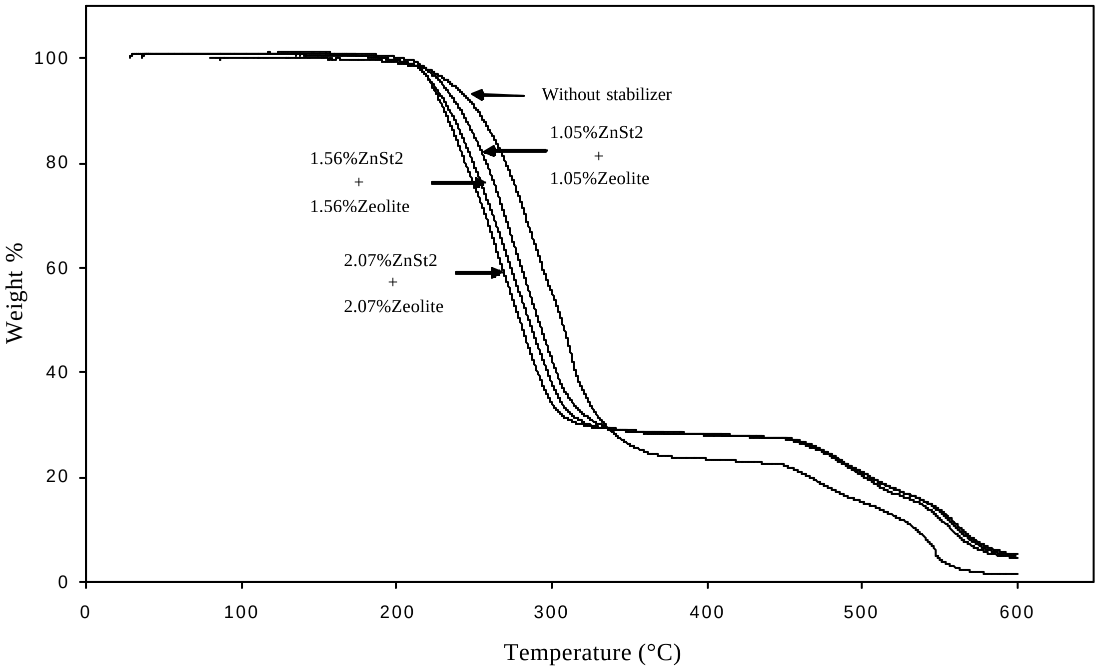


Figure 6.43. TGA curves of unstabilized plastigel and the plastigels stabilized with $ZnSt_2$ and zeolite.

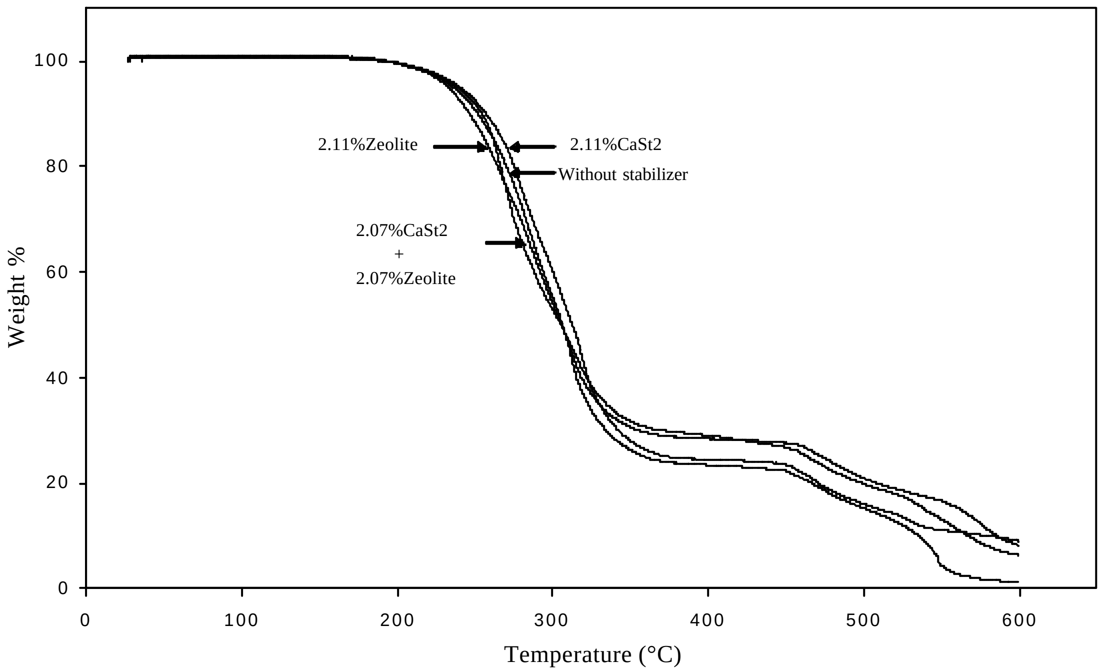


Figure 6.44. TGA curves of unstabilized plastigel and the plastigels stabilized with $CaSt_2$ or zeolite

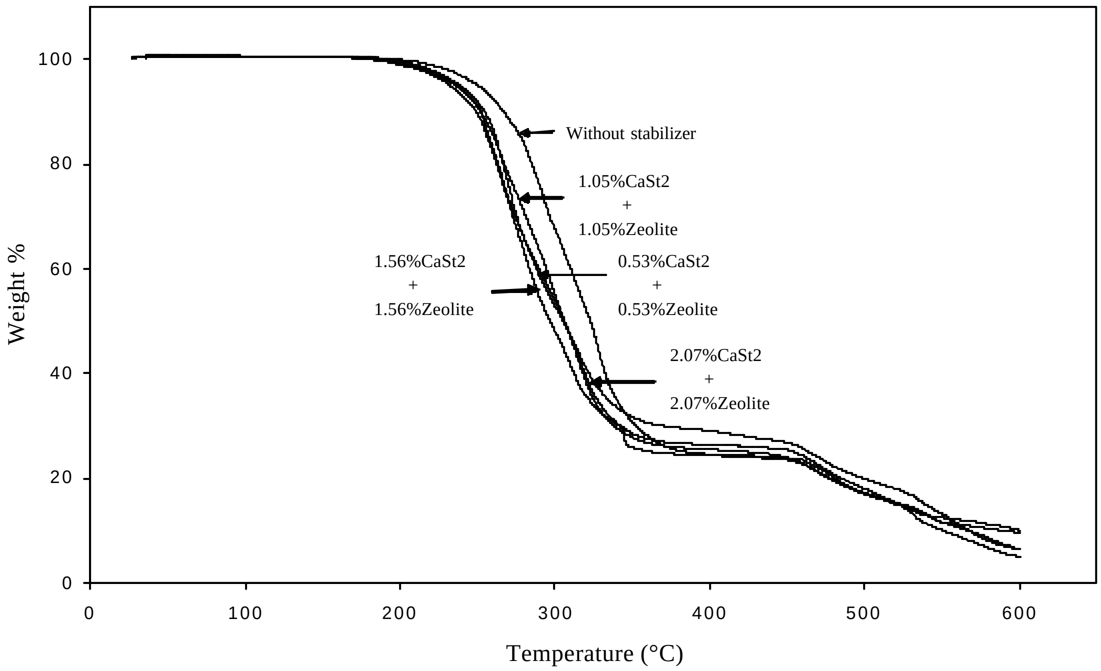


Figure 6.45. TGA curves of unstabilized plastigel and the plastigels stabilized with $CaSt_2$ and zeolite.

Table 6.23. Residual mass of PVC plastigels stabilized with $ZnSt_2$ and zeolite at 400 °C and 600 °C.

% Additive $ZnSt_2$	% Additive Zeolite	Residual mass % at 400 °C	Residual mass % at 600 °C
-	-	23.48	1.38
2.11	-	27.72	2.16
-	2.11	28.42	8.23
1.05	1.05	28.05	5.19
1.56	1.56	28.22	4.93
2.07	2.07	27.42	4.53

Table 6.24. Residual mass of PVC plastigels stabilized with $CaSt_2$ and zeolite at 400 °C and 600 °C.

% Additive $CaSt_2$	% Additive Zeolite	Residual mass % at 400 °C	Residual mass % at 600 °C
-	-	23.48	1.38
2.11	-	24.49	9.06
-	2.11	28.42	8.23
0.53	0.53	25.30	10.14
1.05	1.05	26.45	4.97
1.56	1.56	24.35	6.43
2.07	2.07	29.04	6.42

Table 6.25. Onset temperature of mass loss and the residual mass of PVC plastigels stabilized with $ZnSt_2$ and zeolite at 225 °C.

% Additive		Onset temperature of mass loss	Residual mass % at 225 °C
$ZnSt_2$	Zeolite		
-	-	194.5	97.17
2.11	-	198.6	94.89
-	2.11	191.8	96.87
1.05	1.05	204.4	96.44
1.56	1.56	193.1	94.35
2.07	2.07	187.8	90.70

Table 6.26. Onset temperature of mass loss and the residual mass of PVC plastigels stabilized with $CaSt_2$ and zeolite at 225 °C.

% Additive		Onset temperature of mass loss	Residual mass % at 225 °C
$CaSt_2$	Zeolite		
-	-	194.5	97.17
2.11	-	190.4	97.52
-	2.11	191.8	96.87
0.53	0.53	182.5	96.78
1.05	1.05	186.8	96.97
1.56	1.56	183.3	96.39
2.07	2.07	192.7	97.35

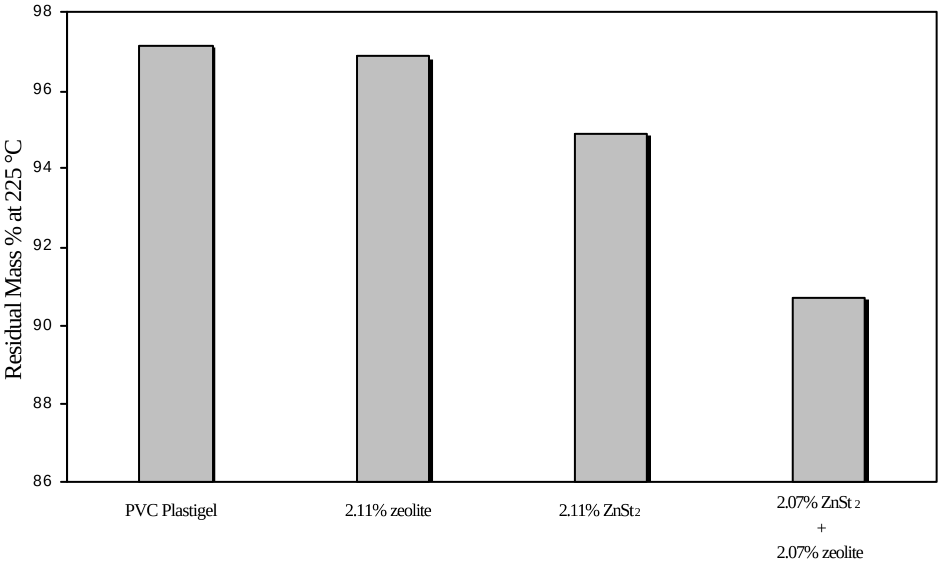


Figure 6.46. Residual mass % values of PVC plastigel stabilized with $ZnSt_2$ and zeolite at 225 °C.

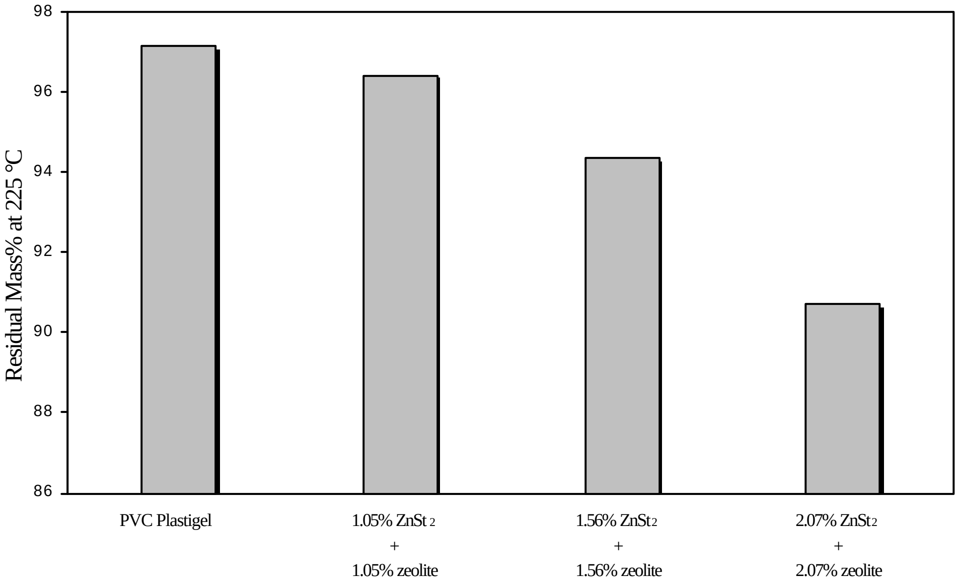


Figure 6.47. Residual mass % values of PVC plastigel stabilized with $ZnSt_2$ and zeolite at 225 °C.

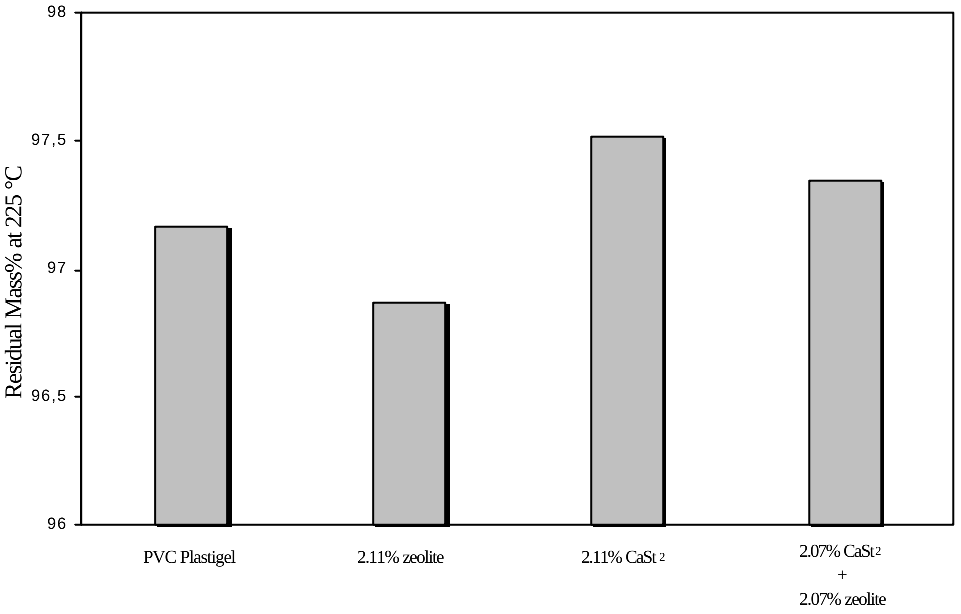


Figure 6.48. Residual mass % values of PVC plastigel stabilized with $CaSt_2$ and zeolite at 225 °C.

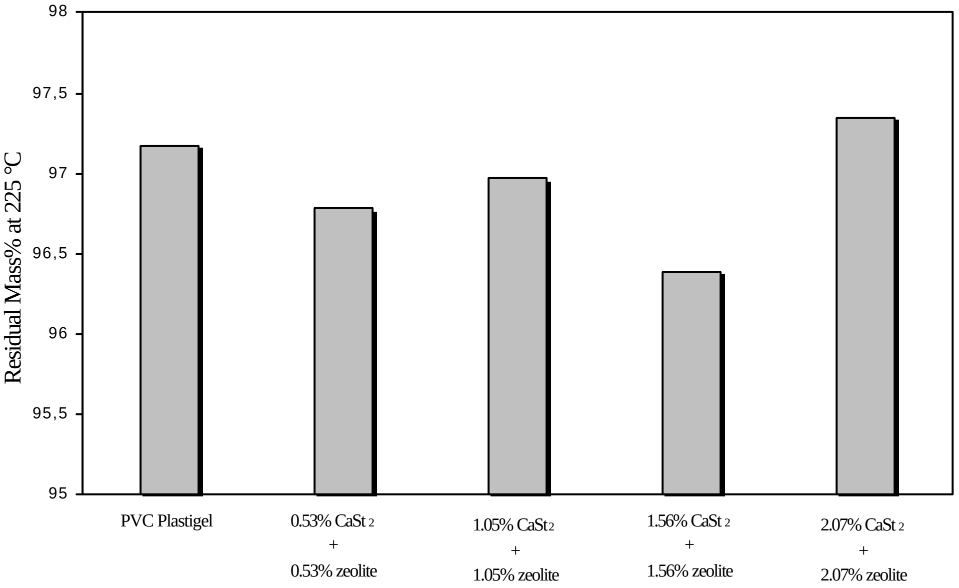


Figure 6.49: Residual mass % values of PVC plastigel stabilized with $CaSt_2$ and zeolite at 225 °C.

6.4. Kinetic Study of Dehydrochlorination of PVC Plastigels

In this part of the study, the kinetic parameters (rate constants and activation energies) of the thermal degradation of unstabilized and stabilized PVC plastigels were determined by using 763 PVC Thermomat. Plastigel films and PVC produced by Petkim in the reaction vessels degraded at 140 and 160 °C in PVC Thermomat. HCl gas evolved from reaction vessels and transferred into the measuring vessels by a nitrogen gas stream. In measuring vessels, deionized water absorbed HCl gas and the conductivity of this solution increased with the increasing amount of HCl gas evolved from PVC plastigel.

6.3.1. Kinetic Study of PVC and PVC Plastigels

The kinetic study was performed not only to investigate the thermal degradation of PVC and PVC plastigels but also to expose the effect of plasticizer and its concentration on dehydrochlorination of PVC at 160 °C. Fig.6.50 shows the change of conductivity of aqueous solution with respect to time for PVC, DOP, and PVC plastigels prepared by 33 wt. %, 43 wt. % DOP. It was observed that firstly, the conductivity values of all the samples except DOP were constant, in other words, HCl was not evolved from the PVC plastigels then dehydrochlorination of PVC occurred and HCl started to evolve and changed the conductivity of the aqueous solution. So the induction time is the period up to inflection point of this curve. The induction time values for PVC, PVC plastigels having 33 wt. % DOP and 43 wt. % DOP were determined as 2.3, 2.98, and 1 h at 160 °C respectively. The results indicated that small amounts of DOP delayed the induction time of PVC but high amounts of it promoted the dehydrochlorination of PVC. These results are in good agreement with those obtained by other investigators. Minsker et al., 1987 tested the addition of small amounts of phthalates, sebacates and adipates to PVC decreased the rate of dehydrochlorination, due to an inhibition effect on the growing of polyene sequences. On the other hand, Marcilla et al., 1995 found that the presence of DOP accelerated the process of decomposition of PVC and observed the destabilizing effect when polar compounds were added to PVC.

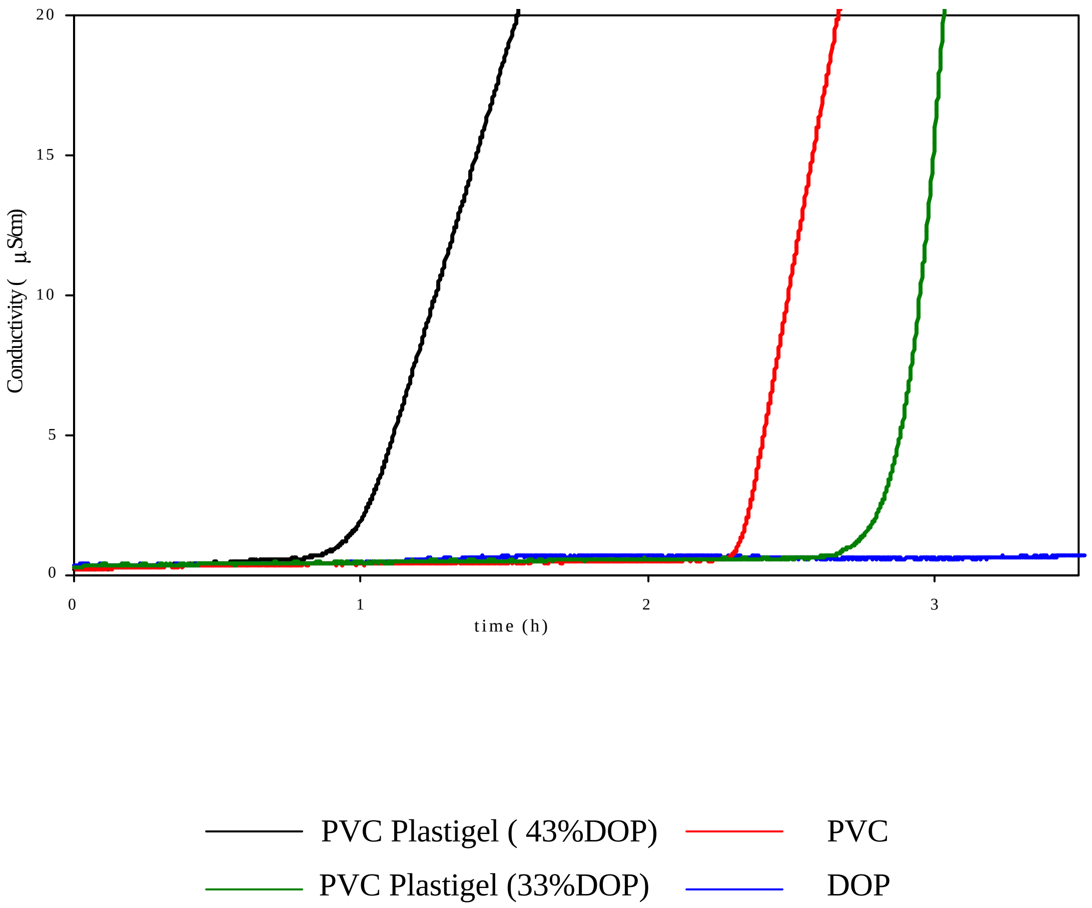


Figure 6.50. The change of conductivity of the aqueous solution with respect to time for PVC, PVC plastigels and DOP at 160 °C.

The curves which show the conductivity change with respect to time were used to determine the rate constant of dehydrochlorination of any sample. The slopes (*a*) of these curves were related with the rate of change of the conductivity (*K*) change with respect to time of the solution. The concentrations of the solutions were evaluated by using the Equation (5). Thus rate of dehydrochlorination of PVC were determined by using the amount of HCl that transferred into the deionized water.

$$a = \frac{\Delta K}{\Delta t} \qquad (31)$$

The conductivity of an electrolyte solution is the sum of the contributions of all the ionic species in the electrolyte.

$$ÄK = F.\Delta C_i.U_i \qquad (5)$$

where;

DK is the change of conductivity

DC_i is the change of concentration of ion that conducts the electricity.

U_i is the mobility of ions dissolved in water at 25 °C.

When the dehydrochlorination of PVC is taken as a first order reaction (Titow, 1985);

PVC (s) dePVC (s) + HCl (g) (32)

where;

dePVC= Dehydrochlorinated PVC

Rate of dehydrochlorination depends on concentration of potential double bonds or concentration of unreacted HCl in PVC.

$$\frac{dC_{HCl}}{dt} = k.(C_o - C_{HCl}) \qquad (33)$$

Where; $\frac{dC_{HCl}}{dt}$ = Rate of dehydrohlorination (μmol/gr PVC. s)

k= Rate constant of the reaction (s^{-1})

C_o= Concentration of potential double bonds to be formed when 100% of HCl is eliminated per 1 g of PVC

C_{HCl} = Concentration of evolved HCl from the sample.

When 1mole HCl is eliminated, 1 mole double bond forms.

C_o=16.5x10^3 µmol/g.PVC

Since $C_{HCl} <<< C_o$

C_o-C_{HCl} can be taken as 16.5x10^3 µmol/g.PVC

$$\frac{dC_{HCl}}{dt} = k.C_o \tag{34}$$

$\frac{dC_{HCl}}{dt}$ can be calculated from the slope of conductivity versus time graph by taking the derivative of Eq.5 with respect to time.

$$\frac{dK}{dt} = F.\Sigma|Z_i|.\frac{dC_{HCl,w}}{dt}.U_{HCl} \tag{35}$$

where;

$C_{HCl,w}$ is the concentration of HCl in water.

Assumption; all HCl evolved from PVC was absorbed by water.

$$\frac{dC_{HCl,w}}{dt}.V_w = \frac{dn_{HCl}}{dt} \tag{36}$$

n_{HCl} =Moles of evolved HCl gas.

V_w= Volume of water in measuring vessel

V_w= 6x10^{-5} m^3

$$\frac{dC_{HCl}}{dt} = \frac{dn_{HCl}}{dt}.\frac{1}{m.CF} \tag{37}$$

m=Mass of plastisol in reaction vessel

$CF =$ Fraction of PVC in PVC plastisol

$$k = \frac{dC_{HCl}}{dt} \cdot \frac{1}{C_o} = \frac{dn_{HCl}}{dt} \cdot \frac{1}{m.CF} \cdot \frac{1}{C_o} \tag{38}$$

Two rate constants were calculated for each dehydrochlorination reaction. Initial rate constants were determined by using the initial region of the curves where HCl gas started to release, and linear region rate constants were evaluated by using the linear region of the curve where the acceleration effect of HCl and the products formed at the end of dehydrochlorination on degradation process could be observed. The calculated rate constants and induction, stability periods for PVC and PVC plastigels are reported in Table 6.27. Although small amount of DOP improved the induction and stability periods of PVC, it was not as effective as high amount of DOP to reduce the dehydrochlorination rate of PVC. The greater efficiency with high amount of DOP was due to the greater size of the octyl group, which minimized the possible dehydrochlorination reaction by separating of the neighboring polymeric chains.

Table 6.27. Induction, stabilization time values and rate constants at 160 °C for PVC and PVC plastigels

Sample	Induction time (h)	Stabilization time (h)	Initial rate constant ki.10^6(min^{-1})	Linear region rate constant klr.10^5 (min^{-1})
PVC	2.50	3.23	2.53	1.43
PVC Plastigel (33% DOP)	2.98	3.19	1.06	3.64
PVC Plastigel (43%DOP)	1.01	2.39	9.34	1.23

6.3.2. Kinetic Study of PVC Plastigels Containing 33% DOP

The PVC plastigels prepared by 33 wt. % DOP and stabilized with $ZnSt_2$ and zeolite were tested in PVC Thermomat at 140 °C and 160 °C. Fig.6.51 and Fig.6.52 show the kinetic curves of dehydrochlorination of the samples. Additionally Table 6.28 and Table 6.29 reported the determined induction and stability time values and the calculated rate constants for these samples.

As shown in Fig.6.51 and Fig.6.52 the kinetic curves can be divided two sections; an initial low increase in the conductivity of the aqueous solution followed by a more rapid change in the conductivity This means that small amounts of HCl are released at the beginning of the heat treatment, then more rapid dehydrochlorination occurs after the consumption of the stabilizers.

PVC plastigel presents a longer induction period than the samples stabilized with $ZnSt_2$ and zeolite at 140 °C. The sample which was stabilized with 2.44% zeolite has the longest induction and the stability time (Fig.6.51 and Table 6.28). Also the PVC plastigel stabilized with 2.44%$ZnSt_2$ and 2.44%zeolite has longer induction and stability time values than the sample stabilized with only 2.44% $ZnSt_2$. Therefore in the presence of zeolite, a stabilizer effect leading a long induction period which corresponded to the first section of the kinetic curve of dehydrochlorination was observed. The stabilizing effect of zeolite on the increase in the induction period of the sample was considered the result from the absorption of HCl which was thought to reduce the autocatalytic effect of HCl evolved at the initial stages of dehydrochlorination. Besides this, the increase in the linear region rate constants, in other words, the increasing rate of dehydrochlorination after the consumption of $ZnSt_2$ for all samples indicated the autoacceleration effect of HCl and the produced $ZnCl_2$ (Eq.29).The initial and linear region rate constants of unstabilized PVC plastigel were determined as $1.06x10^{-6}$ and $3.64x10^{-5}$ min^{-1} at 140 °C whereas these rate constants were evaluated as $1.62x10^{-4}$ and $6.60x10^{-4}$ min^{-1} at 140 °C by Baltacýoðlu et al.,1999 (Table 4.3). At low $ZnSt_2$ and zeolite levels the traces in the induction time were very stable indicating the power of this soap to inhibit dehydrochlorination but as soon as this was finished the acid evolved instantaneously at 140 and 160 °C. Also the induction and stability periods at 160 °C were lower then the periods at 140 °C since dehydrochlorination occurred rapidly at high temperature and this confirmed by the high rate constants (Table 6.28 and 6.29).

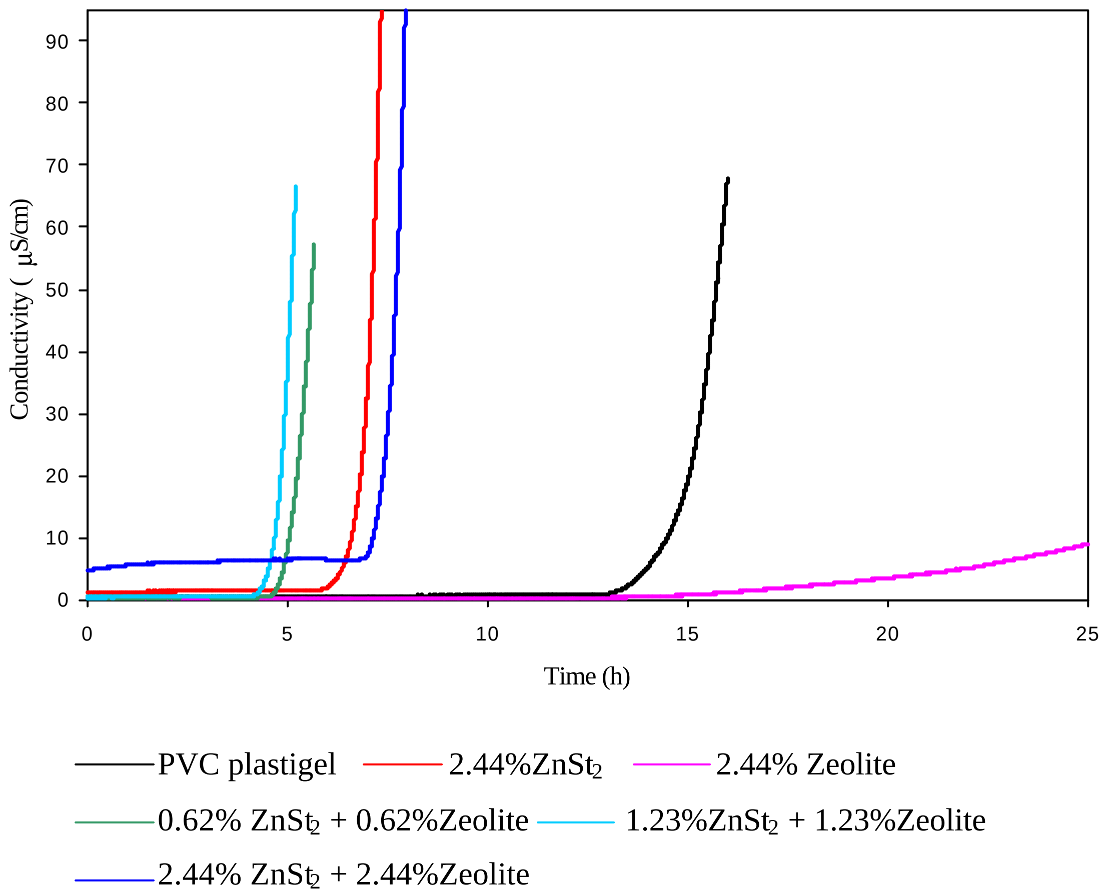


Figure 6.51. The change of conductivity of aqueous solution with respect to time at 140 °C for PVC plastigels having 33% DOP.

Table 6.28. Induction, stabilization time values and rate constants at 140 °C for PVC plastigels having 33% DOP.

Additive wt.%		Induction time (h)	Stability time (h)	Initial rate constant kix10^6 (min^{-1})	Linear region rate constant klrx10^5 (min^{-1})
ZnSt$_2$	Zeolite				
-	-	14.00	15.71	1.06	3.64
2.44	-	6.70	7.13	5.37	2.68
-	2.44	16.00	>30.5	0.17	0.11
0.62	0.62	5.00	5.61	7.38	9.56
1.23	1.23	4.50	5.10	7.37	6.49
2.44	2.44	7.00	7.75	1.38	16.61

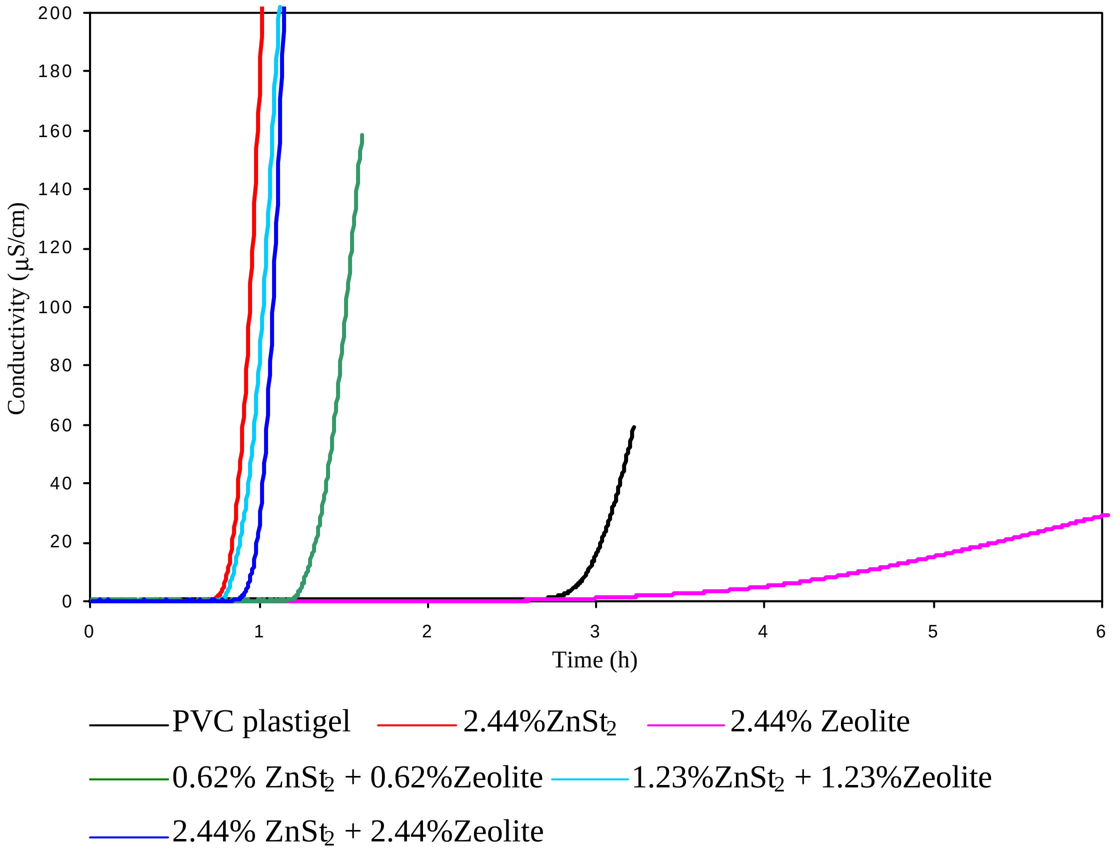


Figure 6.52. The change of conductivity of aqueous solution with respect to time at 160 °C for PVC plastigels having 33% DOP.

Table 6.29. Induction, stabilization time values and rate constants at 160 °C for PVC plastigels having 33% DOP.

Additive wt.%		Induction time (h)	Stabilization time (h)	initial rate constant kix10^6(min^{-1})	Linear region rate constant klrx10^5 (min^{-1})
$ZnSt_2$	Zeolite				
-	-	2.98	3.19	6.33	9.88
2.44	-	0.70	0.89	97.17	66.65
-	2.44	3.50	7.43	4.08	0.56
0.62	0.62	1.25	1.43	40.31	25.58
1.23	1.23	0.75	0.96	95.96	46.62
2.44	2.44	0.90	1.04	15.27	87.27

6.3.3. Kinetic Study of PVC Plastigels Containing 43% DOP

The PVC plastigels prepared by 43% DOP and 2%viscobyk were tested in PVC Thermomat at 140 and 160 °C. Fig.6.53 and 6.54 show the change of conductivity of aqueous solution with respect to time for PVC plastigels stabilized with $ZnSt_2$ and zeolite at two different temperatures. Also the induction, stability periods and the rate constants of dehydrochlorination which were computed from the slopes of the kinetic curves are shown in Table 6.30 and 6.31

The sample stabilized with 2.11% zeolite presents a longer induction time than the others at 140 °C due to the absorbing the produced HCl. Also it has the highest stability time as shown in Table 6.30. Ven et al., (2000) described a linear relationship between HCl-capacity of layered double hydroxides with different counterions and their action as heat stabilizer in PVC. And the rapid dehydrochlorination after 13 h for the sample stabilized with zeolite can be explained by the lack of HCl-capacity of zeolite. When 2.11% $Znst_2$ was used to stabilize the PVC plastigel, it neither delayed the induction time nor decreased the rate of dehydrochlorination. At low $ZnSt_2$ and zeolite levels at 140 °C, the synergism between these heat stabilizers on thermal degradation of PVC was observed due to the slow dehydrochlorination of PVC, in other words, due to the low linear region rate constant. As $ZnSt_2$ amount in PVC plastisol was increased, linear region rate constant increases accordingly.

At 160 °C, all the samples are thermally degraded in 3 hours as shown in Fig.6.54. So the induction periods of the sample decrease with increasing temperature. Also the amount of HCl evolved from the samples seems to be higher than previously since it gets up to more than 295 μS/cm. The sample which was unstabilized had the lowest rate constants for initial and linear regions. When zeolite was a primary stabilizer at 160 °C, it showed a stabilizing effect by increasing the induction and stability periods. This effect was considered to result from the absorption of HCl which catalyzed the dehydrochlorination of PVC. So zeolite captured catalytic, highly mobile HCl before elimination of further HCl occurred. But when the HCl-capacity of zeolite was not sufficient to absorb the evolved HCl, the acid catalyzed the degradation reaction by releasing from the sample. Therefore zeolite provided long induction and stability periods, but it did not prevent or decrease the rate of dehydrochlorination of PVC. Nevertheless, it had lower rate constants than the samples having $ZnSt_2$.

These results were confirmed by the color test of the PVC plastigel films. Since the development of color unstability was attributed to the conjugated double bonds and the evolution of HCl in dehydrochlorination process, the samples represented low induction and stability periods, also high rate constants discolored at the end of 90 min (Table 6.11).

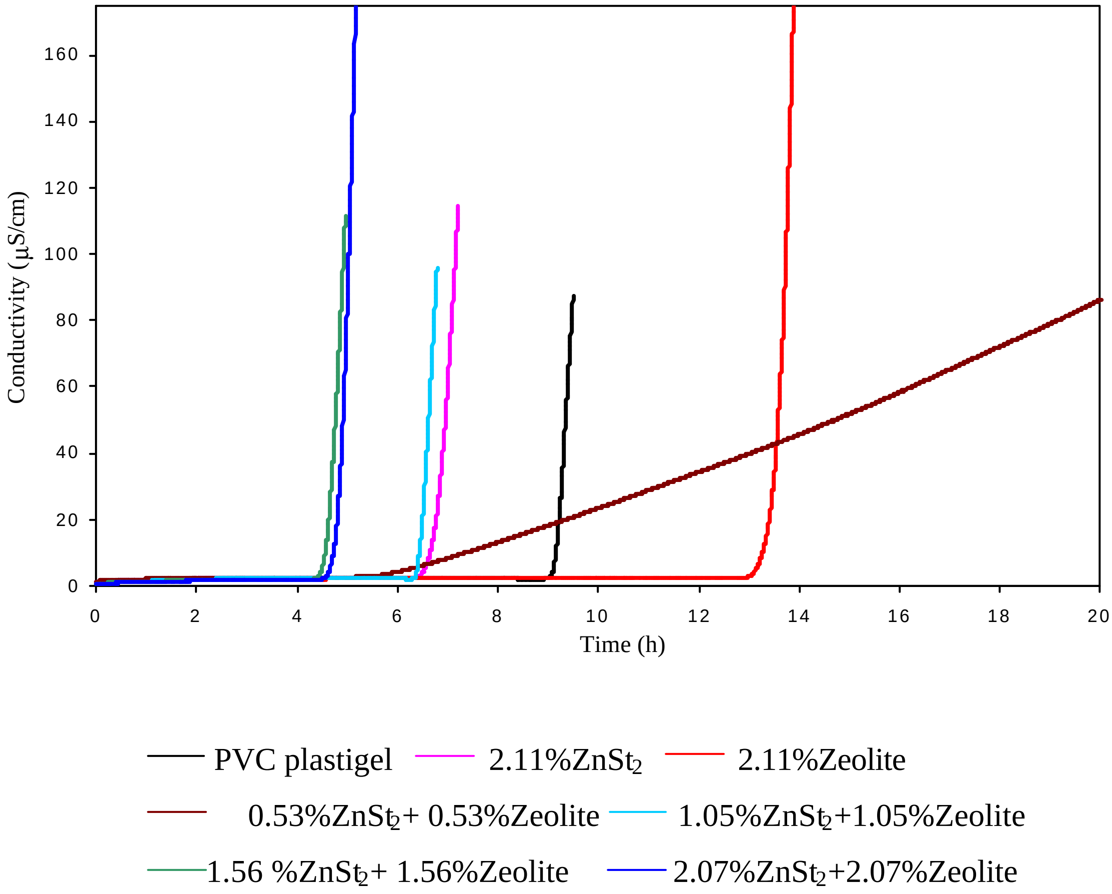


Figure 6.53. The change of conductivity of aqueous solution with respect to time at 140 °C for PVC plastigels stabilized with $ZnSt_2$ and zeolite.

Table 6.30 :Induction, stabilization time values and rate constants at 140 °C for PVC plastigels stabilized with $ZnSt_2$ and zeolite

% Additive		Induction time (h)	Stabilization time (h)	Initial rate constant kix10^6 (min^{-1})	Linear region rate constant klrx10^4 (min^{-1})
$ZnSt_2$	Zeolite				
-	-	9.00	14.95	1.62	0.04
2.11	-	6.50	13.59	35.15	2.64
-	2.11	13.00	22.73	1.22	1.37
0.53	0.53	6.00	9.36	9.98	1.12
1.05	1.05	6.40	6.63	9.48	1.22
1.56	1.56	4.50	4.77	12.34	1.38
2.07	2.07	4.70	4.92	46.51	2.87

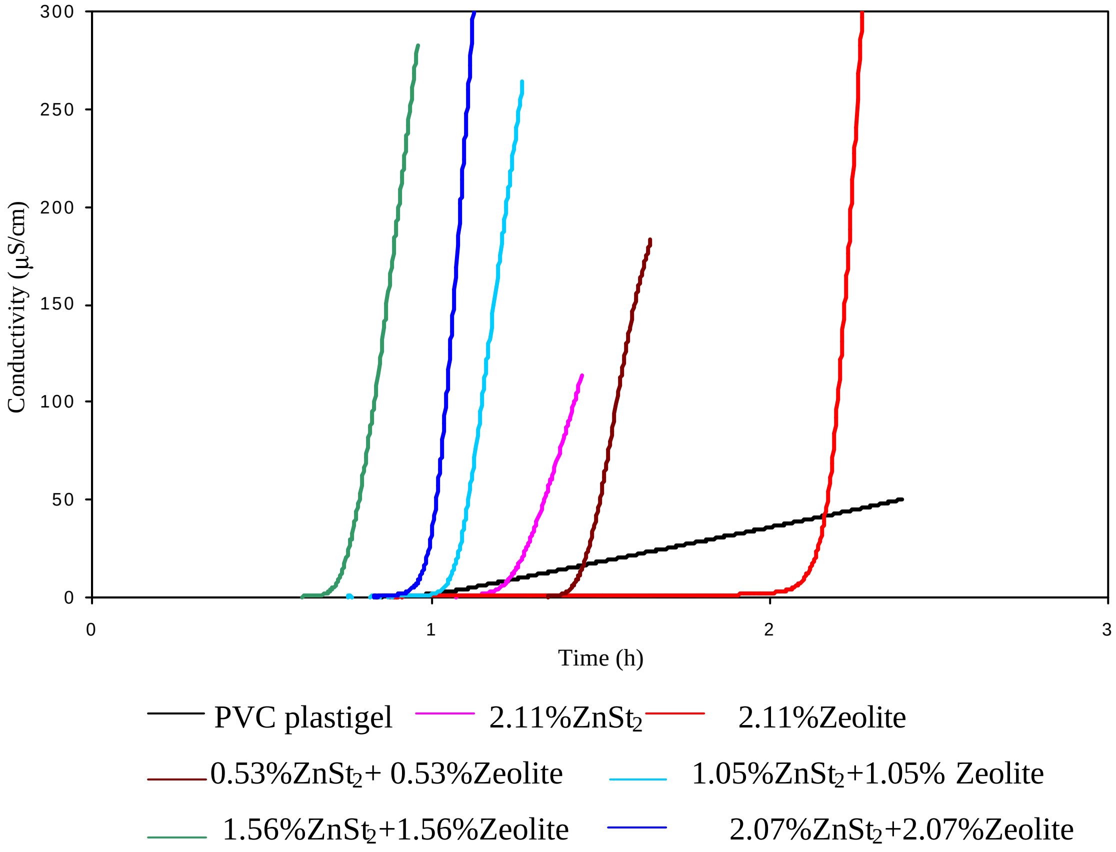


Figure 6.54. The change of conductivity of the aqueous solution with respect to time at 160 °C for PVC plastigels stabilized with $ZnSt_2$ and zeolite.

Table 6.31. Induction, stabilization time values and rate constants at 160 °C for PVC plastigels stabilized with $ZnSt_2$ and zeolite

% Additive		Induction time (h)	Stabilization time (h)	Initial rate constant kix10^5 (min^{-1})	Linear region rate constant klrx10^4 (min^{-1})
$ZnSt_2$	Zeolite				
-	-	1.01	2.39	0.93	0.17
2.11	-	1.15	1.34	12.89	4.51
-	2.11	2.10	2.17	4.22	2.84
0.53	0.53	1.25	1.50	6.90	6.20
1.05	1.05	1.05	1.11	17.51	6.59
1.56	1.56	0.70	0.79	26.54	7.95
2.07	2.07	0.95	1.02	18.80	16.60

Fig.6.55 and 6.56 show the conductivity of aqueous solution with respect to time for PVC plastigels stabilized with $CaSt_2$ and zeolite at 140 and 160 °C. The induction, stability periods and the calculated rate constants from the kinetic curves are reported in Table 6.32 and 6.33. Since $CaCl_2$ was produced at the end of the reaction between $CaSt_2$ and HCl (Eq.30) the traces in these figures obtained for the samples stabilized with $CaSt_2$ and zeolite, were not very stable as the traces of the samples stabilized with $ZnSt_2$ were. Unlike $ZnCl_2$, alkaline earth chloride did not promote dehydrochlorination.

At 160 °C, the stabilization time was increased with the increasing amount of $CaSt_2$. Additionally the samples stabilized with both $CaSt_2$ and zeolite had better stabilizing effects than the sample stabilized with $CaSt_2$ individually.

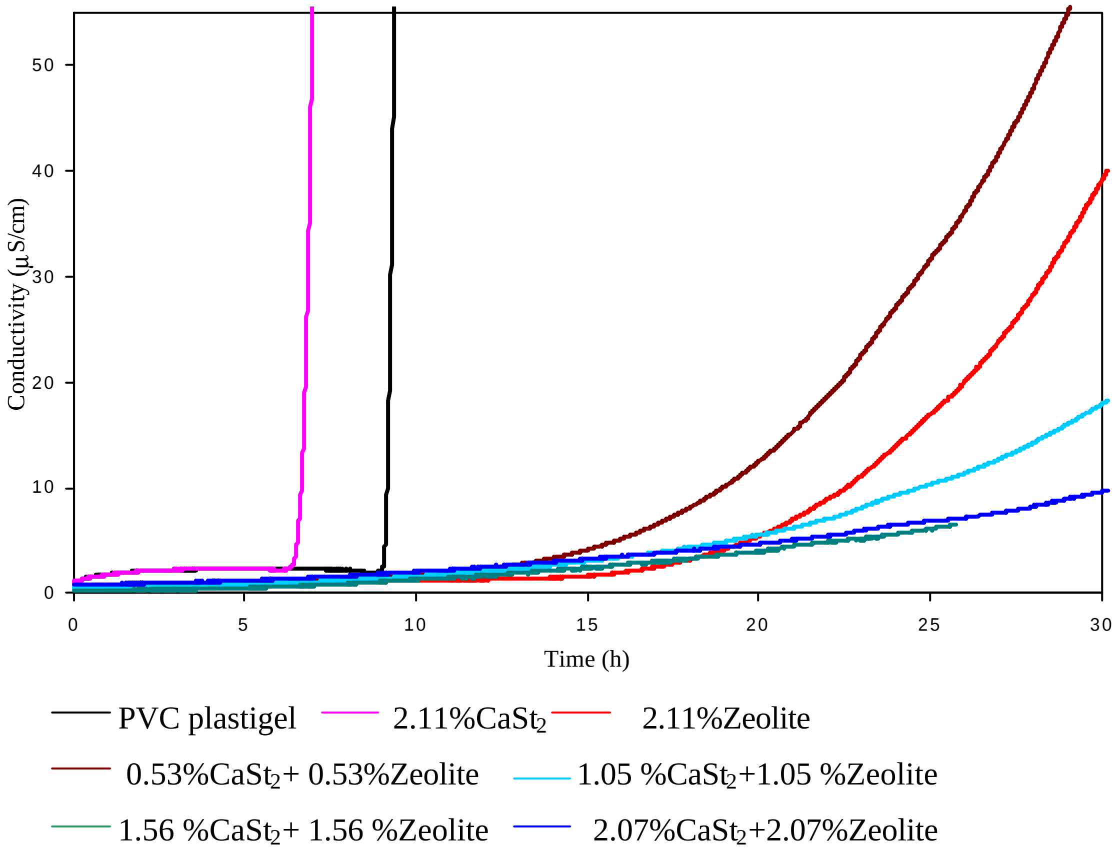


Figure 6.55. The change of conductivity of aqueous solution with respect to time for PVC plastigels stabilized with CaSt$_2$ and zeolite at 140 °C.

Table 6.32. Induction, stabilization time values and rate constants at 140 °C for PVC plastigels stabilized with CaSt$_2$ and zeolite

% Additive		Induction time (h)	Stabilization time (h)	Initial rate constant kix10^7 (min^{-1})	Linear region rate constant klrx10^6 (min^{-1})
CaSt$_2$	Zeolite				
-	-	9.00	14.95	16.20	3.87
2.11	-	6.00	>26	5.27	2.80
-	2.11	13.00	22.73	12.20	13.74
0.53	0.53	10.00	28.39	3.78	2.75
1.05	1.05	5.00	>26	1.32	0.73
1.56	1.56	4.00	>26	2.63	2.64
2.07	2.07	5.00	>26	0.04	0.32

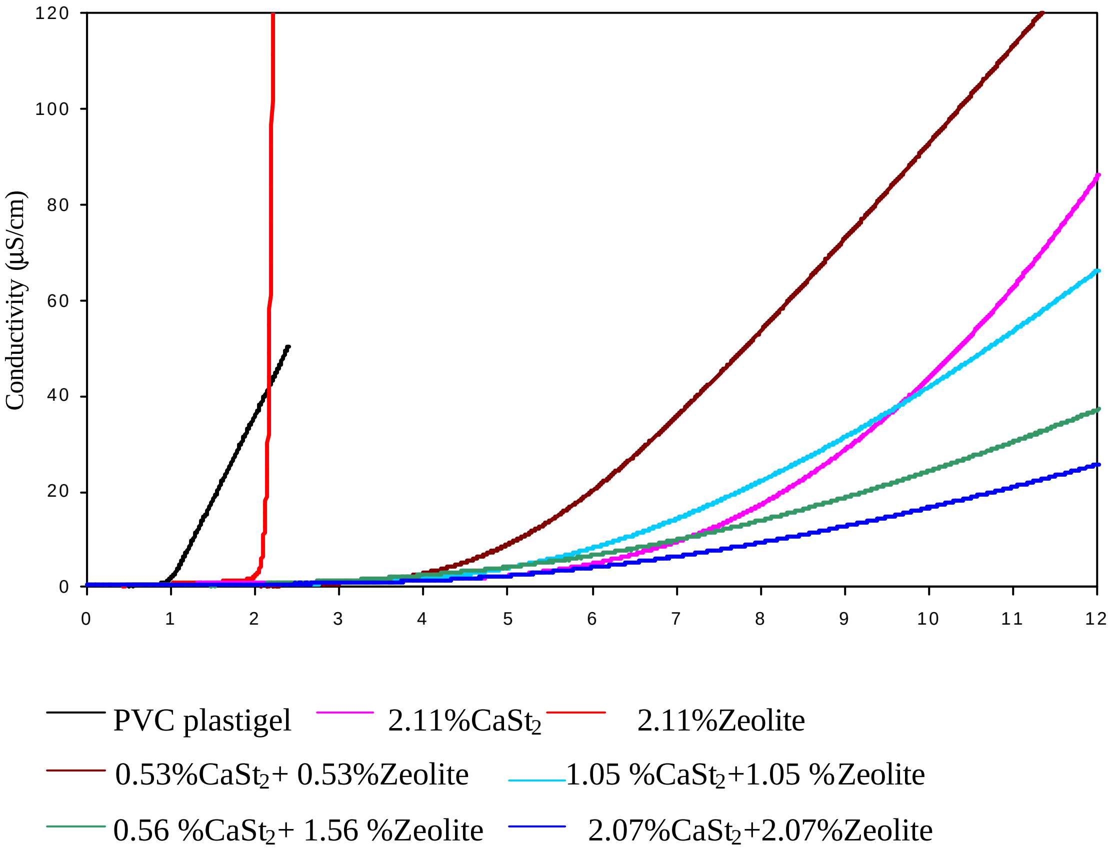


Figure 6.56. The change of conductivity of aqueous solution with respect to time at 160 °C for PVC plastigels stabilized with $CaSt_2$ and zeolite at 160 °C.

Table 6.33. Induction, stabilization time values and rate constants at 160 °C for PVC plastigels stabilized with $CaSt_2$ and zeolite

% Additive		Induction time (h)	Stabilization time (h)	Initial rate constant kix10^7 (min^{-1})	Linear region rate constant klrx10^6 (min^{-1})
$CaSt_2$	Zeolite				
-	-	1.01	2.39	93.12	17.27
2.11	-	7.00	22.35	3.52	14.81
-	2.11	2.10	2.17	421.55	284.18
0.53	0.53	4.00	7.82	44.30	8.86
1.05	1.05	4.50	10.77	23.97	6.59
1.56	1.56	4.00	13.78	4.53	7.46
2.07	2.07	4.00	16.57	8.05	3.22

Although the results of PVC Thermomat indicated the evolving of HCl from the PVC plastigels due to the dehydrochlorination of PVC at 140 and 160 °C, any mass loss of the samples was not detected by thermogravimetric analysis (Fig.6.42 to Fig.6.45). The onset temperatures where the first mass loss was observed were higher than 160 °C according to TGA results. It might be concluded that the amount of evolved HCl from the samples were as low as, thermogravimetric analysis could not detect it. Therefore it was essential to test PVC plastigel films by PVC Thermomat to determine the kinetic parameters of dehydrochlorination of PVC at low temperatures since dehydrochlorination started at 100 °C.

6.3.4. Activation Energies of Dehydrochlorination Reactions

The activation energies of the dehydrochlorination reactions for initial and linear regions were calculated for the samples having 33%, 43% DOP.

The rate constant can be explained by Arrhenius Equation as;

$$k = A.e^{-E/R.T} \tag{35}$$

where;

k = Rate constant
A = Preexponential factor
E = Activation energy (J/mole)
R = Gas constant (8.314 J/mole.K)
T = Absolute temperature (K)

The activation energy was determined experimentally by carrying out the reaction at two different temperatures (140 and 160 °C)

$$\ln\frac{k_2}{k_1} = -\frac{E}{R}.\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{36}$$

For the dehydrochlorination of unstabilized sample prepared by 43% DOP the activation energy values were calculated as 129.70 and 111.27 kj/mole for initial and linear region. Beltran et al., 1997 determined the activation energy of the degradation of PVC plastisol as 87.78 kj/mole, where the overall reaction order was 0.81. In that study, thermogravimetric analysis was used to calculate the kinetic parameters by integrating the corresponding differential equations, using the Runge-Kutta algorithm.

As shown in Table 6.34 to 6.36, the activation energy values in linear region are generally lower than the values in initial region for all the samples due to the high rate of dehydrochlorination of PVC after the consumption of stabilizers and acceleration effect of the evolved acid. It was observed that the addition of the stabilizers into the PVC plastisol prepared by 33% DOP had a stabilizing effect only for linear region by the increasing the activation energy values for linear region.

When zeolite was used as a primary stabilizer, it not only increased the induction period, but also increased the activation energy at initial region. Although the sample stabilized with 2.11% $ZnSt_2$ presented higher activation energy than the sample having 2.11% $CaSt_2$ for initial region, the activation energy of this sample was lower for linear region due the acceleration effect of the produced $ZnCl_2$ on the second step of dehydrochlorination of PVC (Table 6.35 and 6.36). The sample stabilized with both $ZnSt_2$ and zeolite (except 2.07%$ZnSt_2$ and 2.07%zeolite) clearly indicated the high activation energy values for linear region as compared with unstabilized PVC plastigel due to the ability of zeolite to absorb HCl, reducing further acid-catalyzed dehydrochlorination of PVC.

The PVC plastigel stabilized with 2.07% $ZnSt_2$ and 2.07% zeolite presented highest activation energy values for linear region (Table 6.35). Neither of the samples stabilized with $ZnSt_2$ nor zeolite individually got up to these values. Therefore the rate of dehydrochlorination of PVC was reduced by increasing the activation energy of this reaction.

Table 6.34 Activation energies of initial and linear regions of the kinetic curves for the samples having 33% DOP.

Additive %		Activation Energy (kj/mole)	
$ZnSt_2$	Zeolite	Initial region	Linear Region
-	-	132.66	74.12
2.44	-	214.95	238.56
-	2.44	235.91	120.81
0.62	0.62	126.03	73.06
1.23	1.23	190.52	147.52
2.44	2.44	178.44	123.14

Table 6.35 Activation energies of initial and linear regions of the kinetic curves for the samples stabilized with $ZnSt_2$ and zeolite.

Additive %		Activation Energy (kj/mole)	
$ZnSt_2$	Zeolite	Initial region	Linear region
-	-	129.72	107.41
2.11	-	96.46	39.75
-	2.11	263.05	54.16
0.53	0.53	143.53	127.02
1.05	1.05	216.47	125.21
1.56	1.56	227.77	129.99
2.07	2.07	103.69	130.28

Table 6.36 Activation energies of initial and linear regions of the kinetic curves for the samples stabilized with $CaSt_2$ and zeolite.

Additive %		Activation Energy (kj/mole)	
$CaSt_2$	Zeolite	Initial region	Linear region
-	-	129.72	107.41
2.11	-	29.96	123.65
-	2.11	262.97	53.95
0.53	0.53	182.70	86.85
1.05	1.05	215.21	163.33
1.56	1.56	40.20	77.11
2.07	2.07	393.77	171.39

6.3.5. Preexponential Factors of Dehydrochlorination Reactions

Preexponential factors (A) of initial and linear regions of the kinetic curves for PVC plastigels were evaluated by using the Eq. 35. These values were reported in Table 6.37 to Table 6.39.

Table 6.37. Preexponential factors of initial and linear regions of the kinetic curves for PVC plastigels having 33%DOP.

Additive %		Initial preexponential factor	Linear region preexponential factor
$ZnSt_2$	Zeolite		
-	-	$6.36x10^{10}$	$8.63x10^{4}$
2.44	-	$8.26x10^{21}$	$3.99x10^{25}$
-	2.44	$1.17x10^{23}$	$2.10x10^{10}$
0.62	0.62	$6.44x10^{10}$	$1.64x10^{5}$
1.23	1.23	$9.21x10^{18}$	$2.91x10^{14}$
2.44	2.44	$5.12x10^{16}$	$6.26x10^{11}$

Table 6.38. Preexponential factor of PVC plastigels stabilized with $ZnSt_2$ and zeolite

Additive %		Initial preexponential factor	Linear region preexponential factor
$ZnSt_2$	Zeolite		
-	-	4.15×10^{10}	3.63×10^{7}
2.11	-	5.57×10^{7}	16.49
-	2.11	2.27×10^{27}	468.51
0.53	0.53	1.42×10^{13}	2.36×10^{11}
1.05	1.05	2.27×10^{22}	1.55×10^{11}
1.56	1.56	7.95×10^{23}	6.63×10^{11}
2.07	2.07	6.05×10^{7}	1.50×10^{12}

Table 6.39. Preexponential factor of PVC plastigels stabilized with $CaSt_2$ and zeolite

Additive %		Initial preexponential factor	Linear region preexponential factor
$CaSt_2$	Zeolite		
-	-	4.26×10^{10}	4.27×10^{8}
2.11	-	2.16×10^{-3}	1.22×10^{10}
-	2.11	2.22×10^{27}	91.42
0.53	0.53	4.85×10^{16}	2.65×10^{5}
1.05	1.05	2.19×10^{20}	3.32×10^{14}
1.56	1.56	0.03	4.13×10^{3}
2.07	2.07	2.54×10^{41}	1.26×10^{16}

As seen in Table 6.34 to 6.39 activation energy and preexponential factor values are very different than from each other while the reaction rate constants in the same region are close to each other (Table 6.28 to Table 6.33) since the reactions follow different mechanisms. In order to confirm these results, kinetic compensation effect was investigated by plotting lnA vs. E curves as shown in Fig.6.57 to Fig.6.59. Gupta and Viswanath (1998) and Arkýþ (2000) found a linear relation between ln A and E values as;

$\ln A = 0.221E - 7.17$

$\ln A = 0.254E - 9.6$

for the dehydrochlorination of PVC by using metal oxides and organotin stabilizers respectively.

Linear relation between activation energy and preexponential values were observed for both initial and linear regions. The equations of the lines for the samples having 33% DOP were determined as;

lnA=0.2778E-10.682 (initial region)

lnA=0.2882E-9.9506 (linear region)

The equations of the lines for the samples having 43% DOP and stabilized with $ZnSt_2$ and zeolite are;

lnA=0.2795E-9.6722 (initial region)

lnA=0.2726E-9.9506 (linear region)

The equations of the lines fort he samples having 43% DOP and stabilized with $CaSt_2$ and zeolite are;

lnA=0.2818-13.588 (initial region)

lnA=0.281-11.761 (linear region)

These equations are consistent with the other authors (Gupta and Viswanath, 1998, Arkýþ, 2000). Therefore this linear relation confirmed the kinetic compensation effect for the dehydrochlorination reactions.

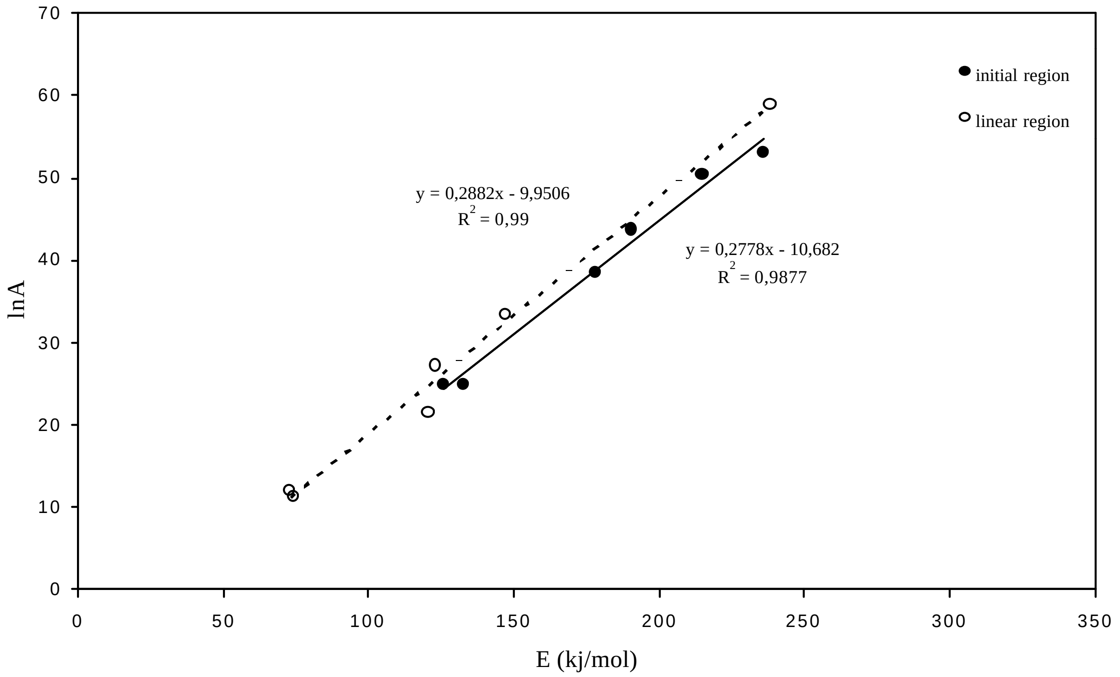


Figure 6.57. Kinetic compensation effect curve for the samples having 33%DOP

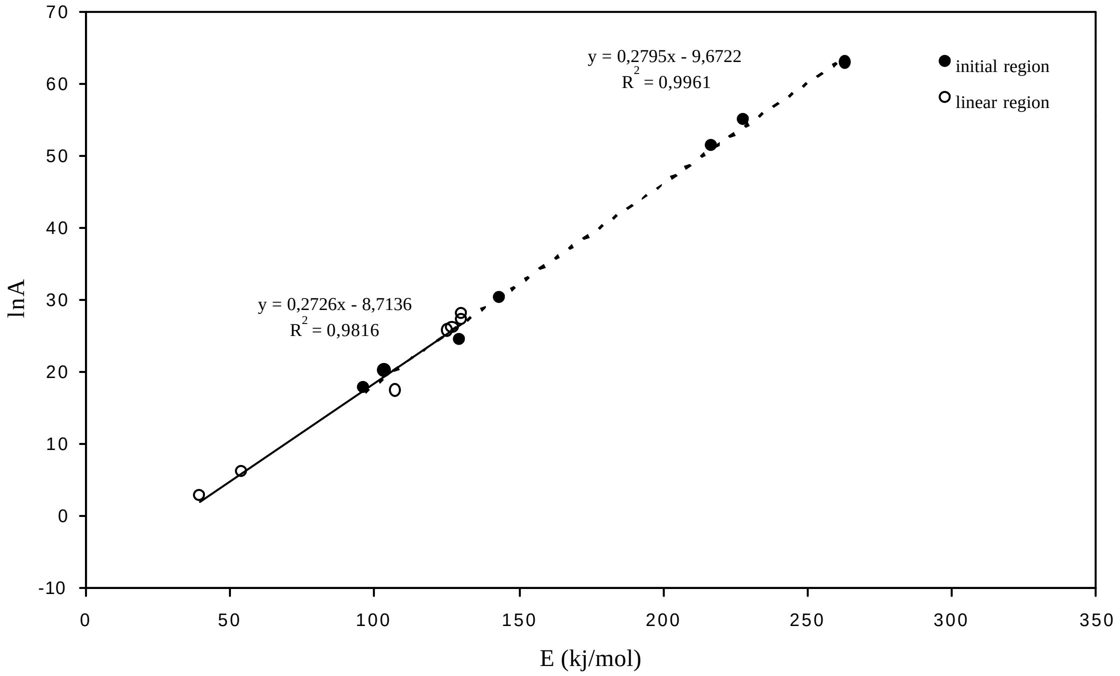


Figure 6.58. Kinetic compensation effect curve for the samples having 43%DOP and stabilized with $ZnSt_2$ and zeolite

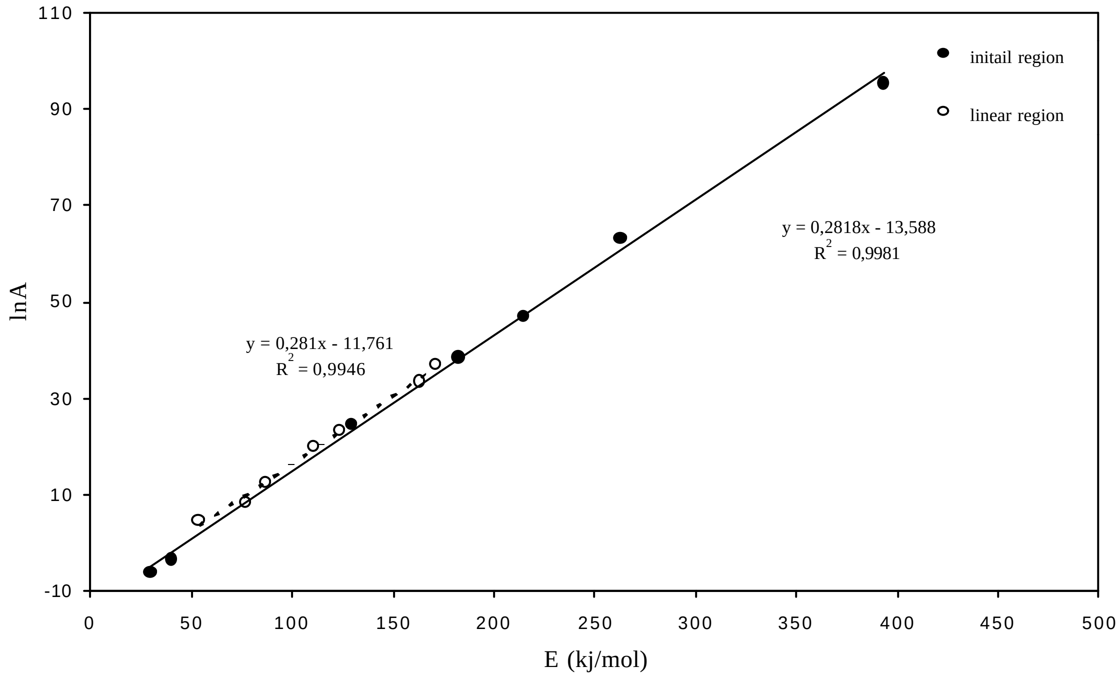


Figure 6.59. Kinetic compensation effect curve for the samples having 43%DOP and stabilized with $CaSt_2$ and zeolite

In this project, dehydrochlorination of PVC was investigated by spectroscopic and thermal analysis techniques. Also PVC Thermomat was used in order to obtain the information about the release of HCl from PVC plastigels and determine the kinetic parameters of dehydrochlorination reaction of the samples.

When the induction periods of PVC, PVC plastigel having 33% DOP and PVC plastigel 43% DOP were compared; this period was reached to highest value 2.98h for PVC palstigel having 33% DOP. This result indicated that the small amounts of DOP delayed the induction time of PVC but higher amounts of it promoted the dehydrochlorination of PVC. Since the higher the plasticizer content, the more flexible PVC film is, the evolved HCl could diffuse easier in the film with high plasticizer content. Thus shorter induction periods are observed for low plasticizer content. These are in good agreement with those obtained by other investigators. (Minsker et al., 1987, Marcilla et al., 1995). The initial and linear region rate constants of PVC plastigel having 33% DOP were calculated as $1.06x10^{-6}$ and $3.64x10^{-5}$ min^{-1} at 140 °C whereas these rate constants were evaluated as $1.62x10^{-4}$ and $6.60x10^{-4}$ min^{-1} at 140 °C by using the concentration of formed polyene sequences in PVC (Baltacýoðlu et al.,1999). In this study, the rate of dehydrochlorination and the rate constants were determined by the concentration of evolved HCl gas from the sample but Baltacýoðlu et al., found the rate constants from the concentration of formed double bonds in PVC. Although the total number of double bonds of the polyene sequences was practically equal to the HCl molecules split off (Patel et al., 1992), the rate constants that were calculated in this study and the rate constants that were calculated by Baltacýoðlu et al., 1999 were not equal to each other. The rate constants evaluated from the concentration of evolved HCl were lower than the values calculated by the concentration of double bonds due to the slow diffusion of HCl gas in PVC. Also all the formed HCl were not evolved from the sample to the surroundings although double bonds were formed due to the dehydrochlorination of PVC. Therefore the total number of double bonds of the polyene sequences was different than the HCl molecules split off and released to the surroundings.

CHAPTER 7

CONCLUSIONS

In this project, PVC dehydrochlorination was studied in different respects. The materials and the prepared PVC plastisols were characterized by spectroscopic and thermal analysis techniques.

Optical microscopy on dynamic heating allowed the gelation and fusion behaviors also the morphology of PVC plastisols. While unstabilized PVC plastisol had non porous structure except the entrapped air bubbles due to the mixing of plastisol in the sample PVC plastisols stabilized with $ZnSt_2$/$CaSt_2$ and zeolite had porous structure allowing easy release of the eliminated HCl gas to the surroundings. The complete gelation of PVC plastisols was observed at 185 °C.

The morphology of PVC plastigel films were studied by scanning electron microscope (SEM). SEM with energy dispersive X-ray (EDX) analysis was used to obtain elemental compositions in polymer and particle phases. The porous structure of PVC plastisols when they were stabilized with metal soaps and zeolite were confirmed by SEM micrographs. It was observed that for all samples, the weight % values of carbon (C) in the range 70.06-81.20% at 140 °C were close to the weight % of carbon of the plasticizer (DOP) 73.81% since DOP was not absorbed by PVC particles and it covered the surface where EDX analysis was performed. This indicated the incomplete gelation at low temperature. 1.00-1.76 % Zn and 0.60-1.11 % Ca were present respectively in $ZnSt_2$ and $CaSt_2$ containing films in polymer phase showed a good dispersion of the metal soaps were present.

The thermal stability of PVC plastigels in terms of color were obtained by heating them in a static vacuum oven. It was observed that $ZnSt_2$ was a good heat stabilizer for PVC plastisol at the beginning of heating, but $ZnCl_2$ formed at further heating times acted as accelerator on dehydrochlorination reaction causing sudden blackening of the sample. When zeolite was used as a primary stabilizer it prevented the early blackening of the film.

UV spectroscopy gave information about the formation of the conjugated double bonds by PVC dehydrochlorination. Concentrations of conjugated 6-n double bonds causing the discoloration of the PVC were evaluated and the minimum concentration was determined as $2.84x10^{-4}$ mol/l for the synergistic mixtures of 0.53 wt.% $CaSt_2$ and 0.53 wt.%zeolite.

The evaporation of the plasticizer (DOP) was investigated from the FTIR band at 1600 cm^{-1} and the formation of organic acid from the reaction between metal soaps and HCl produced by dehydrochlorination of PVC was investigated from the FTIR band at 1540 cm^{-1} for the gelled and heated samples. FTIR results indicated $ZnSt_2$ was consumed at a faster rate than $CaSt_2$. For 90 min heating at 160 °C, the COO^- peak of $CaSt_2$ at 1540 cm^{-1} was higher in intensity than the COO^- peak of $ZnSt_2$. This showed that $ZnCl_2$ formed from $ZnSt_2$ accelerated dehydrochlorination of PVC.

Thermogravimetric analysis was studied to investigate the loss of mass caused by elimination of HCl and the evaporation of the plasticizer. The sample stabilized with 1.05%$Znst_2$ and 1.05%zeolite presented the highest onset temperature (204.4 °C). This result indicated that these stabilizers prevented early dehydrochlorination when they were used at low levels.

Measurements in PVC Thermomat gave information about the release of HCl from the PVC plastigels to the surroundings. The rate of elimination of HCl was determined from PVC plastigels. The induction and stability periods, and the kinetic parameters were determined by using the rate of HCl elimination at 140 and 160 °C The induction time of the sample having 2.11%zeolite was determined as 2.10h, whereas this period for the unstabilized sample was 1.01h at 160 °C. The stabilizing effect of zeolite on the increase in the induction period of the sample was considered the result from the absorption of HCl which was thought to reduce the autocatalytic effect of HCl evolved at the initial stages of dehydrochlorination. Since the induction time of the sample having 0.53% $ZnSt_2$ and 0.53% zeolite was 1.25 h the synergistic effect on thermal stability was observed at low levels of them. The linear relation between the activation energy and preexponential factor values were confirmed the compensation effect for the dehydrochlorination reactions. Although the results of PVC Thermomat indicated the evolving of HCl from the PVC plastigels due to the dehydrochlorination of PVC at 140 and 160 °C, any mass loss of the samples was not detected by thermogravimetric analysis. The onset temperatures where the first mass loss was observed were higher than 160 °C for the PVC plastigels on dynamic heating at 10 °C/min.

The synergistic effect of metal soaps and zeolite could not be observed at all levels of stabilizers due to the heterogeneous reaction which involved gas, liquid, and solid phases. Because PVC and zeolite were solid, metal soaps were liquid at 140 and 160 °C. Since the metal soaps, zeolite and PVC were not in the same phase, they did not substitute to labile chlorine atoms so the dehydrochlorination was initiated.

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