

# Efficient Thermal Stabilization of Polyvinyl Chloride with Tannin-Ca Complex as Bio-Based Thermal Stabilizer

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## Abstract

The potential use of tannin-Ca complex derived from tannins as bio-based thermal stabilizer and antioxidant additive for polyvinyl chloride (PVC) was investigated in this work. For this project, Reapak B-NT/7060 was applied as reference thermal stabilizer. Variable compositions: (1, 2, and 3) part per hundred ratio (phr) of tannin-Ca complex in the presence of 10 phr Dioctyl phthalate (DOP) as plasticizer in all PVC formulations were prepared by melt mixing by internal mixer at 165°C. Tannin-Ca complex was characterized by FT-IR spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) analysis as well as by means of differential scanning calorimetry (DSC). The tannin derivative stabilization efficiency under inert atmosphere was determined by using thermogravimetric analysis (TGA). In addition, its thermal stabilization effect has been assessed in air as oxidizing atmosphere by DSC in dynamic conditions. According to TGA thermograms, the initial degradation temperature ( $T_i$ ) and optimum degradation temperature ( $T_{op}$ ) for the main degradation stage of PVC stabilized with this derivative were about 280°C and 310°C, respectively. While these were about 255°C and 293°C, respectively for PVC stabilized with commercial thermal stabilizer. Global results of TGA, DSC, SEM and EDX show that the tannin-Ca complex provides the best properties and results in stabilizing both against thermal degradation and thermal oxidation degradation of PVC.

## Keywords

PVC, Natural Polyphenols, Tannin-Calcium Complex, Bio-Based Thermal Stabilizer

## 1. Introduction

Because it is easily modified, polyvinyl chloride, PVC becomes one of the most important commodity polymers.

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PVC is widely applied in many areas and used in almost every aspect of our lives. Commercially, PVC increasingly produced for using in various industries such as building and constructions, packaging, electrical, automotive, furniture/office equipment, clothing, footwear and so on.

Nevertheless, it is characterized by poor heat and UV resistance and at its processing. PVC loses HCl and consequently, loses all its physical and mechanical properties as the end result. From this point, the addition of thermal stabilizers is, therefore, required to prevent thermal degradation during process. Because all these changes are accompanied by deterioration some of the useful properties of this polymer, it has become practically, to process of PVC with the presence of heat stabilizers [1] [2].

Thermal stabilizers are considered as essential additives to protect this polymer during processing as well as during the useful life of the polymer when oxygen, heat of atmosphere and sunlight are the most important degradative agencies. Certainly, the potential use of thermal stabilizers for PVC stabilization comes into the center of attention of polymer additives and they play a key role in the formulations of PVC and in determining their physical properties and process ability. Commonly used thermal stabilizers for PVC belong to one of four categories: lead salts, metal soaps, organic-tin compounds, and some auxiliary stabilizing materials. In the United States, USA, tin stabilizers dominate the market and represent state of the art. Europe has traditionally used lead based stabilizers for PVC. However, they will completely switch away from lead in the next several years. On the whole, the most common replacement is solid Calcium/Zinc stabilizers [2] [3].

Therefore, the replacement of lead-based thermal stabilizer, especially by green and renewable resources, such as the materials from plant resources, constitutes major contemporary challenges in terms of both economic and environmental aspects (environmental friendly and biodegradable). Generally natural polymer stabilizer additives which impart low toxicity, total or partial biodegradability are economically and technically viable to substitute the conventional heavy metal-based products [3].

On the other hand, bio waste materials or byproducts from industrial processing of some crops, nowadays are a cost for agri-food companies. All those materials contain chemicals and raw material and they until now have been exploited only partially. Antioxidants rich fractions were extracted from hazelnuts, chestnuts and especially grape seeds. The main chemical components of these extracts are tannins and plant polyphenolic compounds, which represent the major family of natural phenolic antioxidants and are chemical analogues to synthetic stabilizers widely used in plastic industry as well [4].

Among the natural polyphenolic compounds, tannins extracted from many plant parts (from forestry or viticulture byproducts) are available in high quantities. From a historical point of view, they are being used in the leather tanning and adhesives industries. Condensed tannins are polyphenolic polymers based on a flavonoid repeat units and have a large amount of phenolic rings in their structure with the hydroxylation pattern providing potent metal ions chelating and antioxidant activity [5] [6].

In Warren J. Grigsby [7] study, both native tannins and chemically modified tannins have been evaluated as additives in synthetic and biodegradable plastics such as polylactic acid and polypropylene. Based on his preceding works, pine bark tannin (PBT) is used and preferentially esterified with hexanoate or other ester chains to improve tannin hydrophobicity and miscibility within the plastics. Warren J. Grigsby [8] in his next study, the polypropylene and an aliphatic polyester have been also used as parallel plastic systems to assess the functional attributes provided by the tannin-based additives. It is found that tannin esters have inhibited the UV degradation effects in both polypropylene and aliphatic polyester, and have extended the oxidative induction time of polypropylene.

To the best of our knowledge, the projects that involved in this study, in which tannin-Calcium complex used as PVC thermal stabilizer additives, were unprecedented. Therefore, evaluation of the performance of tannin-Calcium complex as potential additive and thermal stabilizer to PVC has been carried out by our project. This study actually tackles three objectives: 1) to use renewable natural materials from byproducts resources; 2) to produce polymer additive as thermal stabilizer for PVC starting from available bio friendly raw materials; and 3) to find green thermal stabilizer-antioxidants, which can efficiently hinder the degradation of PVC during the processing and uses without any danger of possible health damage when releases from the polymer during application.

## 2. Experimental

### 2.1. Materials

PVC (k-value 65) with S6558 trade name, was provided from Bandar Imam Petrochemical Co. (Iran); Tannins

used in this study after isolated it from eucalyptus bark. Sodium hydroxide was supplied by Fluka; and Calcium hydroxide from Aldrich. Dioctylphthalate, DOP which is used as PVC plasticizer was provided from Iranian petrochemical industries (Farabi for petrochemical industries). Reapak B-NT/7060, Commercial thermal stabilizer type (Ca/Zn-based powder) supplied by Reagents, Italy; was selected as reference stabilizer and used for comparison.

## 2.2. Instrumentals

The PVC powder and other ingredients of the formulations were dry hand blended at room temperature. The compounding was carried out using an internal mixer Brabender type: measurement and control system.ms, model: Lab. Station-Plasti-Corder, W50-2002, Germany.

Determination of torques during melt-mixing of PVC with additives samples (expression of relative melt viscosity) versus time was carried out in Brabender internal mixer, a couple of roller rotors speed at 80 rpm, mixing temperature was at 165°C for 4 minutes.

Compression molding machine type minipress, Toyseiki, Japan, which was used for making PVC samples as sheets with 1.5 mm thickness.

The thermal stability of PVC samples was evaluated by using a thermo gravimetric analyzer (TGA) type: TGA/DSC-1 from Mettler Toledo (Switzerland). The samples with an average mass of 8 - 10 mg were heated from 25°C to 600°C at a 20°C/min of heating rate under N<sub>2</sub> atmosphere at flowing rate 50 ml/min. Differential scanning calorimetric, DSC analysis was carried out by used a DSC model DSC 1 (2011) from Mettler Toledo (Switzerland). The samples with an average mass of 8 - 10 mg were heated from 25°C to 350°C at heating rate 20°C/min and under the air as atmosphere at flowing rate 50 ml/min.

Fourier Transform Infrared (FTIR) Spectroscopy was measured with BRUKER FTIR EQUINOX 55 IR Spectrum Scanner (Bruker, Germany). The FTIR sample was tested as KBr mixture disk with tannins or with tannin-Ca complex.

## 2.3. Methods

### 2.3.1. Isolation of Eucalyptus Tannins

100 g of Eucalyptus outer bark was dried and grinded to fine powder. The bark powder was extracted with 2% w/w (per weight of dried bark) sodium hydroxide aqueous solution under reflux for 24 hours. The liquor/bark ration of 20:1. After extraction, the isolation tannins were filtered out and dried at 70°C. The extraction was repeated twice more. Solids were separated by filtration and liquid fraction was dried in oven (60°C) overnight. The isolated tannins were dried and used as raw material for synthesis tannin-Ca complex without further purification.

### 2.3.2. Preparation of Tannin-Calcium Complex

10 g of tannins powder were dissolved in 100 ml distillation water at 60°C with continuous stirrer. The pure and filtrated of the saturation aqueous solutions of Ca(OH)<sub>2</sub> was added gradually to the tannin solution with continuous mixing by magnetic stirrer, the addition process continuous until the pH was raised to 12. After that, the mixture was allowed to stand up for 24 hours. Brown and thick precipitate was obtained which was filtered, then washed with excess of distillation water to pH about 6 and dried for 24°C at 60°C.

### 2.3.3. Samples Preparation

Preparation of PVC Mixtures with Tannin-Calcium Derivative were prepared as follow: PVC was thermally mixed with tannin-Calcium derivative at percentages (1, 2, and 3) part per 100 ratio, phr and in the presence of 10 phr dioctyl phthalate, DOP as plasticizer in all samples. The mixing process was carried out by using 60 g of PVC and the appropriate weight of tannins derivative and DOP. All samples of PVC were prepare firstly by thoroughly hand mixing, then the mixture transferred into the mixing chamber of internal mixture (**Table 1**).

The conditions of thermal mixing were carried out at 165°C with rotating speed at 80 rpm for 4 minutes, this period start after full addition the polymer formulation into mixing chamber. Samples of PVC with commercial thermal stabilizer at 2 phr and DOP at 10 phr was prepared under the same conditions and used for comparison.

The specimens for the tests were produced using compression molding method at 200°C for 10 min (under 5 MPa for 8 min and the pressure increased to 30 MPa for the last 2 min).

**Table 1.** Formulations of the PVC samples.

PVC samples	PVC compound (phr <sup>*</sup> )	Tannin-Ca complex (phr)	DOP (phr)	Reapak B-NT/7060 (phr)
PVC/0phr tannin-Ca	100	0.0	10	2
PVC/1.0phr tannin-Ca	100	1.0	10	0
PVC/2.0phr tannin-Ca	100	2.0	10	0
PVC/3.0phr tannin-Ca	100	3.0	10	0

\* phr: part per hundred ratio; DOP: dioctyl phthalate.

### 3. Results and Discussion

The reactivity of tannins is determined both by its particular structure with specific functional groups, their positions, and by the chemical modifications. Tannins have phenolic hydroxyl groups and at different positions on the molecular structure, the presence of hydroxyl groups in tannins has enable it to utilization as raw material for synthesis of products with a lot of applications. In recent decades, tannins as ligand to prepare metal ions complex have been increasingly considered as a potential way to used tannins on a large scale, for example, for removing some metal ions from environmental systems [9] [10].

Tannins act as ligand with metal ions to formation of the complex in which the metal coordinates with hydroxyl functional groups. Upon coordination, some of the wavenumber values of tannins functional groups are shifted. The FTIR spectra of unmodified tannins was compared with the spectrum of tannin-calcium metal chelating complex, **Figure 1** and **Figure 2**, respectively.

The FTIR spectrum of tannins and tannin-Ca chelating complex exhibited significant features in the stretching vibration at  $3380\text{ cm}^{-1}$ ,  $1680\text{ cm}^{-1}$ ,  $1480 - 1600\text{ cm}^{-1}$ , and  $800 - 900\text{ cm}^{-1}$  regions. The most significant changes with respect to the unmodified tannins concern the bands at  $1000$ ,  $1400$ ,  $1600$  and  $3400 - 3470\text{ cm}^{-1}$ . The FTIR spectra of tannin-Ca complex shows decrease in the intensity of the characteristic bands in the region  $3300 - 3470\text{ cm}^{-1}$  (OH stretching vibration) which is lower in intensity with respect to that of unmodified tannins due to de-protonation of the OH groups on binding. The sharp band at  $860\text{ cm}^{-1}$  and the strong one at  $1400 - 1480\text{ cm}^{-1}$  which can be attributed to formation O-Ca ionic bonds [11]. These bands can be considered as characteristic bands for tannin-Ca chelating complex formation. It is well known from literature data that tannins can complex with more metal ions because they have suitably oriented functional hydroxyl groups (catechol units) in their chemical structure. Literature resources provide papers on metal ion chelating mechanisms by tannins and chemically modified tannins. These include ion-exchange, surface adsorption, chemisorption, complexation, and adsorption-complexation [9] [10].

It is commonly believed that ion-exchange is the most prevalent mechanism. Metal ion reacts with neighboring phenolic groups (OH at C3' and C4') **Figure 3**, of the tannins to release protons with formation of coordination bonds with an existing metal ion, a possible mechanism of ion exchange could be considered as divalent metal ion (as  $\text{Ca}^{2+}$ ) attaching itself to adjacent hydroxyl groups (and oxyl groups in the tannin-Na phenoxide salt), which could donate two pairs of electrons to metal ions. As a result, forming chelated compounds and releasing two hydrogen ions into solution [9] [10] [12].

To obtained detailed information about the physical nature of tannin derivative, the scanning electron microscopy (SEM) method was used. The morphological changes of the tannins before and after chemical modification have also been studied by (SEM). **Figure 4** shows micrographs obtained for tannins (a) and (b); and for tannin-Ca complex (c) and (d) powders at two magnifications. The shape and the particle morphology of tannins and tannin-Ca complex as shown in **Figure 4**, appears as non crystalized particles with non homogenous particles sizes ranging from 1 micrometer to 5 micrometer. Furthermore, **Figure 4(d)** shows the presence of smaller particle (100 - 500) nm on aggregated on the surface of tannin-Ca Complex.

The effect of metal binding to the tannins on the morphological properties of the final product caused some changes in the surface morphology. The tannin-Ca particles looks more spherical with more smooth surfaces and the diameters of this particles are smaller in comparison with that of the particle shape and sizes of tannins before loaded with  $\text{Ca}^{2+}$  ions.

The energy dispersive X-ray analysis (EDX) spectroscopy was employed on the tannins, **Figure 5(a)** and on tannin derivative, **Figure 5(b)** to obtain information about the mineral element in these materials.

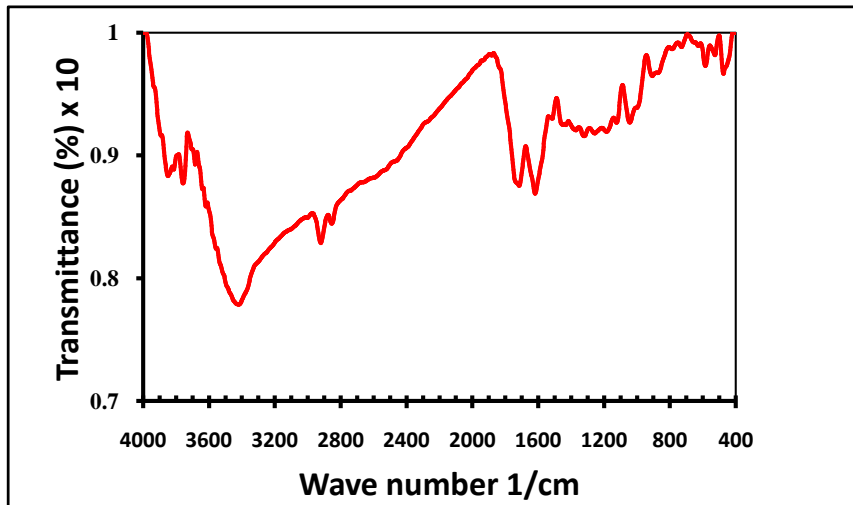


Figure 1. FTIR spectrum of unmodified tannins.

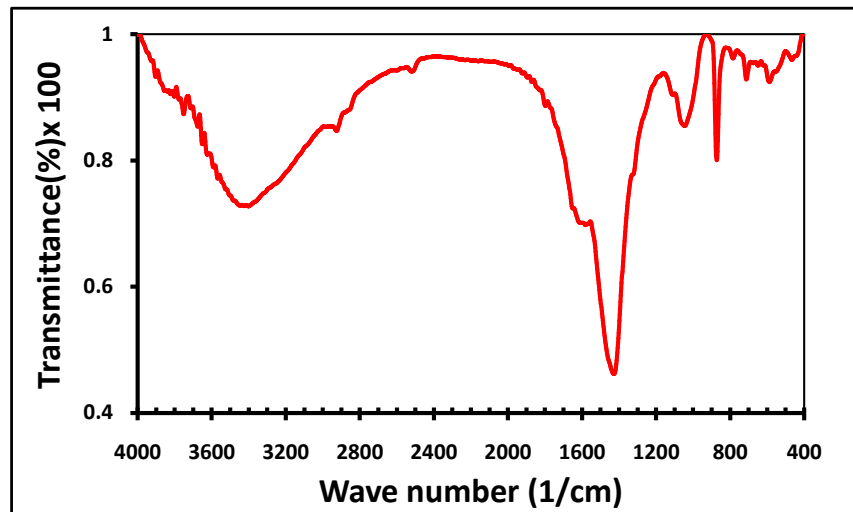


Figure 2. FTIR spectrum of tannin-Ca complex.

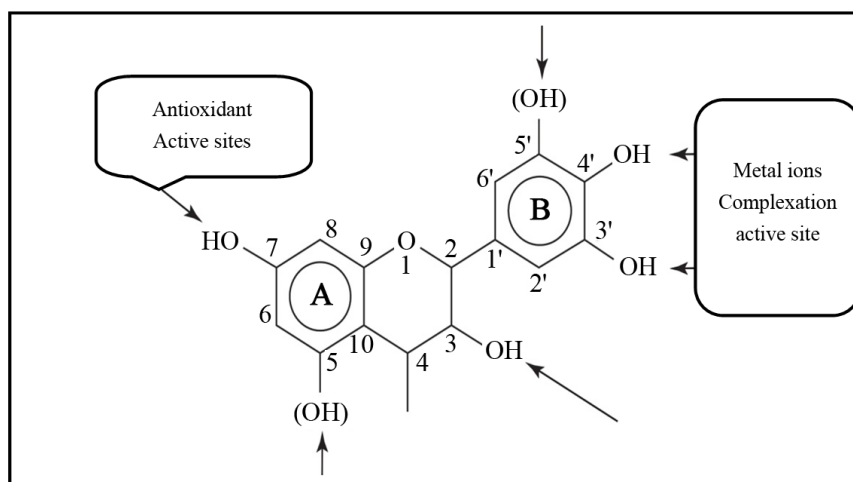
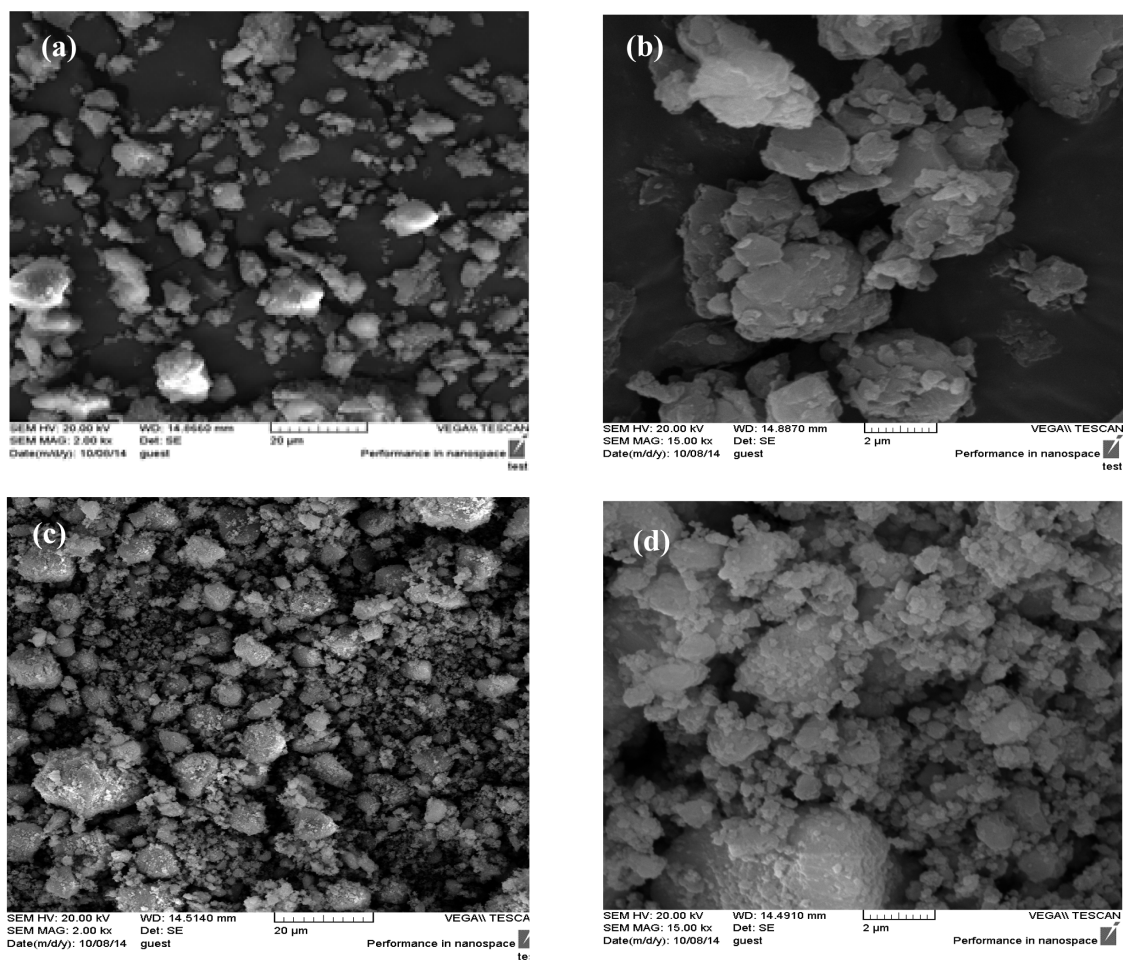
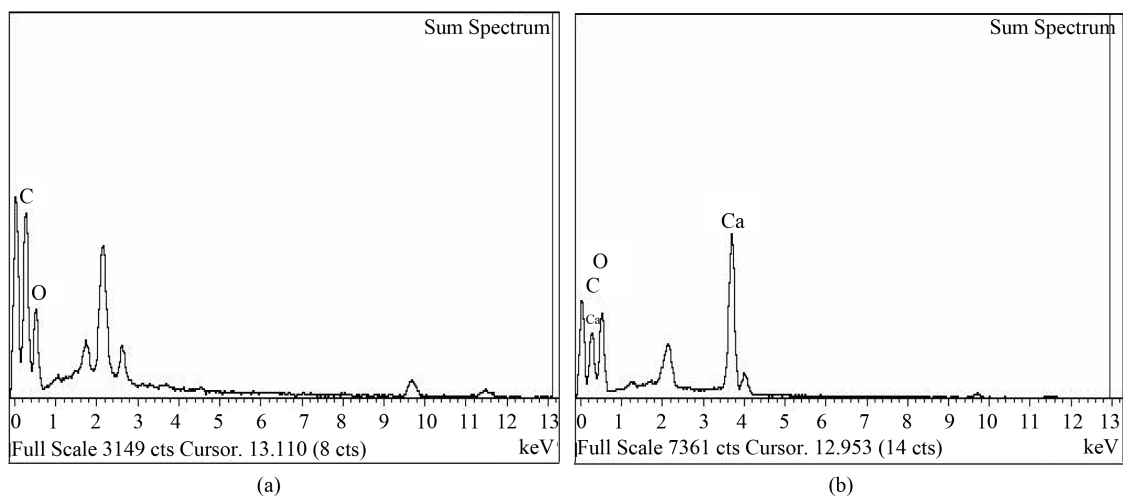


Figure 3. Probable flavonoid unit into a condensed tannin.





**Figure 4.** SEM images of un modified tannin at 2.00 kx (a) magn. and at 15.00 kx (b); and of tannin-Ca complex powder at 2.00 kx magn. (c) and at 15.00 kx (d).



**Figure 5.** EDX spectra of tannins before modification (a); and EDX spectra of tannin-Ca complex (b).

In the present study, energy dispersive X-ray analysis (EDX) of the raw material as well as the product were characterized. The results of EDX analysis suggests that C and O contributed the two major elements of the tan-

nins before reaction with calcium hydroxide where the phenolic structures represents the main ingredients. Ca or other metals are not evident, **Figure 5(a)**. On the other hand, calcium element as well as carbon and oxygen were observed in the powder sample of tannin-Ca complex, **Figure 5(b)**. The registered alkali earth (Ca) metal peaks normally characterized by the presence of these metals. which is additionally confirmed by FTIR analysis, as previous described.

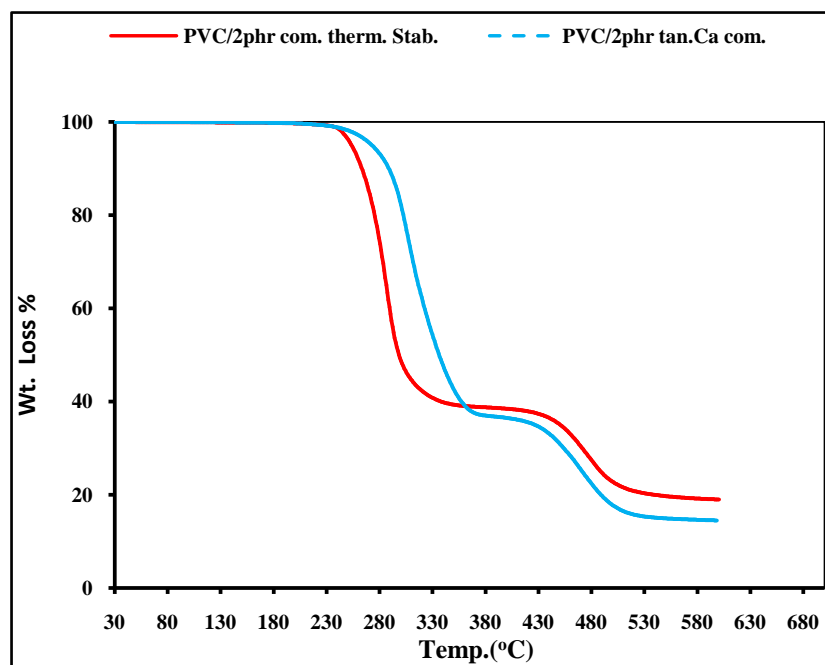
**Table 2** summarizes the main elements composition into both tannins and tannin-Ca complex. The result of the EDX provide an evidence of metallic calcium ion ( $\text{Ca}^{2+}$ ) in the tannin-Ca complex which not found in native tannins. EDX show that the tannin-Ca complex contain 14.53% from this metal when comparison with pure tannins which not contain it in addition the carbon and oxygen which the main structure of this 100% natural based derivative for used as PVC additive.

However, it is generally well known that the thermal degradation and thermal oxidation degradation of polyvinylchloride, PVC occur by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds and also by autocatalytic free radicals reactions. The main process involved in thermal degradation of PVC stabilized with commercial thermal stabilizer (2 phr) appears to have the onset temperature (5% wt. loss) around  $255^{\circ}\text{C}$ , **Figure 6**.

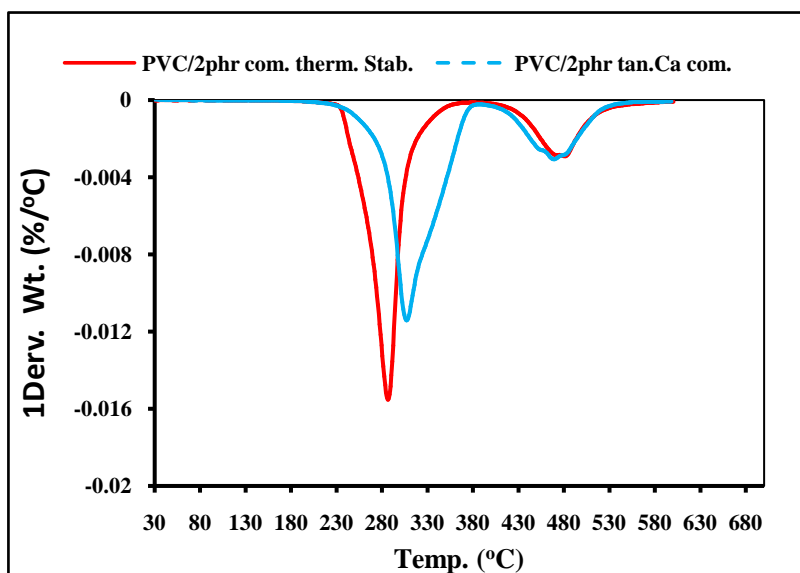
The weight loss percentage from PVC stabilized with 2 phr commercial thermal stabilizer sample reach to about 55% in the first degradation stage with temperature at maximum degradation rate ( $T_{\text{max}}$ ) or optimum degradation temperature ( $T_{\text{op}}$ ) at  $290^{\circ}\text{C}$ , as clearly demonstrate into **Figure 6** (TGA) and **Figure 7** (DTG). After the main degradation step which can be totally or partially prevented by thermal stabilizers, the chemical structure and physical properties of this polymer will be different in whole.

**Table 2.** Elements composition of tannins and tannin-Ca complex.

Elements	Tannins		Tannin-Ca complex	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	58.78	65.51	29.10	38.41
O	41.22	34.49	56.37	55.85
Ca	0	0	14.53	5.74



**Figure 6.** TGA thermograms of PVC stabilized with 2 phr commercial thermal stabilizer and of PVC stabilized with 2 phr tannin-Ca complex.



**Figure 7.** DTG thermograms of PVC stabilized with 2 phr commercial thermal stabilizer and of PVC stabilized with 2 phr tannin-Ca complex.

From these thermograms, it is clearly evident that the tannin-Ca complex improved PVC thermal stability. Both  $T_i$  and  $T_{op}$  of PVC stabilized with 2 phr tannin-Ca complex were found to be 272°C and 303°C, respectively. All these values are higher than that of PVC stabilized with commercial one. On the other hand, the PVC have degradation rates in the presence of tannin-Ca complex lower than that of PVC with commercial thermal stabilizer. These results suggest that the PVC stabilized with tannin-Ca complex is more resistant to thermal degradation (lower mass loss %) and the tannin derivative have highly activity to increase the thermal stability of this polymer, whereas during and after thermal treatment (thermal mixing) of PVC with this additive, the tannin-Ca complex start to work as thermal stabilizer by HCl scavenging mechanism. Furthermore, this additive can save the PVC from thermal degradation during the course of thermal compression for about 10 min. During TGA run and when all amount of this derivative is completely consume, the PVC start to degrade, as a natural result to the heat energy effect on polymer system.

**Figure 8** and **Figure 9** represent the thermal degradation behavior of PVC in the presence of different compositions from tannin-Ca complex. All samples even at lower composition (1phr) of tannin-Ca complex, show the excellent effect of this derivative in increased the thermal resistance of PVC against the degradation conditions.

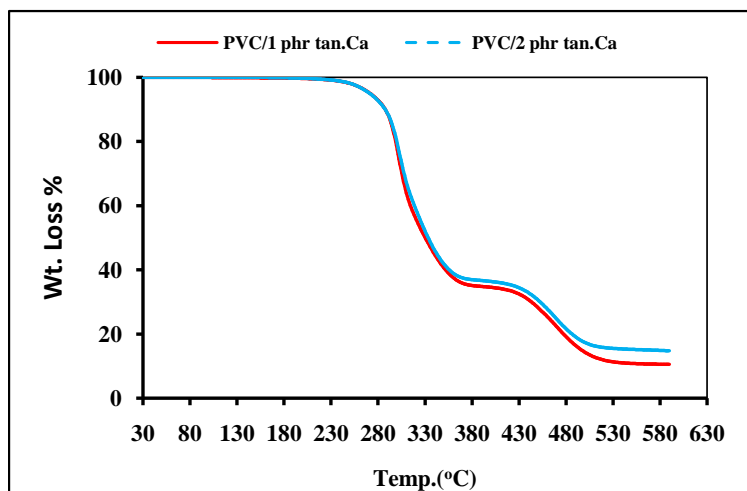
On the contrary, at continuous heating process, the second degradation stage appears around 300°C which consist of loss the by products of chains scission, cyclisation and thermal oxidation reactions (if the thermal degradation occurs under oxidation atmosphere) [1]. As clearly appear from **Figure 8** and **Figure 9**, there are on significant effect for this derivative on PVC stabilization at this stage.

From the thermograms, it is evident that the tannin-Ca complex improved PVC thermal stability. Whereas the  $T_i$  and  $T_{op}$  of PVC stabilized with tannin-Ca complex were found to be 285°C and 310°C, respectively. Whereas for PVC stabilized with commercial thermal stabilizer, these temperatures were about at 255°C and at 295°C, respectively. On the other hand, the PVC have degradation rate in the presence of tannin-Ca complex lower than that by effect of commercial thermal stabilizer, **Table 3**. These results suggest that the PVC stabilized with tannin derivative is more resistance to thermal degradation (lower mass loss %).

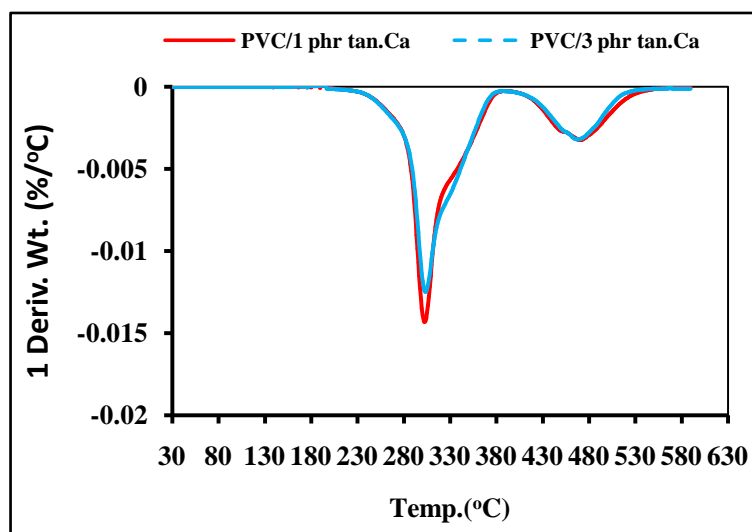
Generally, all the thermal data in **Table 3** show that the resistance of PVC against thermal degradation in the presence of tannin-Ca complex are higher than that in the presence of commercial stabilizer. In addition, the degradation rate of PVC in the presence of tannin-Ca complex at all concentration values are lower than that of PVC stabilized with commercial thermal stabilizer. This result suggests that the tannin-Ca complex may work as thermal stabilizer for PVC by different mechanism or by other mechanism in addition to the main mechanism which dependent on reaction and trapped the HCl.

Clearly, the ability of tannins to work as antioxidant will added more qualification to increase the perfor-





**Figure 8.** TG thermograms of PVC stabilized with 1 phr and 3 phr tannin-Ca complex.



**Figure 9.** DTG thermograms of PVC stabilized with 1phr and with 3 phr tannin-Ca complex.

**Table 3.** Thermal data from TGA and DTG thermograms for PVC stabilized with commercial thermal stabilizer and tannin-Ca complex.

PVC samples	$T_{i(5\% \text{ wt. loss})}^*$ °C	$T_{10\% \text{ wt. loss}}^*$	$T_{60\% \text{ wt. loss}}^*$	$T_{op}^{\circ \text{C}^*}$	Degrad. rates <sup>***</sup> (wt%)/min
PVC/(2phr) Com. Therm. Stab.	255	280	350	295	15.7
PVC/(1phr) Tan.-Ca	285	292	370	310	8.88
PVC/(2phr) Tan.-Ca	280	295	380	310	7.77
PVC/(3phr) Tan.-Ca	280	300	390	312	7.0

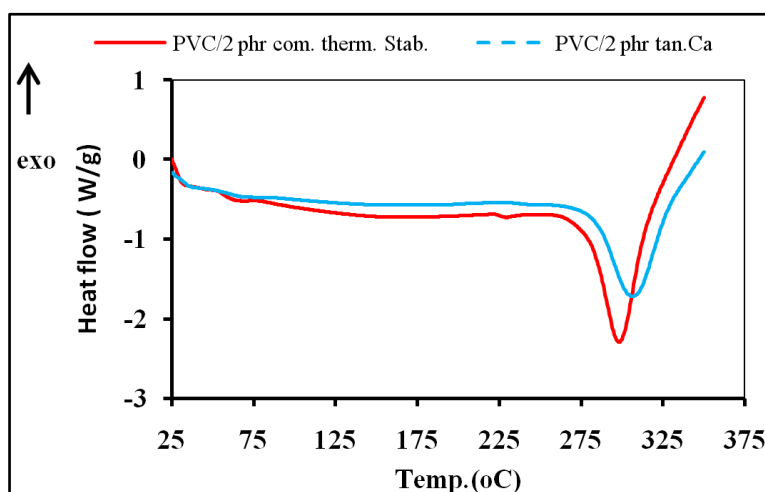
\*Where are  $T_i$  and  $T_{op}$  are the initiation degradation temperature (corresponding to 5% weight loss); and optimum degradation temperature *i.e.* temperature at maximum degradation rate, respectively, of the main degradation stage (first step). \*\* $T_{10\%}$  and  $T_{60\%}$  are the temperatures for 10% weight loss and for 60% weight loss, respectively. \*\*\*The rate of weight loss percentage (degradation rate) during first degradation stage of PVC samples.

mance of tannin-Ca to act as thermal stabilizer and antioxidant (in the same time) for PVC. In other words, tannin derivative have ability to work as primary and secondary thermal stabilizer for PVC.

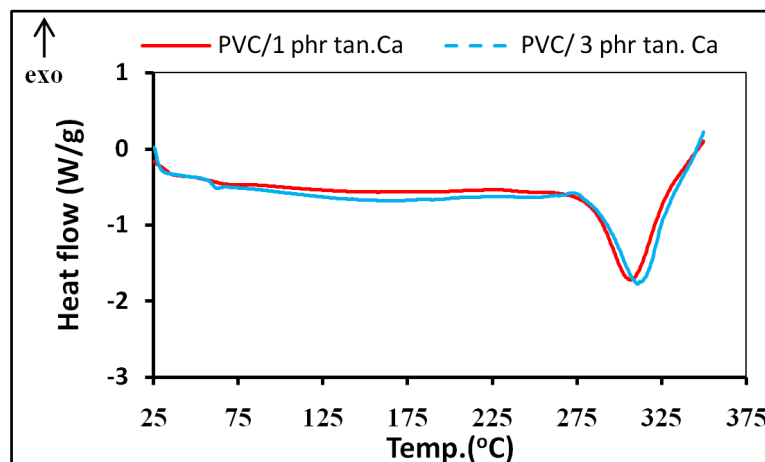
For that reason, the degradation of PVC is always associated with evolution of HCl, the main attempts to stabilize of PVC involved the addition of thermal stabilizers. Despite this, the stabilization process was more complex than simply reacting with hydrogen chloride. The ability of tannin derivative to react with HCl and to act as antioxidant as well as other properties such as high efficiency, relatively high molecular weight, low cost, low water dissolving, 100% natural and low evaporation make this product have more advantages as thermal stabilizer for PVC and can be used as a single component to create greatly thermal stability in this polymer.

Concurrently, in this study, differential scanning calorimetry, DSC as another thermal analysis technique were used effectively in investigated the effect of tannin-calcium complex at different levels on the thermal behavior and thermal degradation of PVC under air as oxidized atmosphere. In the presence of oxygen (or air), thermal degradation of PVC usually is companies with thermal oxidation degradation reactions and the rate of degradation process becomes even more rapid in presence of oxygen and HCl. To prevent autooxidation of this polymer both primary and secondary antioxidants may be used. Therefore, if there are any additives that can act as thermal stabilizer and antioxidant in the same time will be have more benefit. As many papers and researches showed that the tannins as natural polyphenol are well known to have antioxidation activity [13]-[15].

Once again, all PVC samples were heated from 25°C to 350°C by the dynamic DSC heating scans, DSC curves were tracked to detection the degradation and oxidation behaviors of PVC in the presence of these additives, **Figure 10** and **Figure 11**.



**Figure 10.** DSC scans of PVC stabilized with 2 phr com. ther. stab; and of PVC stabilized with 2 phr tannin-Ca complex (b).



**Figure 11.** DSC scans of PVC stabilized with 1 phr and; of PVC stabilized with 3 phr tannin-Ca complex.

Simply, it can be observed from the DSC scans of PVC, **Figure 10** and **Figure 11**, the degradation of PVC is endothermic reaction because the degradation process consist of elimination reactions and take place as reverse to the organic addition reactions that can occur into the double bond of alkenes [16]. The main DSC peaks which appears at around  $T_{op}$  300°C in DSC scan of PVC stabilized with 2 phr tannin-Ca complex and at 295°C in DSC scan of PVC stabilized with 2 phr commercial thermal stabilizer, represented the main degradation step of PVC. These peaks reflect the action, efficiency and effect of tannin-Ca complex on the thermal stability of PVC as comparison with that of the reference stabilizer.

The onset temperatures  $T_i$  and the peak temperatures  $T_{op}$  (which corresponds to maximum reaction rate) of degradation and the energy of degradation which are associated with the resistance of polymer to degradation reaction are summarized in **Table 3**. Based on these results, it can be considered that the tannin-Ca complex can act as potential thermal stabilizer with good activity.

As clearly shown in **Figure 11**, the thermal stability of PVC slightly increase with increased the tannin-Ca complex percentage. Whereas the  $T_i$  appears at 280°C and the  $T_{op}$  reach to 312°C for PVC stabilized with 3 phr of the tannin derivative. The tannin complex exhibit their stabilizing efficiency mainly through effective absorption of the degradation products (HCl gas) by their metal ion coordination salts which reacted with HCl and give  $\text{CaCl}_2$  and hydroxyl groups into tannins as main reaction products to stabilization mechanism. And secondary by ability of tannins to work as antioxidant.

Therefore, the performance of tannin derivative to protect the polymer against thermal degradation and thermal oxidation can be estimated from DSC curves by a relatively more thermally stable PVC. The main thermal data of DSC scans were summarized in **Table 4**, all the parameters obtained from DSC analysis indicate to the high performance of tannin-Ca complex to increase the thermal stability of PVC. Furthermore, after this peak, there are rapid exothermic reaction occur in all PVC samples, this reaction associated with the thermal oxidation degradation of PVC, which consist of both oxidation and degradation reactions [1] [2]. Once again, the advantage effect of this derivative appear in delay the temperatures and the rates of this peaks.

The activity of tannins derivatives to increase the thermal stability of PVC is shown by the high temperature ( $T_i$  and  $T_{op}$ ) of the degradation peak as well as the higher temperature degrees during which no detectable to any endothermic (or exothermic) reaction. That means there are limited or no degradation occur in the polymer sample until this temperature. This behavior can be attributed the ability of tannin-Ca complex to reacted with HCl *i.e.* it can act as scavenger to the main catalyst for low thermal stability of PVC.

The degradation temperature that related to thermal oxidation degradation in the second stage appear at 315°C for PVC sample stabilized by 2 phr commercial thermal stabilizer. While in the presence of tannin chelation complex at 2 phr this temperature appear at 325°C, **Figure 10**. This temperature reaches to about 330°C for PVC sample with 3 phr tannin complex, **Figure 11**. And also the heat energy for degradation of PVC especially stabilized with 2 phr or 3 phr of tannin complex were lower than that obtained for PVC with the reference stabilizer, **Table 3**. This entails that tannin-Ca complex shows greater thermal stability effectiveness during DSC temperature range.

Tannins, and most of plants phenolic compounds are the most active natural antioxidants in plants and can be used in synthetic system such as polymers. They are known to act as antioxidants not only because of their ability to donate hydrogen or electrons to prevent or interrupt oxidation reactions, but also because they are stable radical intermediates. The ability of tannin chelation complex to react with HCl, and on the other hand to their ability to act as phenolic antioxidant give to tannins derivatives double effect in PVC thermal oxidation process.

From the DSC scans, in **Figure 10** and **Figure 11**, there are relativity small change in the DSC baseline for

**Table 4.** Results of DSC dynamic characterization PVC stabilized with commercial thermal stabilizer and tannin-Ca complex.

PVC samples	$T_i^*$ (°C)	$T_{op}^*$ (°C)	Heats of degradation (W/g)	Degradation rates (W/g)/min
PVC/(2phr) com. Ther. Stab.	270	295	107.3	0.75
PVC/(1phr) Tan.-Ca	280	305	151.2	1.0
PVC/(2phr) Tan.-Ca	280	305	101.0	0.75
PVC/(3phr) Tan.-Ca	280	312	95	0.8

\* $T_i$  and  $T_{op}$  are the initiation degradation temperature and optimum degradation temperature, respectively.

glass transition temperature,  $T_g$  of PVC. The  $T_g$  values of PVC in all other samples appears in the same range of 58°C - 65°C. This relatively low values of  $T_g$  for PVC related to minimum or non considerable changes in the molecular structure of this polymer. These findings can be attributed to the stabilization effect of commercial thermal stabilizer and of tannin complex. The relatively low values of  $T_g$  which confirms the activity of additive as stabilizer.

The results show that the rate of degradation-oxidation reaction in the samples of PVC with tannin derivatives (2 phr) appear at lower rate than that of reference sample *i.e.* (2 phr commercial thermal stabilizer). This behavior suggests that the tannins into tannins chelation complexes contribute in the stabilization of PVC as chelating phenolic thermal stabilizer. Therefore, the time of thermal stability to PVC samples stabilized with this derivative (or stabilized by this systems) reached to higher values than in the case of using normal commercial thermal stabilizers.

#### 4. Conclusion

A preliminary investigation is reported on the thermal stability efficiency of tannin-Ca complex for PVC. Several analytical techniques were employed in order to evaluate PVC thermal stability in the presence of this derivative. TGA, and DSC experimental results confirmed that the tannin-Ca complex increased PVC thermal stabilization against thermal-oxidation degradation, compared with the commercial stabilizer. The results of this study point out that the tannin-Ca complex is an efficient stabilizer for PVC, even though in a lower extent (1 phr). Thus, it is possible to recommend the use of this bio-based additive as thermal stabilizer for PVC, according to the performance of tannin derivative. In this study, the most importance of performing further work aimed to evaluate the flame retardant and UV-stabilization effects of this derivative as long-term stabilization of PVC.

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#### References

- [1] Owen, E.D. (1984) Degradation and Stabilisation of PVC. Elsevier Applied Science Publishers LTD., London. <http://dx.doi.org/10.1007/978-94-009-5618-6>
- [2] Starnes, W.H. (2002) Structural and Mechanistic Aspects of the Thermal Degradation of Poly(Vinyl Chloride). *Progress in Polymer Science*, **27**, 2133-2170. [http://dx.doi.org/10.1016/S0079-6700\(02\)00063-1](http://dx.doi.org/10.1016/S0079-6700(02)00063-1)
- [3] Pierfrancesco, C., Mario, M., Jozef, R., Lyda, M.-R. and Cosimo, C. (2009) Effect of Natural Antioxidants on the Stability of Polypropylene Films. *Polymer Degradation and Stability*, **94**, 2095-2100. <http://dx.doi.org/10.1016/j.polymdegradstab.2009.07.023>
- [4] Dóra, T., Luca, M., Eniko, F. and Béla, P. (2014) Study of the Effect of Natural Antioxidants in Polyethylene: Performance of  $\beta$ -Carotene. *Polymer Degradation and Stability*, **102**, 33-40. <http://dx.doi.org/10.1016/j.polymdegradstab.2014.02.012>
- [5] Elaine, C.R. and Elisabete, F. (2012) Tannin-Phenolic Resins: Synthesis, Characterization, and Application as Matrix in Biobased Composites Reinforced with Sisal Fibers. *Composites: Part B*, **43**, 2851-2860. <http://dx.doi.org/10.1016/j.compositesb.2012.04.049>
- [6] Laurent, R., Chahinez, A., Eric, D. and Hélène, F. (2013) Depolymerisation of Condensed Tannins in Ethanol as a Gateway to Bio Sourced Phenolic Synthons. *Green Chemistry*, **15**, 3268-3275. <http://dx.doi.org/10.1039/c3gc41281d>
- [7] Grigsby, W.J., Bridson, J.H., Lomas, C. and Elliot, J.-A. (2013) Esterification of Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid). *Polymers*, **5**, 344-360. <http://dx.doi.org/10.3390/polym5020344>
- [8] Grigsby, W.J., Bridson, J.H., Lomas, C. and Frey, H. (2014) Evaluating Modified Tannin Esters as Functional Additives in Polypropylene and Biodegradable Aliphatic Polyester. *Macromolecular Materials and Engineering*, **299**, 1251-1258. <http://dx.doi.org/10.1002/mame.201400051>
- [9] Graciela, P., Juanita, F. and Jaime, B. (2003) Removal of Metal Ions by Modified Pinus radiata Bark and Tannins from Water Solutions. *Water Research*, **37**, 4974-4980. <http://dx.doi.org/10.1016/j.watres.2003.08.008>

- [10] Mahmut, O., Cengiz, S. and Şengil, İ.A. (2006) Studies on Synthesis, Characterization, and Metal Adsorption of Mimosin and Valoniatannin Resins. *Journal of Applied Polymer Science*, **102**, 786-797. <http://dx.doi.org/10.1002/app.23944>
- [11] Rabek, J.F. (1970) *Experimental Methods in Polymer Chemistry*. John Wiley & Sons, New York, 221-253.
- [12] de Yuso, A.M., Lagel, M.C., Pizzi, A., Fierro, V. and Celzard, A. (2014) Structure and Properties of Rigid Foams Derived from Quebracho Tannin. *Materials & Design*, **63**, 208-212. <http://dx.doi.org/10.1016/j.matdes.2014.05.072>
- [13] Wei, S.-D., Zhou, H.-C., Lin, Y.-M., Liao, M.-M. and Chai, W.-M. (2010) MALDI-TOF MS Analysis of Condensed Tannins with Potent Antioxidant Activity from the Leaf, Stem Bark and Root Bark of *Acacia confuse*. *Molecules*, **15**, 4369-4381. <http://dx.doi.org/10.3390/molecules15064369>
- [14] Formagio, A.S.N., Volobuff, C.R.F., Santiago, M., Cardoso, C.A.L., do Carmo Vieira, M. and Pereira, Z.V. (2014) Evaluation of Antioxidant Activity, Total Flavonoids, Tannins and Phenolic Compounds in Psychotria Leaf Extracts. *Antioxidants*, **3**, 745-757. <http://dx.doi.org/10.3390/antiox3040745>
- [15] Rosales-Castro, M., González-Laredo, R.F., Bae, Y.-S., Kim, J.K., Morre, J. and Karchesy, J.J. (2014) Characterization and Antioxidant Properties of the Condensed Tannins from Alaska Cedar Inner Bark. *Records of Natural Products*, **8**, 217-227.
- [16] Woo, L., Ling, M.T.K. and Chan, E. (1991) The Oxidative Induction Test Applied to Medical PVC and Other Polymers. *Journal of Vinyl and Additive Technology*, **13**, 199-203. <http://dx.doi.org/10.1002/vnl.730130408>