

# Evaluation of Lignin-Calcium Complex as Thermal Stabilizer for Poly Vinyl Chloride

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## ABSTRACT

Chemical modification of lignin was carried out by reacted it with HI acid, then the modified lignin treated with calcium hydroxide to prepare calcium-lignin chelating complex, this derivative was examined as thermal stabilizer for PVC, thermal degradation of PVC neat as blank and containing three weight percents (1, 2, and 4) into polymer was accelerated by heat treatment at 190°C for 2 h then PVC films were casting from THF solvent with thickness 0.03 mm. Thermal stabilization activity of this derivative was investigated by using infrared spectroscopy, according to the results obtained Calcium-lignin complex have suitable activity to increased PVC stability at low concentration depending on it's ability to reaction with HCl as well as the chemical structure of lignin that contain phenolic properties.

**Keywords:** Lignin, Modification of Lignin, Poly (Vinyl Chloride), Thermal Degradation, IR Study

## 1. Introduction

Lignin has a highly branched chemical structure consisting of phenol propane unites which are connected mainly together by ether or C-C linkages [1,2]. Because of variety functional groups in lignin that provide many potential reactive sites for chemical modifications and applications, one of these modification method that used to increase lignin activity were by reacted it with formaldehyde in alkaline solution to form methylol groups into lignin matrix [3,4], or by synthesized polymer from lignin on the basic of some functional groups such as phenylene, hydroxyl and methoxyl [5].

There are other studies show that the modification lignin by oxidation reaction (obtained through several sources and methods) can be used as chelating agent for some type of metal ions [6,7]. German C. Quintana and his co-worker study the capacity for removal of heavy metals from liquid streams by formation of complexes with lignin's oxidized by acid treatment and their conclusions refer to lignin capable of adsorbing Cadmium ions from aqueous solution and a slight increase in adsorption capacity when lignin was oxidized [8]. Another study show the used of native lignin as will as modification lignin as additive for low density polyethylene which can act as antioxidant and UV-stabilizers [9].

On the other hand, Poly (vinyl chloride), PVC, is one

of the leading thermoplastic materials. It stands second in the world after polyethylene so far as production is concerned. However, PVC shows low thermal stability [10]. It is generally accepted that poly(vinyl chloride), PVC, is an unstable polymer when exposed to high temperatures during it's moldings and applications. Therefore, the poor thermal stability of PVC still remains one of its main problems [11]. The purpose of this work was to study the chemical modification of lignin by chelated it with Ca ion then evaluated its effect on thermal stability of poly (vinyl chloride).

## 2. Experimental

### 2.1. Modification of Lignin

15 g Lignin (Kraft lignin) from paper industries—Basrah was modified by refluxed it with 60 ml of 30% solution of HI acid (May & Baker Ltd.) for 3 h at the end or the reaction period the solution was allowed to cool before filtrated. Modified lignin washed with distillation water several times and finally dried under reduced pressure for 24 h.

### 2.2. Preparation of Calcium-Lignin Chelating Complex

Modified lignin 10 g was dissolved in 250 ml water and added periodically 10% of Ca(OH)<sub>2</sub> as clear and fil-

trated solution with hand stirring. the addition was cautious to precipitate all lignin in the mixture as brown dark powder which was filtered and washed to removal the non reacted  $\text{Ca}(\text{OH})_2$ , finally the product was oven drying for 24 h at  $50^\circ\text{C}$ .

### 2.3. Preparation of PVC Samples

Commercial polyvinyl chloride (supplied from petrochemical industries Basrah) with K-value 66, volume density  $0.45 \text{ gm/cm}^2$  and without thermal stabilizer was mixed thermally by hakee thermal mixer (hakee rheocord torque rheometer) at  $170^\circ\text{C}$  with 60 rpm with Ca-lignin chelating complex at three weight percentage (1, 2, and 4)% w/w and 0% as blank, the samples were compression molded at  $170^\circ\text{C}$  under 5 MPa for 5 min. to get sheets .

### 2.4. Thermal Degradation Condition

Accelerated PVC degradation was performed by fixed the samples in the oven at  $190^\circ\text{C}$  for 2 h under air as atmosphere.

### 2.5. Films Preparation

PVC samples were dissolved in THF then filtrated to remove Ca-lignin chelating or other compounds from PVC polymer. PVC was re-precipitated from THF solution by ethanol and filtrated, fixed concentration from PVC (0.1/5 ml)in THF were casting on class plate to prepare polymer film with 0.03 mm thickness (measured by Starrett micrometer, Jedburgn Scotland), the films were further dried at  $40^\circ\text{C}$  for 24 h.

### 2.6. Infrared Analysis

IR-spectrophotometer that used in our study was Shimadzu-FTIR-8400S infrared sepectrometer for measurement infrared sepecrometry of lignin, modified lignin, and Ca-lignin chelating complex after dried, ground and mixed with KBr and pressed to form pellets. The infrared spectrometry of PVC samples as films specimens were placed in the path of IR beam, all spectrums were recorded in the range  $4000 - 600 \text{ cm}^{-1}$ .

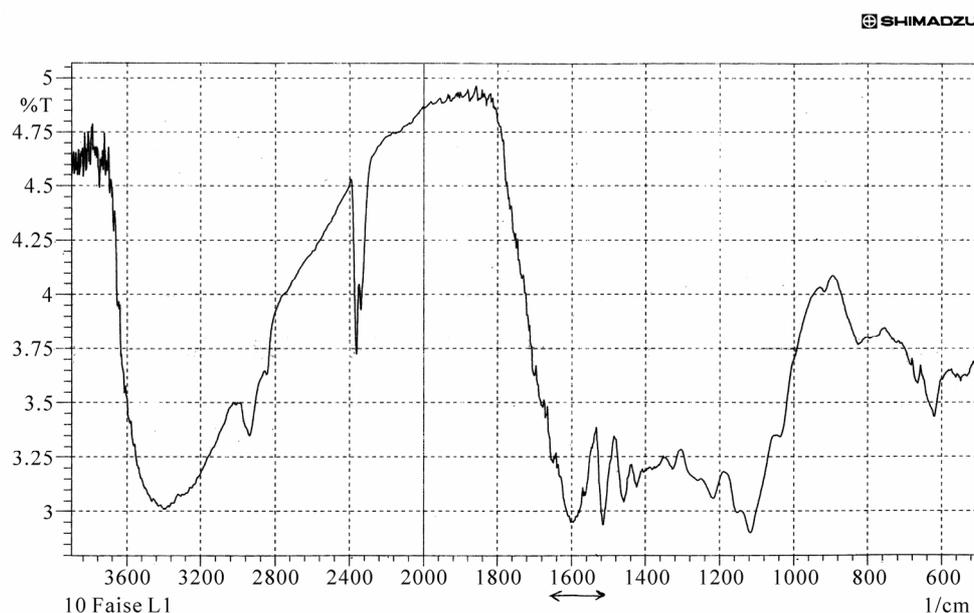
### 3. Results and Discussion

One modification method have been made on the De-etherfication of methoxyl groups of the guaiacyl propane and syringyl propane units by reacted lignin with HI acid this reaction lead to lignin molecule containing more phenolic hydroxyl groups [9].

FTIR spectrum of lignin (**Figure 1**) and modified lignin (**Figure 2**) show the same basic absorption peaks of main chemical groups that contained in lignin.

One of these peaks the broad and strong peak at  $3300 - 3400 \text{ cm}^{-1}$  that attributed to hydroxyl groups and the peaks at  $1600 \text{ cm}^{-1}$  and  $1520 \text{ cm}^{-1}$  corresponding to the absorption of double bonds of alkene and aromatic skeletal vibration. But the main differences in the chemical structure between lignin and modified lignin can be represented by that peak of phenolic hydroxyl at  $1220 \text{ cm}^{-1}$  which become more intense and the peak at  $1120 \text{ cm}^{-1}$  that attributed to the alcoholic hydroxyl and aliphatic ether which appear less intensity.

The chemical reaction of lignin with HI lead to clear



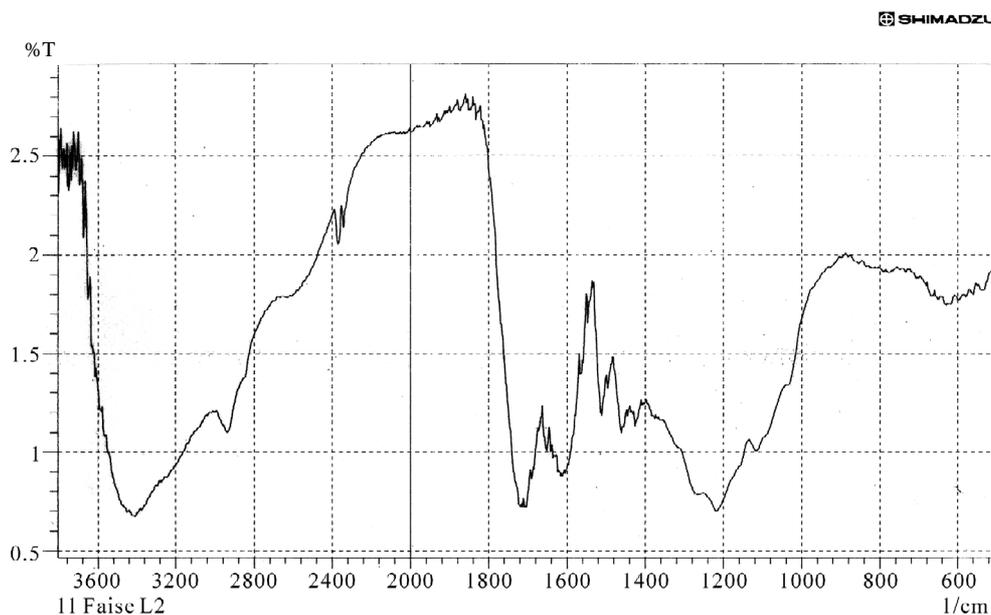
**Figure 1. FTIR spectrum of unmodified lignin.**

increment in the intensity of these peaks due to increased the phenolic hydroxyl into modified lignin [9]. It's expected that the modification of lignin by above reaction lead to increased reactivity to some metal ions to form complex salts or chelating complexes; **Figure 3** gives evidence of the chemical bonding occurring as consequence of the reaction modified lignin with  $\text{Ca}(\text{OH})_2$  to formation chelating complex .

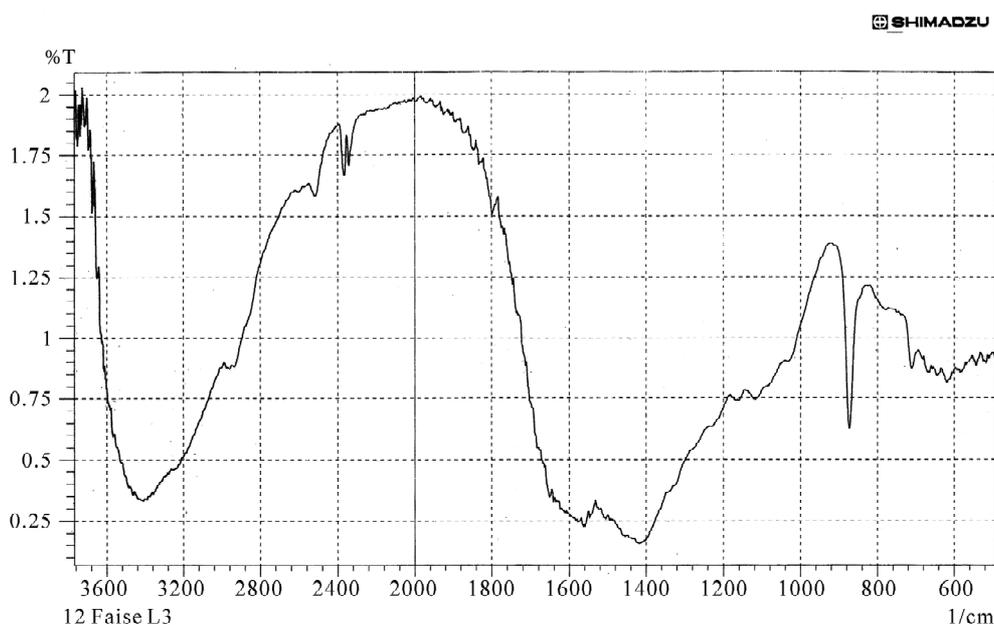
The major differences between the two FTIR spectrum obtained from modified lignin and Ca-lignin chelate

showed in **Figure 2** and **Figure 3**, the presence of clear and broad peak at  $1400\text{ cm}^{-1}$  and the sharp peak at  $860\text{ cm}^{-1}$  that attributed to formed ionic bond (Ca-O) into this derivative [12]; One the other hand the absence the peak at  $1220\text{ cm}^{-1}$  due to chelating phenolic groups with  $\text{Ca}^{2+}$  ion that refer to formation chelating salt.

Generally, infrared spectroscopy has been proven to be a highly effective means to qualitatively and quantitatively studies in polymer field where are deferent bonds and functional groups present in polymer which have



**Figure 2. FTIR spectrum of modified lignin.**



**Figure 3. FTIR spectrum of Ca-lignin chelating complex.**

different vibration frequencies, and by identifying characteristic frequencies as absorption peaks can be detected and monitoring many functional groups in polymer structure and composites [13,14]. The application of infrared spectroscopy in polymer are concerned with the range  $650 - 4000 \text{ cm}^{-1}$ ; many works used IR or FTIR to study the decomposition and thermal degradation of PVC as well as evolution the thermal, photo-stabilizer and antioxidants additives for this polymer [11, 15-19].

Matuana L. M. (2001) classified the characteristic IR bands of PVC into three regions the first is called the (C-Cl) stretching region in the range from  $600 - 700 \text{ cm}^{-1}$ , the second region is attributed to (C-C) stretching in the region from  $900 - 1200 \text{ cm}^{-1}$  and the third region is at  $1250 - 2970 \text{ cm}^{-1}$  assigned to numerous C-H mode. The IR spectrum of stander PVC without added thermal stabilizer or heat treatment is presented in **Figure 4**; absorption bands of this polymer evidenced at about  $2950 \text{ cm}^{-1}$  which attributed to C-H stretching from  $\text{CH}_2$ ,  $1440 \text{ cm}^{-1}$  wagging of  $\text{CH}_2$ ,  $1300 \text{ cm}^{-1}$  of  $\text{CH}_2$  deformation,  $1250 \text{ cm}^{-1}$  C-H stretching from  $\text{CHCl}$ ,  $1070 \text{ cm}^{-1}$  C-C,  $930 \text{ cm}^{-1}$  rocking of  $\text{CH}_2$ ,  $700 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$  stretching of C-Cl.

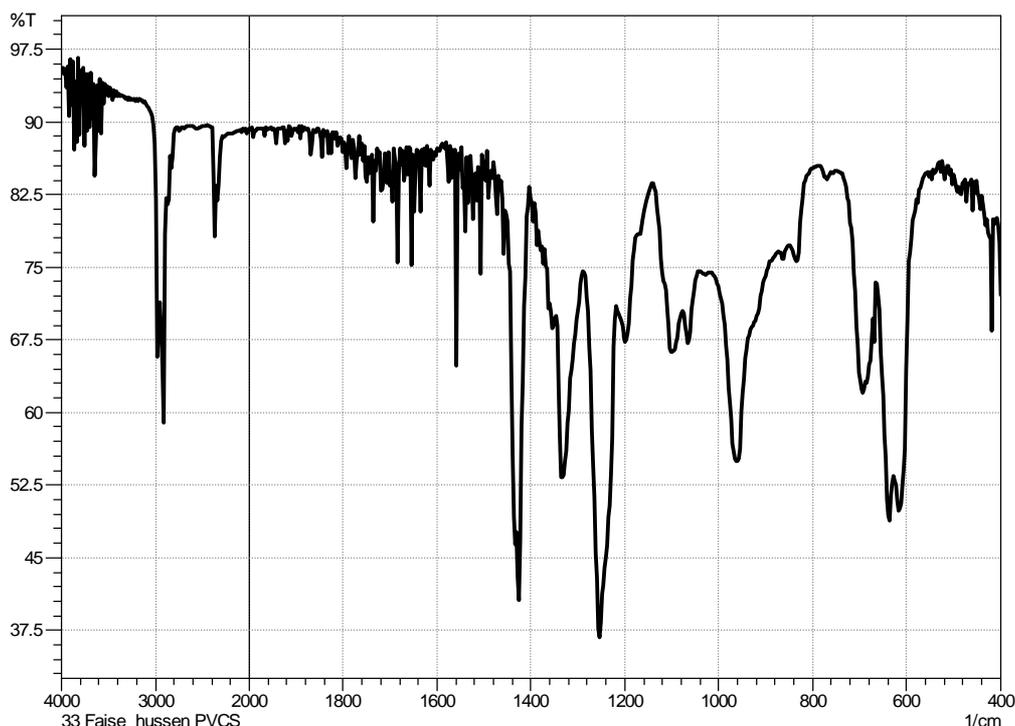
After degradation of PVC by heated it for 2 h. at  $190^\circ\text{C}$  main differences occur in the chemical structure lead to found new chemical groups such as polyene, hydroxyl, carbonyl, cyclic compound and other [20,21], this

new chemical structure can be observed and monitored by IR spectrometry; **Figure 5** shows the IR spectra of PVC after decomposed with out any thermal stabilizer.

This spectrum contain clear and new deference peaks at several position where are not found in IR spectrum of stander PVC; (**Figure 4**) one of these peaks that appear at  $3650 \text{ cm}^{-1}$  which attributed to the free hydroxyl groups stretching vibration which can formed as a result to thermal-oxidation process, while in the state of PVC contain deferent percent from Ca-lignin chelating complex; **Figure 6**, **Figure 7**, and **Figure 8**, where in this samples the peak became much less intense or not found.

Additionally, clear peak can be detected in **Figure 5**, in the region between  $3200 - 3400 \text{ cm}^{-1}$  corresponding to absorption of hydroxyl with hydrogen bond, but this not found in the presence on lignin derivative at all %wt. that mean increased PVC stability to thermal degradation by this additive where appear that the Ca-lignin chelating complex can be play a main role in the PVC stabilizing mechanism by it's chemical structure which can absorbed HCl.

The intensified new strong and sharp at  $1730 \text{ cm}^{-1}$  in **Figure 5** attributed to formation carbonyl groups as aliphatic ketone in PVC after heat treatment and this not found in PVC contain 1% **Figure 6** and became less intense in 2 wt% sample, **Figure 7**; other significant peak used to study the thermal degradation of PVC, polyene



**Figure 4.** IR spectrum of pure PVC (blank).

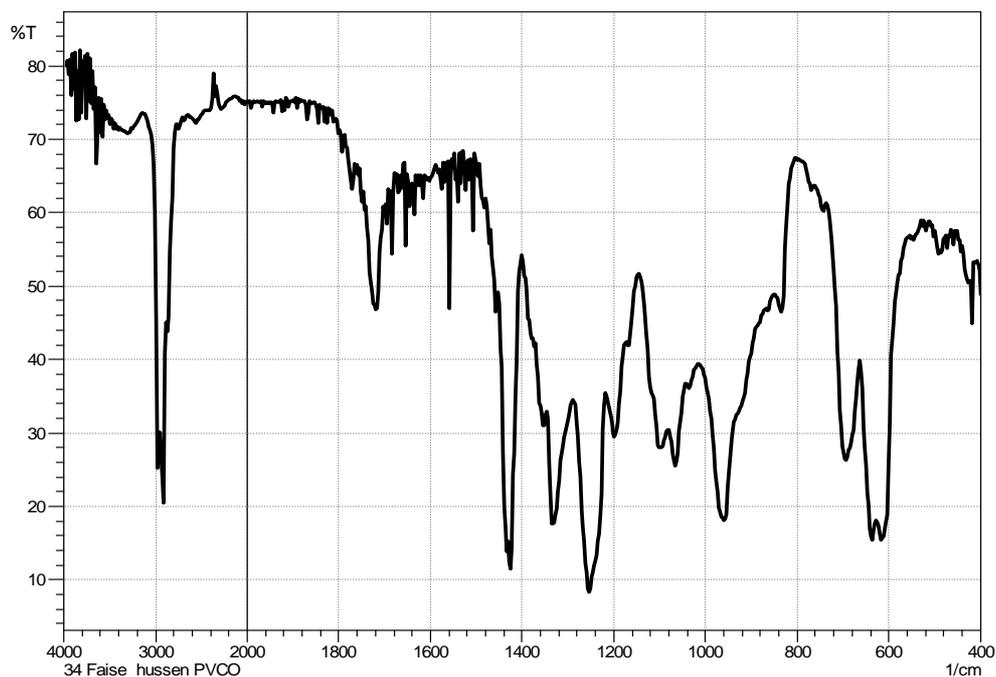


Figure 5. IR spectrum of pure PVC after degradation.

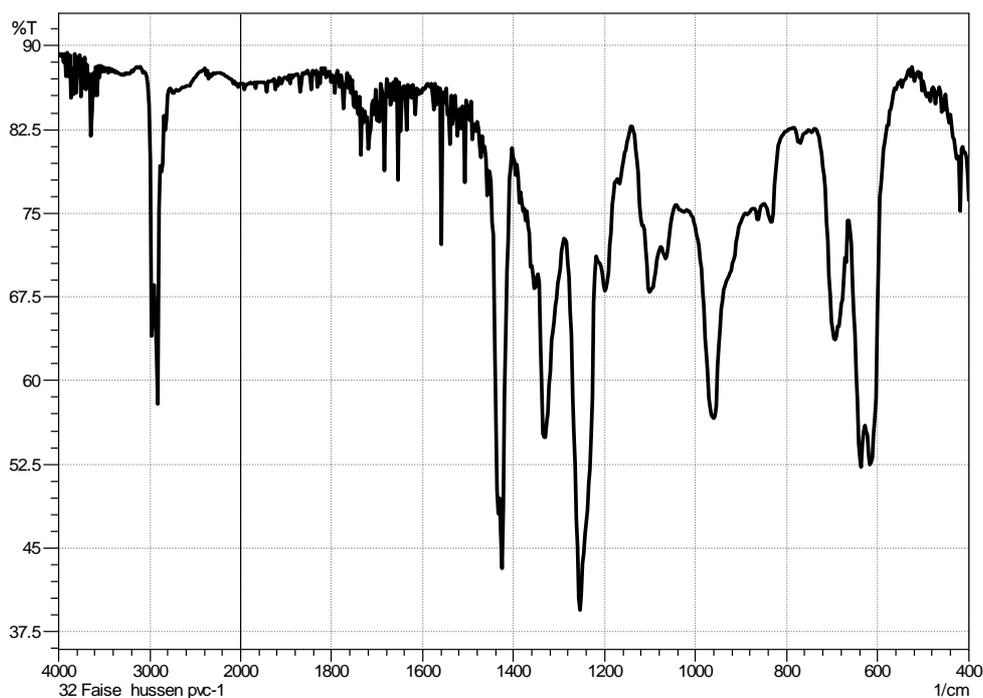


Figure 6. IR spectrum of PVC contain 1% Ca-lig. chelating complex.

that formed in the first state of degradation process (Owen 1984) at  $1602 - 1640 \text{ cm}^{-1}$  which appear in **Figures 5, 7 and 8** and not found in **Figure 6**, that mean the best activity can be achieved at less concentration from this derivative.

The absorption of the polyene and hydroxyl groups are used to follow the extend of polymer degradation by calculation polyene index ( $I_{Pe}$ ) and hydroxyl index ( $I_{OH}$ ) and carbonyl index ( $I_{CO}$ ); as seen from **Figure 9**, **Figure 10** and **Figure 11** the presence of lignin derivative lead

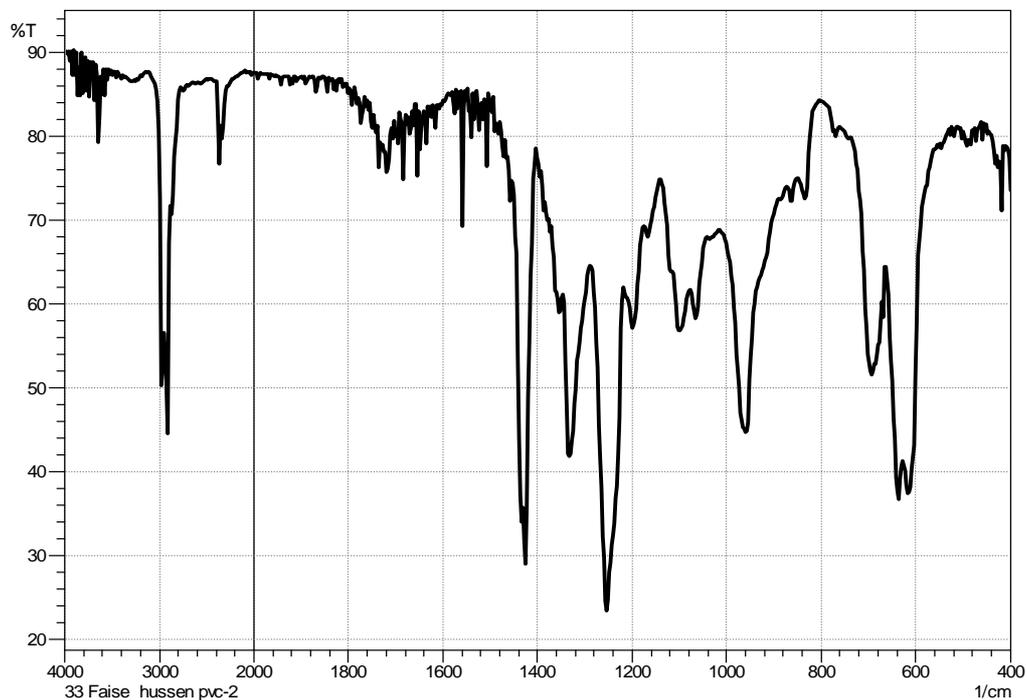


Figure 7. IR spectrum of PVC contain 2% Ca-lig. chelating complex.

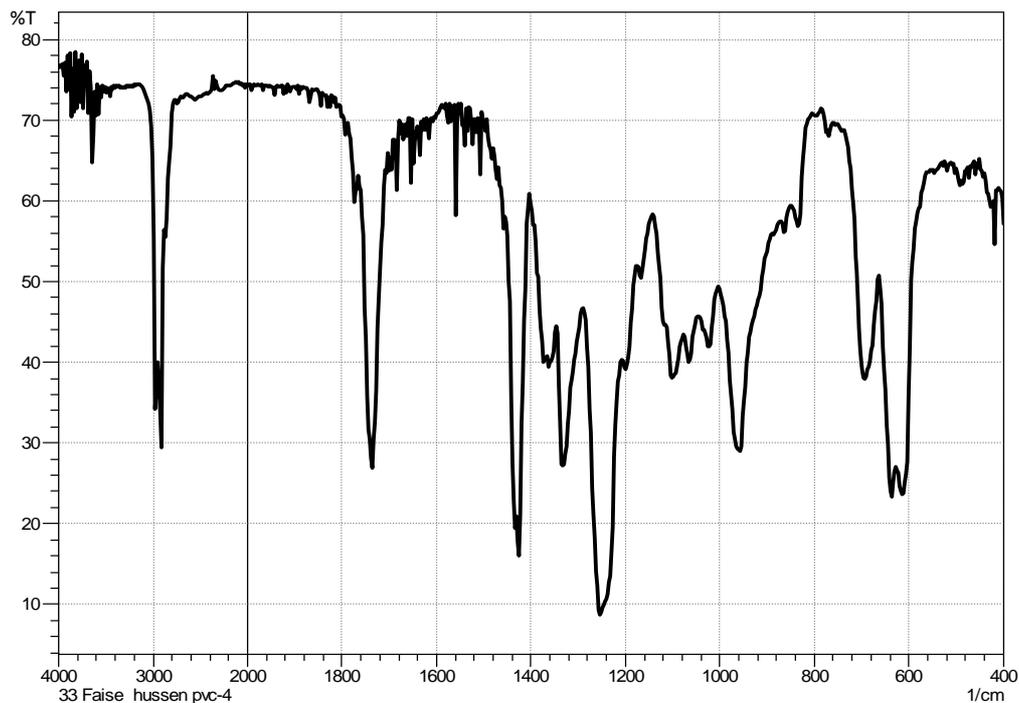


Figure 8. IR spectrum of PVC contain 4% Ca-lig. chelating complex.

to lower growth rate of polyene and hydroxyl indices respectively, with increased the wt% of this additive into PVC samples. Therefore, at 0% from lignin derivative the indices appear at higher values and decreased with

increased wt% into polymer.

#### 4. Conclusions

1) The chemical reaction of lignin with HI acid lead to in-

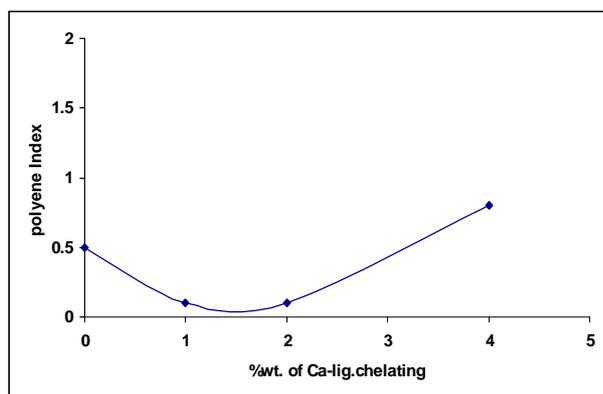


Figure 9. Relationship between the polyene index and wt% of Ca-lignin chelating complex.

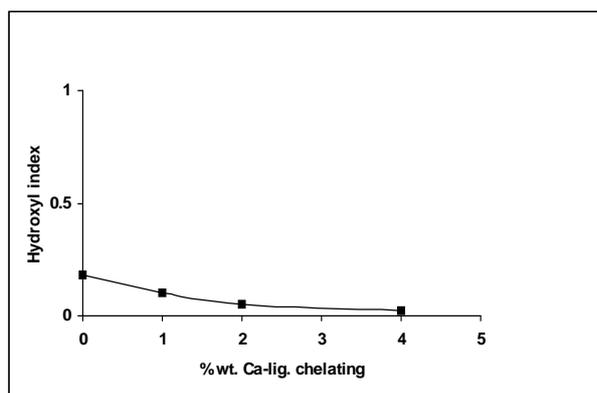


Figure 10. Relationship between the hydroxyl index and wt% of Ca-lignin chelating complex.

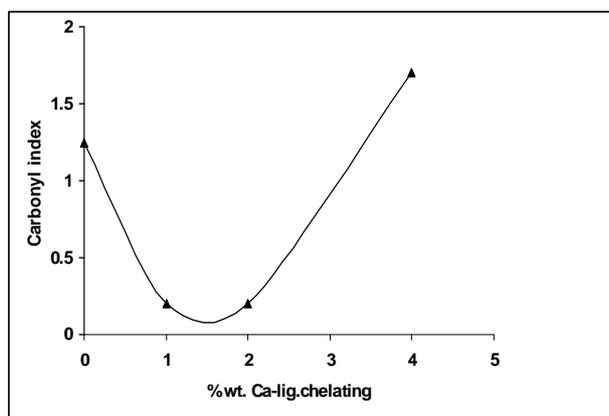


Figure 11. Relationship between the carbonyl index and wt% of Ca-lignin chelating complex.

creased it's contain from hydroxyl group and it's chemical reactivity to reaction with Calcium ion to form Ca-lignin chelating complex.

2) Investigating the influence of this derivative on the thermal stability of PVC showed increased thermal sta-

bility of PVC by the action of it's chemical structure to absorbed HCl from polymer system.

3) Ca-lignin chelating complex have thermal stabilizer effect with high activity at 1 wt% and less activity at above percentage.

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