

# **Antal Kerpely Doctoral School of Materials Science and Technology**



## **Flame Retarding-Stabilizing Behavior of Plasticized Poly(vinyl chloride) Containing Novel Heavy Metal Free Modifier**

Thesis Booklet

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## RECOMMENDATION FROM THE SUPERVISOR TO

**Mr. Ali Ibrahim Moslem**

PhD Candidate at University of Miskolc Antal Kerpely Doctoral School of  
Materials Science and Technology

Mr. *Ali Ibrahim Moslem* (M.Sc. in Materials Engineering, Engineering College, Babylon University, IRAQ) had joined our Antal Kerpely Doctoral School at University of Miskolc four years ago. He has 10 years experience in higher education, e.g. Lecturer at Technical Institute of Babylon, Iraq. He had a well-prepared research plan, namely the fire behavior of plasticized PVC and opening new perspectives in this field. Mr. *Ali Ibrahim Moslem* (Al-Mosawi) already had significant experience in the field of polymer flame retardancy and published several papers. However, his scientific interest is much broader; he also familiar with rubber technology, composite materials and polymer processing .

Mr. *Ali Ibrahim Moslem* successfully completed his doctoral studies, planning his experiments well — sometimes in too much detail. As an experienced speaker, he performed excellently in his seminar lectures .

Wanhua BorsodChem Zrt provided opportunity to carry out important parts of its experimental work in its laboratory; using the company's infrastructure. He learned every workflow (mixing, roll-milling, sample preparation, L.O.I. tests, DSC, DMA, different heat stability tests, rheological measurements and so on) and gained a good manual practice, too. (Thanks again to BorsodChem for the help.) If it was necessary, he also joined the tasks of the laboratory. I have to highlight out that he considered it very important to observe the material under study; the “direct touch” during the research.

His first studies served as a good comparison with traditional flame retardants ( $Sb_2O_3$ ) to evaluate designed new materials. During the experiments with nanocement (Oxydtron), he noticed that the material also has other beneficial effects, namely significantly improving the thermal stability of PVC. I think this observation is a good indication of his researcher's character and ability.

Mr. *Ali Ibrahim Moslem* is able to compile an article independently and quickly. He has multiple exceeded the doctoral school's requirement, his publication list speaks for itself. (He published 30 papers during his PhD study and obtained 500 credits.)

In all, his overall achievements can be highly valued; he has largely met the requirements of the Antal Kerpely Doctoral School of Material Science of Technology. I can only wish him to achieve his goals for both the successful completion of his doctoral studies and the realization of his dreams in his future scientific and personal life.

Kazincbarcika, 3<sup>rd</sup> May 2021



Dr. Kálmán Marossy  
professor emeritus

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## **Abstract**

There is no universal super-material in the universe, but there are compounds that can have more than one characteristic that make it unconventional, and one of these is discovered in this study, which is Oxydtron (nano cement). Oxydtron has proven excellent efficiency as a flame retardant and surprisingly also showed excellent heat stabilizing effect. Tests carried out were limiting oxygen index, static heat stability, congo-red, differential scanning calorimetry, dehydrochlorination, capillary rheometry analysis, dynamic mechanical analysis, and color change measurement . These thermal tests proved the ability of Oxydtron to improve the properties of poly(vinyl chloride) at high temperatures reducing the risks associated with the combustion of plasticized poly(vinyl chloride) by increasing its thermal stability, flame retardation, and rate of degradation was effectively decreased. These tests has been shown that Oxydtron is not only a material used to improve the properties of concrete; but also a material that has shown a significant indication in the stabilization process of plasticized poly(vinyl chloride), this can lead to open a new horizon in the poly(vinyl chloride) industry .

As well, the structural changes in the poly(vinyl chloride) layer located directly under the flame zone (heat affected zone-HAZ), which is exposed to high temperatures without burning, have been checked by scanning electron microscopy (SEM) and FLIR analysis. Images obtained from SEM and FLIR analysis for the heat affected zone of limiting oxygen index samples showed a significant decrease in the chlorine content in the poly(vinyl chloride) structure accompanied by considerable stability of the carbon content when compared to the untested samples images. But after adding Oxydtron, the chlorine percentage was maintained at acceptable levels. Also, the effect of the processing method on poly(vinyl chloride)'s properties has been studied. The results obtained from the L.O.I test showed that the extrusion method was better than the rolling method for L.O.I. This behavior because the heat will be distributed uniformly in the screw-extrusion process, which reduces thermal stresses in the final product.

## **1 Introduction**

It is well recognized that heavy metals are found in many of the additives used to improve the performance of poly(vinyl chloride), such as stabilizers and flame retardants. Despite their environmental and health threats, they are now widely used [1-5]. The accumulation of these heavy metals that comes from stabilizers and flame retardants in soil, water (whether in rivers, lakes, groundwater), or even in the air leads to environmental pollution, which will lead to flame retardants transfer to organisms in that polluted environment, including humans. For example, in European countries, concentrations of flame retardants were found in human milk and the bodies of birth cohorts (but their concentrations were lower than in the United States) and household dust. Concentrations of flame retardants were also found in the bodies of birds and their eggs [6-14].

Therefore, accountable to these environmental challenges and responsibilities, most of these flame retardants must be reconsidered in terms of use and finding an environmentally friendly and sustainable alternative. Especially since countries have already started issuing laws prohibiting the use of certain types of flame retardants due to their severe damage to the environment after research has proven this [15-17]. Many of flame retardants currently

in use are included in European Union regulation (EC) No. 1272/2008 and its amendments for materials classification, which have been classified as dangerous materials. So it has become imperative to search for safe alternatives to these materials [18]. Therefore, there must be a precise harmony between environmentally friendly flame retardants and preserving the materials' properties. This matter requires more time and research for a complete shift from traditional flame retardants to those environmentally friendly [1,18-21]. Certain recent flame retardants are now available to comply with the successful flammability tests regulations. Also, the interference of retardants with flame reaction chains will restrict the oxidation of the hydrocarbon. This interference will prevent the process of converting carbon monoxide to carbon dioxide, which causes highly volatile, very smoky fire effluents and rich in incomplete combustion products [22]. From other hand, a significant effort has been made in recent years to develop new stabilization systems for the processing of poly(vinyl chloride), to get as far away as possible from using heavy metal-based stabilizers.

Due to the toxicity of the lead and cadmium stabilizers, they are now in limited use, but despite there are various alternatives now to occupy a place of these stabilizers, such as calcium/zinc, organotin, and barium/zinc systems, but still has its disadvantages for the plasticised vinyl formulator. Therefore, a complete switch to environmentally friendly stabilizers needs more research in this field. With the tendency to replace traditional stabilizers and flame retardants with environmentally friendly ones, the environmental conditions surrounding the product containing this type of stabilizers and retardants must be taken into account and the applications for which it is used. One study revealed that environmentally friendly retardants could be harmful when breaking down by heat and ultraviolet rays [22-24]. Therefore, it is necessary to use these retardants carefully. Obtaining the ideal flame retardant requires great research efforts that may not take as long as research in the past due to scientific research development. Simultaneously, the chemical stability of environmentally friendly stabilizers and flame retardants in different conditions is of critical importance to increase safety level when using these retardants.

## **2 Knowledge Gap**

This study introduces a new material, which does not contain heavy metals and at the same time an excellent stabilizer and flame retardant agent for poly(vinyl chloride), and has never been used in this field, this material is Oxydtron which is a nano-cement. Oxydtron was developed initially for use as additives with Portland cement to improve the properties of cement. The unexpected behavior of Oxydtron as a stabilizer qualifies it to be a substitute or at least a competitor to existing stabilizers. Many heavy metal-free materials are used now as stabilizers and flame retardants for poly(vinyl chloride) and other polymers, but never has been used as a material produced to be a building material before. Therefore, our attention has been focused on testing this interesting material to gain insight into all its thermal properties, especially since it does not have any database. Even the company that manufactures it does not have such data. After more than three years of work, testing, and analysing the results, this material has proven its efficiency and readiness to be a successful alternative for the traditional ones.

### 3 The Objectives

The objectives of our study can be summarized in the following points:

1. Preparing efficient alternative heavy metal free flame retardant comparable to the conventional stabilizers and flame retardants. At the same time, being environmentally friendly and with properties equivalent to traditional materials and could be better than it in many aspects in terms of engineering properties and not only at the environmental level.
2. Providing a database on the properties of this material because it is not available, where I have published many of the properties as articles and compared them with the properties of traditional ones.
3. Making poly(vinyl chloride) significantly safer by using a unique heavy metal-free additive. Where the traditional materials currently used with poly(vinyl chloride), increasing health and environmental risks.
4. Drawing the attention of researchers to such materials, and not only looking for chemical compounds as alternatives.

### 4 Experimental Procedure

#### 4.1 Materials

The percentages of following primary materials used in this study illustrated in Table 1. The description of these materials as follows:

- a. PVC suspension type S-5070 (under trademark Ongrovil®) produced and supplied by BorsodChemZrt., Hungary.
- b. DOP (or DEHP), Bis(2-ethylhexyl) ortho-phthalate plasticizer supplied by DEZA, a. s. CO., Valašské Meziříčí, Czech Republic.
- c. Calcium-Zinc-based stabilizer (under trademark Newstab-50), which supplied by Betaquímica CO., Barcelona, Spain.
- d. Wax-E (under trademark Licowax®E) supplied by Clariant International Ltd, Muttenz Switzerland.
- e. Oxydtron (type A) supplied by Bioekotech Hungary Kft. Oxydtron is a nanocement admixture applied to concrete to enhance workability and durability properties such as heat resistance, acid/alkali resistance, water leakage resistance, and freezing resistance. The composition of Oxydtron includes many compounds in the form of oxides and carbides such as  $Al_2O_3$ ,  $TiO_2$ ,  $Fe_2O_3$ ,  $CaCO_3$ ...etc, with copolymers such as styrene-butadiene; Vinyl acetate [1,25]. I couldn't find anyone who used this nanocement as a polymer additive, especially to improve flame retardancy and thermal stability.

Table 1. Materials used and their ratios

Component type	Quantity	Unit
PVC suspension type S-5070	100	phr
DOP (or DEHP), Bis(2-ethylhexyl) plasticizer	70	phr
Newstab-50, Ca-Zn based stabilizer	1.5	phr
Wax E lubricant	0.3	phr
Oxydtron	1, 3 and 5	wt.%

## 4.2 Selection of Processing Method

Before quantitative sample manufacturing, I initially manufactured several samples in various methods to know the best way to present a perfect product with optimal properties. I used rolling and extrusion for processing materials to compare the final product properties for both methods.

## 4.3 Mixing Procedure

There are two types of mixing processes used in this study: primary and secondary mixing as shown in Figure 1.

**4.3.1 Primary mixing process:** The entire primary mixing process takes about 40 minutes and is accomplished using high-speed fluid mixer type Mischtechnik MTI 10. All the raw materials illustrated in Table 1 (except Oxydtron) had been mixed together with this process to form a poly(vinyl chloride) basic formulation mixture.. The primary mixing process is consists of three stages:

- 1. Initial Mixing:** The mixing process starts at a speed of 600 rpm, wherein the beginning, the PVC powder (suspension type PVC homopolymer), Ca-Zn based stabilizer, and wax lubricant are mixed together for two minutes, then the DOP plasticizer is added to it and mixed all components for three minutes.
- 2. Raising of speed and temperature:** in this stage, the mixing speed increased to 2700 rpm. This speed increment causes the temperature of the mixture to rise steadily from room temperature and reaching to 150 °C, due to the shearing of particles between the components. The mixture stays at 2700 rpm for about 15 minutes while the temperature rises to 150 °C. The stability of speed allows the plasticizer to penetrate PVC particles further to obtain a homogenized structure with optimum production characteristics.
- 3. Cooling of mixture:** In order to cool the mixture, the mixing speed is reduced to 600 rpm and stays at this steady speed for 20 minutes. During a constant speed period, the temperature of the mixture will drop below 45 °C. At the end of this stage, the temperature of the mixture reaches 30 °C.

**4.3.2 Secondary mixing process:** This process involves applying Oxydtron to the PVC basic formulation mixture produced by the primary mixing process with various weight fractures (1, 3, and 5 wt.%). This new mixture is mixed by a small electrical mixer for one minute to uniformly dispersed and homogenized Oxydtron into the mixture.

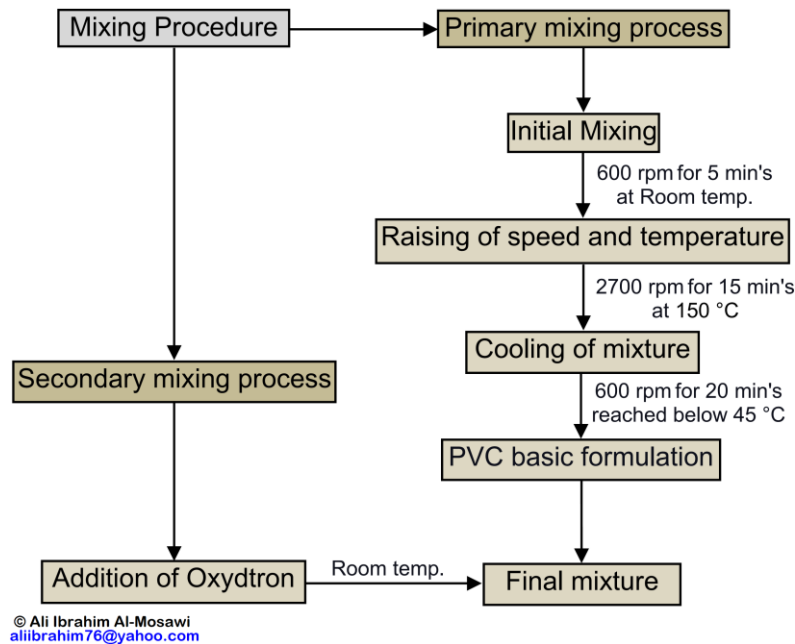


Figure 1. Scheme of Mixing Procedure

#### 4.4 Samples Preparation and Tests

In all tests, four blends of plasticized poly(vinyl chloride) had been made as shown in Table 2. All samples have been prepared according to ISO standards, and all preparation steps have been completed at BorsodChem Zrt., Hungary.

Table 2. Components of test samples

Sample No.	Content
Sample 1	PVC basic formulation
Sample 2	PVC + 1wt.% Oxydron
Sample 3	PVC + 3wt.% Oxydron
Sample 4	PVC + 5wt.% Oxydron

The tests that have been performed are as follows:

1. **Static Heat Stability:** these samples were prepared by using laboratory roll mill type SCHWABENTHAN polymix 150 U, at 170°C temperature, time 5 min, rolling speeds 21 rpm (front roller) and 24 rpm (back roller). The samples produced as sheets with 1mm thickness. Static heat stability test (heat stability testing oven) has been completed by using a Stabilemetr PVC 03 device (heat stability testing oven method) found at BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology and following EN ISO 305:1990 standard [26].
2. **Limiting Oxygen Index (L.O.I):** L.O.I samples were fabricated as a rod by using an extrusion machine type GÖTTFERT with extruder screw diameter of Ø 20 at 170 °C temperature and 60 rpm speed at uniform conditions (pressure, temperature, and compression). L.O.I test was done according to ISO 4589-2 standard [27] by using a Stanton Redcroft FTA flammability unit at BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology.
3. **Differential Scanning Calorimetry (DSC):** A 10 milligrams weight sample from poly(vinyl chloride) containing Oxydron additives. These 10 milligrams have been



cut from L.O.I test samples. The Mettler Toledo DSC823e instrument was used to complete the DSC test to measure the gelation or fusion grade (G.G) by following the ISO 11357-2 standard [28] and using a heating profile of 30 °C to 240 °C with a heating rate 20°C/min.

4. **Color Change Test:** Samples of static heat stability test were used. Datacolor spectraflash SF 300 spectrophotometer found at BorsodChem Zrt., Hungary was used to analyze the color change of these samples. The test was done according to ISO 11664-1 standard [29].
5. **Dynamic Mechanical Analysis (DMA):** The DMA test samples were a strips fabricated by using extrusion machine type GÖTTFERT at 170 °C temperature and 60 rpm speed at uniform conditions (pressure, temperature). This test was done according to ISO 6721-11:2012 standard [30] by using dynamic mechanical thermal analyser MK III manufactured by Rheometric Scientific, Inc. and found at BorsodChem Zrt., Hungary. The temperature range is -60°C to 120°C with heating rate 2°C per min and the test finished within 2 hrs.
6. **Congo-Red Test:** the congo-red test samples were prepared by using twin-screw extrusion machine type SCHLOEMANN BT-50 as pellets with 3mm diameter and 2mm thickness at uniform conditions. Congo-red test: was done by using a Julabo MC-12 circulator oil bath at 200°C shown in Figure 16 according to ISO 182-1:1990(E) standard [31], and found also at BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology.
7. **Capillary Rheometry Analysis:** the samples were produced as pellets with the same procedure, dimensions, and conditions of congo-red test samples. This test was done according to ISO 11443:2014 standard [32] at different temperatures rang (160 °C, 170 °C, and 180 °C) and different dies lengths (15, 30, and 45mm) with (3mm) die hole diameter for all lengths. Laboratory extruder type Göttfert Extrusimeter G20 was used to complete this test with processing speed 60 rpm.
8. **Dehydrochlorination Test:** pellets of poly(vinyl chloride) containing Oxydtron additives with the exact dimensions of congo-red test and capillary rheometry analysis and produced with the same extrusion machine, under the same conditions were used in this test. Two methods were used to calculate the dehydrochlorination rates  $n$  as follows: **(1) Standard Method;** in this method, dehydrochlorination rates have been measured by Metrohm 763 Thermomat found also at BorsodChem Zrt., Hungary. This test was carried out according to ISO 182-3:1993 standard [33] at 190 °C. And **(2) Novel Evaluation Method;** this method was adopted in my thesis to plot dehydrochlorination data. I collected the data stored in the device database after performing each test. Then I analyzed it by a program to get more even kinetic information from the dehydrochlorination tests. The method of analysis is as follows: **(a)** The conductivity can be converted to HCl concentration. The conversion function calculated from the Foxboro data table is the following:

$$\log(c) = -1.05788 + 0.9882 \times \lg(k) + 0.003988 \times (\lg(k))^2$$

Where:  $c$  is HCl concentration in mg/l;  $k$  is specific conductivity in  $\mu\text{s}/\text{cm}$ . If the absorbent water quantity is known the HCl weight (mg) can also be calculated. The instrument is using 50 ml water, so the absorbed HCl is  $c/20$ .

**(b)** If the exact mass of PVC in the sample is known, the dehydrochlorination curve can be converted to the conversion of degradation. Because from pure PVC 58.4% HCl is evolved during total degradation, the conversion is:

$$k_{conv.} = m_{HCl}/0.584 \times m_{PVC}$$

9. Scanning Electron Microscopy: SEM was used to analyze the chemical composition and structure analysis of Oxydtron as shown in Figure 2. Also SEM was used to analyze the chemical composition and structure analysis of heat affected zone (HAZ). This test was carried out using a Carl Zeiss EVO MA10 SEM at the institute of physical metallurgy, metal forming and nanotechnology, University of Miskolc.

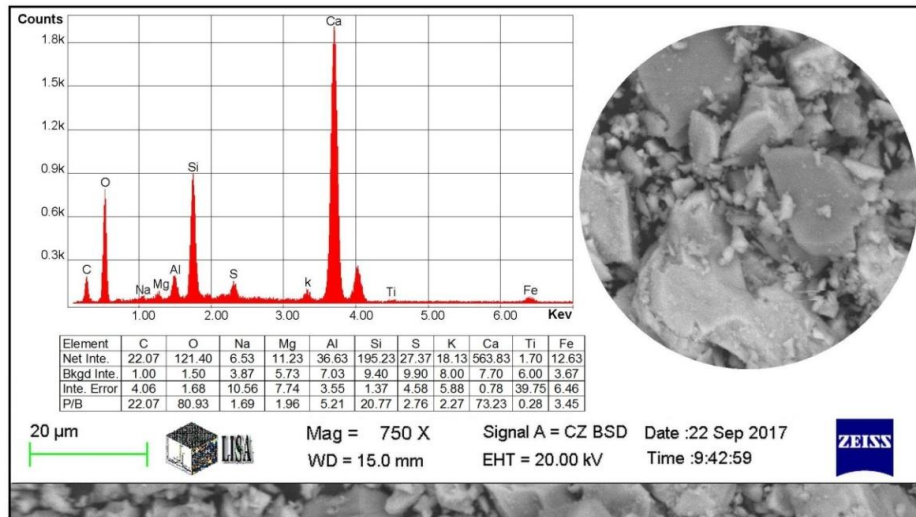


Figure 2. SEM- EDAX analysis for Oxydtron

10. Fourier Transform Infrared Analysis: FTIR analysis was completed by using A Shimadzu IRTracer-100 device found at BorsodChem Zrt. The analysis of chemical compounds of the Oxydtron shown in Figure 3.
11. Oxides Analysis: ICP-AES spectrometer, made by Varian Inc. and found at the institute of chemistry, University of Miskolc, was used to analysis chemical composition of Oxydtron. The results of this analysis are listed in Table 3.
12. Particle Size Distribution Analysis (PSD): HORIBA LA-950V2 laser particle size analyzer was used for analyze particle size distribution gradient as shown in Figure 4.
13. FLIR Thermal Gradient Image Analysis: Thermal analysis for L.O.I extruded and rolled samples by using thermal imaging camera (FLIR Systems) in order to determine the thermal gradient before and after the addition of Oxydtron and the effect of these additions on the heat affected zone (HAZ).

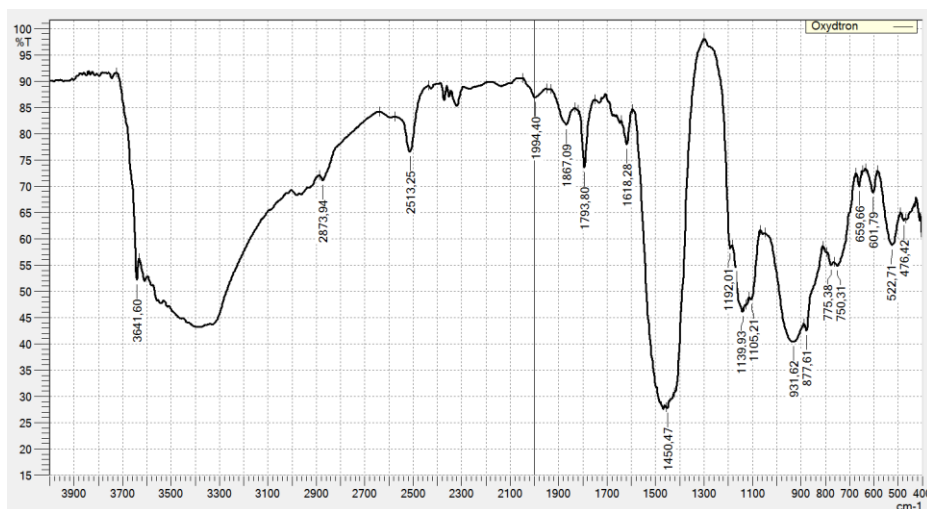


Figure 3. FTIR analysis for Oxydtron

Table 3. Components of test samples

Oxide	Ratio, wt%	Element	Ratio, wt%
Al <sub>2</sub> O <sub>3</sub>	4.47	Al	2.37
CaO	58.0	Ca	41.4
Cr <sub>2</sub> O <sub>3</sub>	0.006	Cr	0.004
Fe <sub>2</sub> O <sub>3</sub>	2.67	Fe	1.87
K <sub>2</sub> O	0.78	K	0.65
MgO	1.20	Mg	0.72
Mn <sub>2</sub> O <sub>3</sub>	0.05	Mn	0.04
Na <sub>2</sub> O	0.31	Na	0.23
SO <sub>3</sub>	2.50	S	1.00
SiO <sub>2</sub>	21.44	Si	10.0
SrO	0.093	Sr	0.079
TiO <sub>2</sub>	0.274	Ti	0.164
ZnO	0.138	Zn	0.111

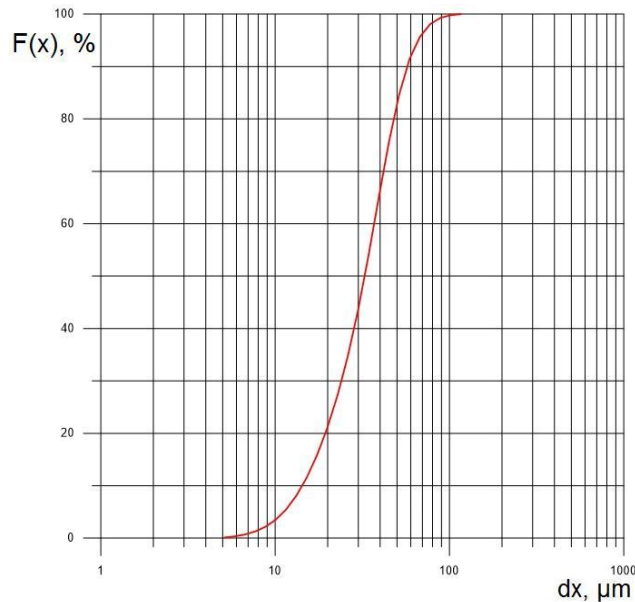


Figure 4. Particle size distribution analysis for Oxydtron

## 5 Results and Discussion

### 5.1 Flame Retardancy Test

The limiting oxygen index test results for plasticized poly(vinyl chloride) containing Oxydtron processing by extrusion and rolling are shown in Figure 5. The first pair of bars in this figure represents poly(vinyl chloride) basic formulation has, the second pair of bars represents poly(vinyl chloride) containing 1wt.% Oxydtron, third pair of bars represents poly(vinyl chloride) containing 3wt.% Oxydtron, and finally, the fourth pair of bars

represents poly(vinyl chloride) containing 5wt.% Oxydtron. The improvement in flame retardation can be seen after adding Oxydtron. Where the value of L.O.I of poly(vinyl chloride) basic formulation was increased from 22.2% (extrusion ) and 21.6% (rolling) to 23.4% (extrusion) and 22.3% (rolling) after adding 1% wt. Oxydtron. Also It also continued to rise to value 25.5% (extrusion) and 24.8% (rolling) after adding 3% Oxydtron. And this rise continued after adding 5% Oxydtron, where the percentage of increase was 27.8% (extrusion) and 26.4% (rolling).

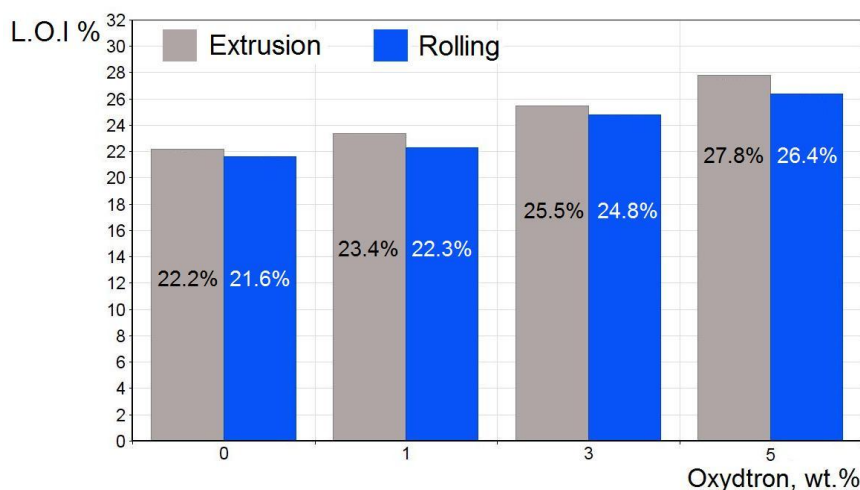


Figure 5. Limiting oxygen index (L.O.I) test results for plasticized poly(vinyl chloride) containing Oxydtron

## 5.2 Static Heat Stability Test

The additional stabilizing synergistic action with the original stabilizer can be observed clearly from the results of the thermal stability test shown in Figure 6, representing the behavior of plasticized poly(vinyl chloride) containing Oxydtron under static heat stability test at 190°C. When comparing the color gradation between the samples before and after Oxydtron additions, we will note that static heat stability of plasticized poly(vinyl chloride) containing Oxydtron better than poly(vinyl chloride) alone. And this means that the Oxydtron is a perfect stabilizer for poly(vinyl chloride), where the Oxydtron will decrease the tendency of poly(vinyl chloride) discoloration.



Figure 6. Static heat stability test at 190°C for plasticized poly(vinyl chloride) containing Oxydtron (OX)

### 5.3 Color Change Measurement

Figure 7,a shows the yellowing behavior ( $\Delta b^*$ ) of poly(vinyl chloride) with different percentages of Oxydtron. From this figure, we note that poly(vinyl chloride)'s tendency to yellowing is very high due to low thermal stability at elevated temperatures for poly(vinyl chloride) [34,35]. After adding Oxydtron to poly(vinyl chloride), the yellowing is significantly reduced; in addition, the transformation period to dark color has been extended. Figure 7,b represents the lightness changes ( $\Delta L^*$ ) of plasticized poly(vinyl chloride) as a function of Oxydtron additives. We can observe from this figure that the lightness appearance of poly(vinyl chloride) begins to deteriorate, which can be seen from the sharp decline of the curve in a short time towards a darker appearance until it becomes entirely black constantly exposed to high temperatures. But this state will be changed after adding Oxydtron, where the thermal resistance of poly(vinyl chloride) will improve, enabling it to maintain a better light appearance for a longer time at the same temperature range and period, where the lightness appearance decreases gradually and not sharply.

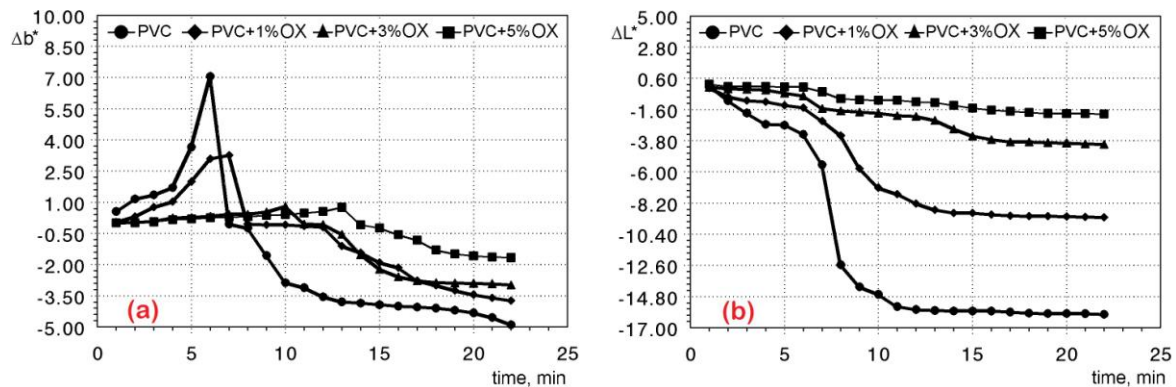


Figure 7. (a) Detecting the yellowish changes of plasticized poly(vinyl chloride) containing Oxydtron (OX), (b) Lightness changes of plasticized poly(vinyl chloride) as a function of Oxydtron (OX) additives

### 5.4 Congo-Red Test

Figure 8 represents the congo-red test for plasticized poly(vinyl chloride) containing Oxydtron. We can noticed from this figure that the time required for beginning and ending of the color change process measured by this test is short; because the thermal stability of poly(vinyl chloride) is low [36,37]. But after adding Oxydtron the stability of poly(vinyl chloride) has been improved. As a result for this behavior the time period for discoloration will extend where the time period for the beginning and ending of the color change for test paper in case of plasticized poly(vinyl chloride) containing Oxydtron will be longer than plasticized poly(vinyl chloride) of basic formulation.

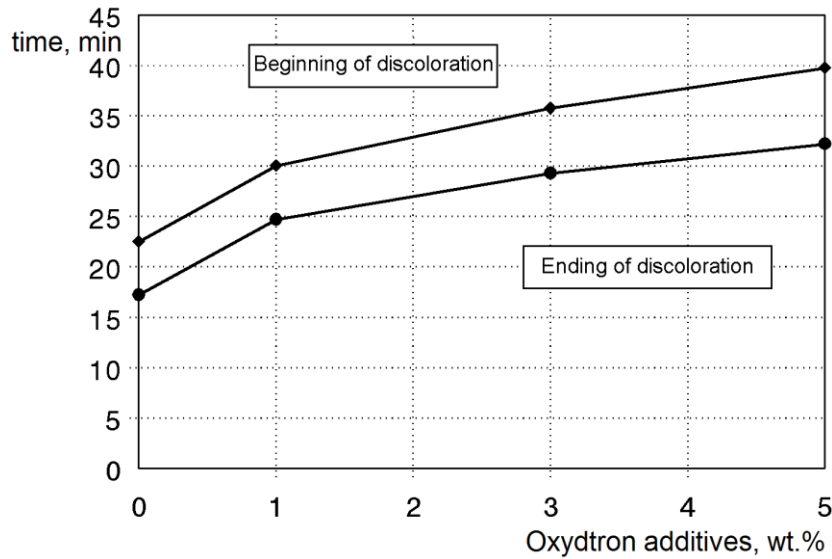


Figure 8. Beginning and ending of discoloration in congo-red test for plasticized poly(vinyl chloride) containing Oxydtron at 200°C

### 5.5 Differential Scanning Calorimetry Measurements (DSC)

Figure 9 represents the DSC measurements for extruded and rolled plasticized poly(vinyl chloride) containing Oxydtron in the same temperature range of 30°C-240°C. From Figure 9, a it can be observed that Oxydtron shifted gelation grade (fusion degree) towards higher temperatures than poly(vinyl chloride) of basic formulation and settled at 201°C. At the same time, the gelation grade continued to drop with the increase of Oxydtron content. The same behavior applies for rolled samples but being slightly wobbly and not ideal as extruded samples, where the history of poly(vinyl chloride) affects the final product properties as shown in Figure 9, b.

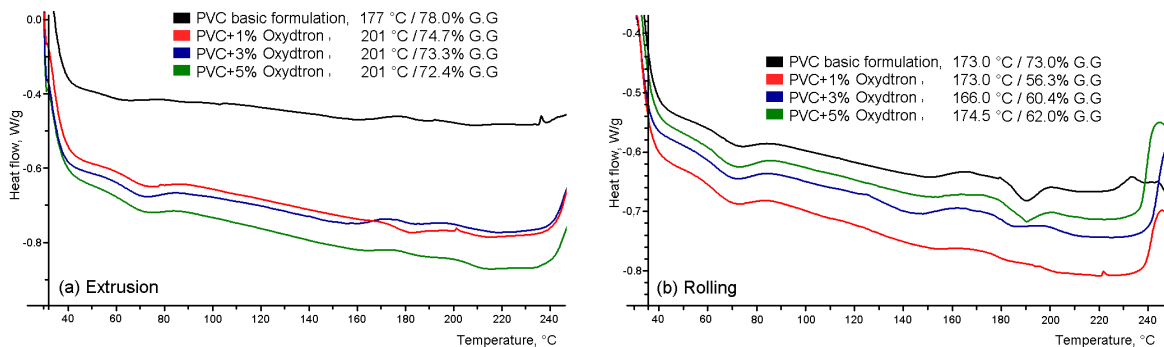
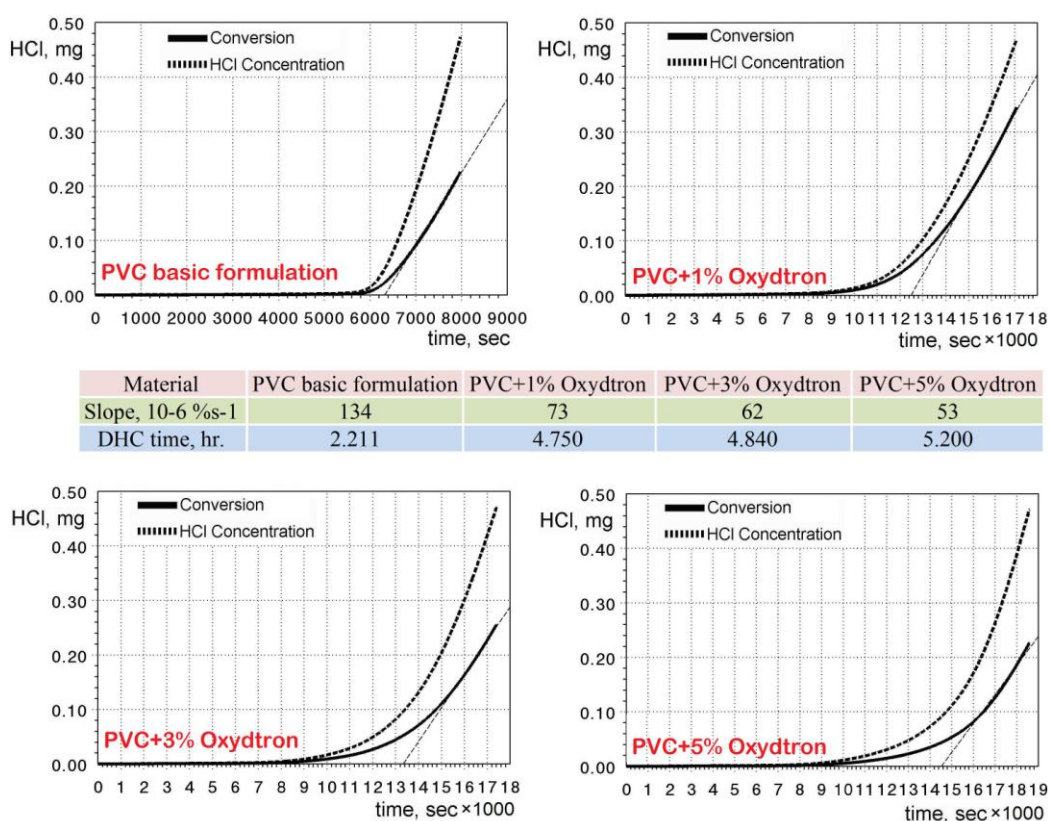


Figure 9. Gelation behavior for (a) extruded, (b) rolled plasticized poly(vinyl chloride) containing Oxydtron measured by DSC at 30°C-240°C temperature range

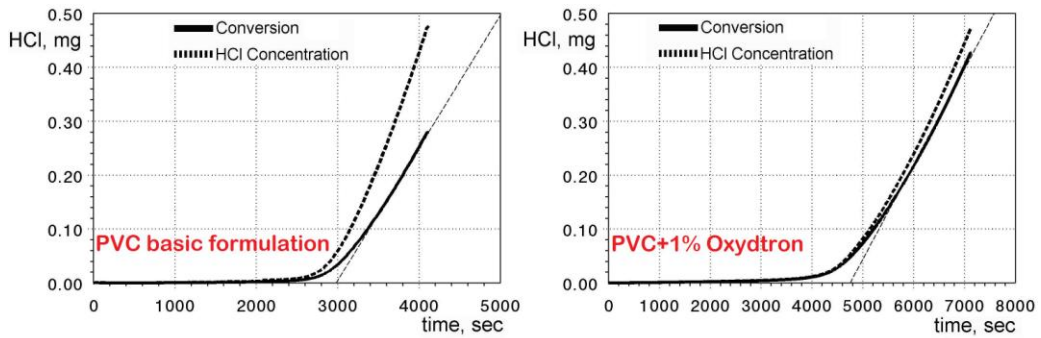
## 5.6 Dehydrochlorination Tests

Figures 10, 11, and 12 represents dehydrochlorination tests for plasticized poly(vinyl chloride) containing Oxydtron at 170°C, 180°C, and 190°C, respectively. The structure of poly(vinyl chloride) becomes less stable at high temperatures, leading to the release of chlorine-containing compounds strongly. As a result, the resistance of poly(vinyl chloride) starts to decrease. From these three figures, we see that the chlorine-containing compounds loss is very rapid from poly(vinyl chloride) structure, and the slope of the curve is very sharp (high inclination). This behavior of poly(vinyl chloride) will be changed after adding Oxydtron additives, where the structure of poly(vinyl chloride) shows more stability at high temperatures and the tendency to release containing compounds has been decreased and the period of degradation extended.

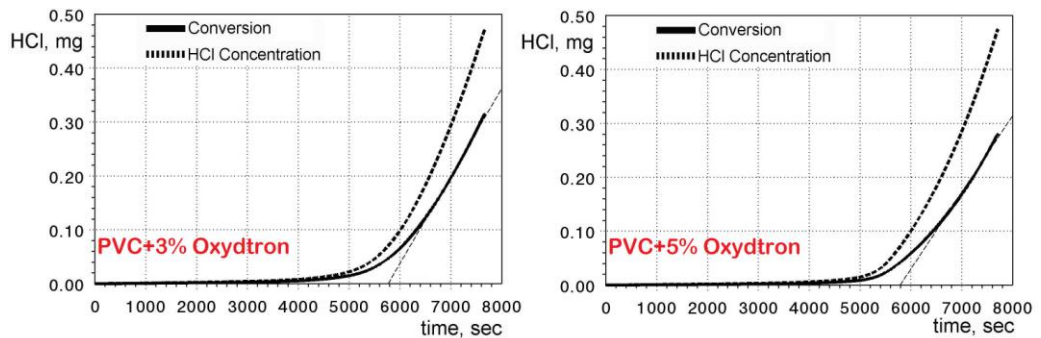
From my perspective, and depending on the results we obtained, the Oxydtron will hinder the formation of allylic chloride groups, leading to the prevention of polyenes formation. This will delay the poly(vinyl chloride) from entering the propagation stage. The optimum improvements of degradation rate obtained by 5 wt.% of Oxydtron addition were 135.2% at 170°C, 88.4% at 180°C, and 146.4% at 190°C longer than poly(vinyl chloride) basic formulation.



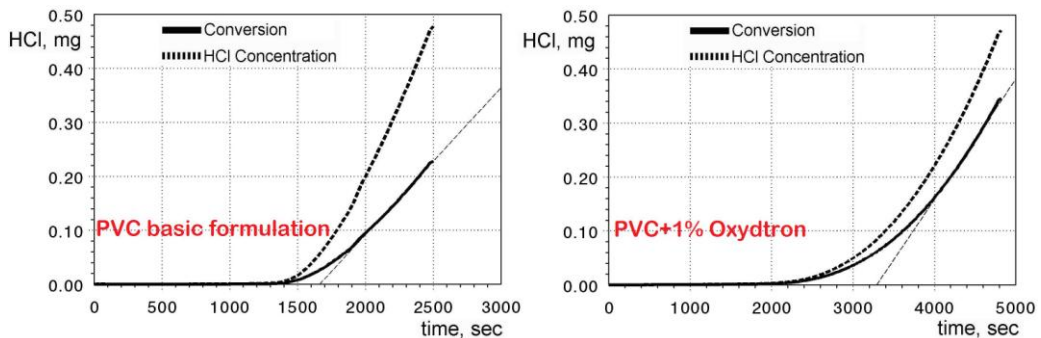
Figures 10. Dehydrochlorination test for plasticized poly(vinyl chloride) containing Oxydtron at 170°C



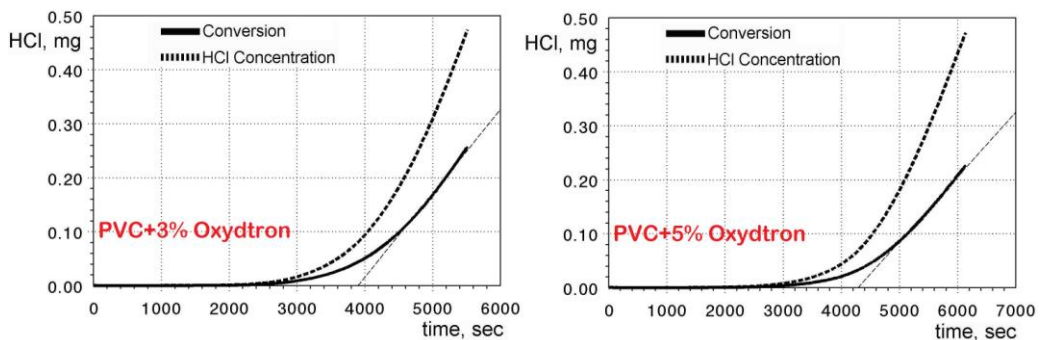
Material	PVC basic formulation	PVC+1% Oxydtron	PVC+3% Oxydtron	PVC+5% Oxydtron
Slope, 10 <sup>-6</sup> %s <sup>-1</sup>	246	176	163	142
DHC time, hr.	1.144	1.983	2.133	2.144



Figures 11. Dehydrochlorination test for plasticized poly(vinyl chloride) containing Oxydtron at 180°C



Material	PVC basic formulation	PVC+1% Oxydtron	PVC+3% Oxydtron	PVC+5% Oxydtron
Slope, 10 <sup>-6</sup> %s <sup>-1</sup>	272	223	155	120
DHC time, hr.	0.694	1.340	1.533	1.710



Figures 12. Dehydrochlorination test for plasticized poly(vinyl chloride) containing Oxydtron at 190°C



## 5.7 Dynamic Mechanical Analysis (DMA)

From Figure 13, which represent the dynamic mechanical analysis (DMA) for plasticized poly(vinyl chloride) containing Oxydtron, we can note that the Oxydtron additives increase the glass transition temperature ( $T_g$ ), where the glass transition temperature shifts to higher temperatures rising from (-3.26 °C) in case of plasticized poly(vinyl chloride) basic formulation to (0.30 °C) when 1% of Oxydtron has been added and continues to rise to (3.50 °C) and (4.66 °C) when added 3% and 5% of Oxydtron respectively. Clearly, there is an interaction between poly(vinyl chloride) and Oxydtron particles, which causes the reduction of the kinetic energy of plasticized poly(vinyl chloride), and reducing the segmental movement as mentioned, which probably prevents the molecules from assembling in crystalline systems, so the relaxation time of this movement increases. So the polymer will consist of long physically crosslinked liquid-like molecules [45].

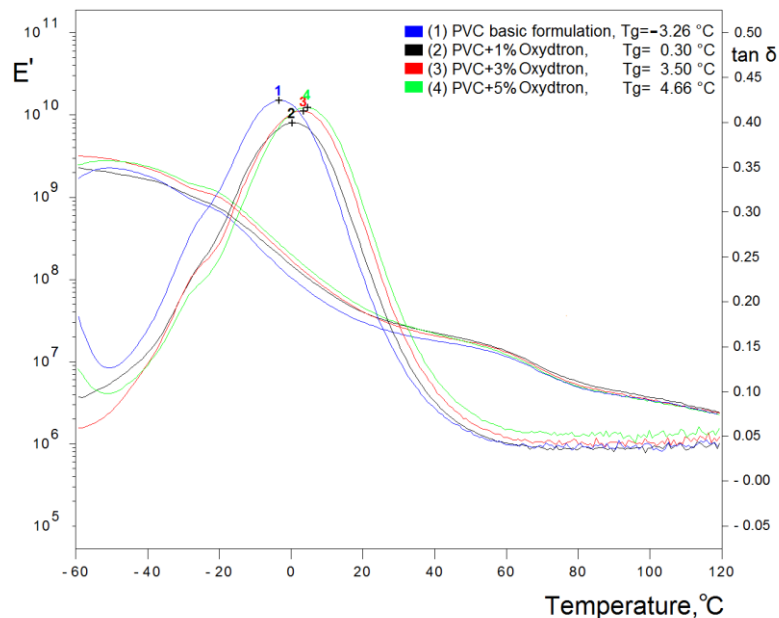


Figure 13. Dynamic mechanical analysis for plasticized poly(vinyl chloride) containing Oxydtron

## 5.8 Capillary Rheometry Analysis (Extrusionometry)

It is known that the inlet pressure drop ( $\Delta p$ ) can be measured practically by using capillaries that are of different lengths while maintaining a constant diameter [38,39]. Figure 14 represents the length correction of plasticized poly(vinyl chloride) containing Oxydtron at 160°C, 170°C, and 180°C respectively. And Table 4 represents Bagley correction and slope values of plasticized poly(vinyl chloride) containing Oxydtron at the same three temperatures. As the plasticized poly(vinyl chloride) melt travels and is extruded from the greater diameter of the barrel to the smaller diameter of the capillary the excess pressure begins to drop due to extensional viscosity [40,41]. From this figure we can see that the length correction will decrease with increasing the temperature because the

poly(vinyl chloride) melt becomes less elastic at higher temperatures. Also we can observe from this figure that the extrapolation of the linear Bagley correction plots of poly(vinyl chloride) basic formulation indicated a good fitting. Also, from the same figure we notice that the Bagley correction value has increased after adding Oxydtron. It is a fact that the shear stress is directly proportional to the pressure drop [42-44], therefore, the shear stress values in the case of plasticized poly(vinyl chloride) containing Oxydtron will be higher than poly(vinyl chloride) basic formulation.

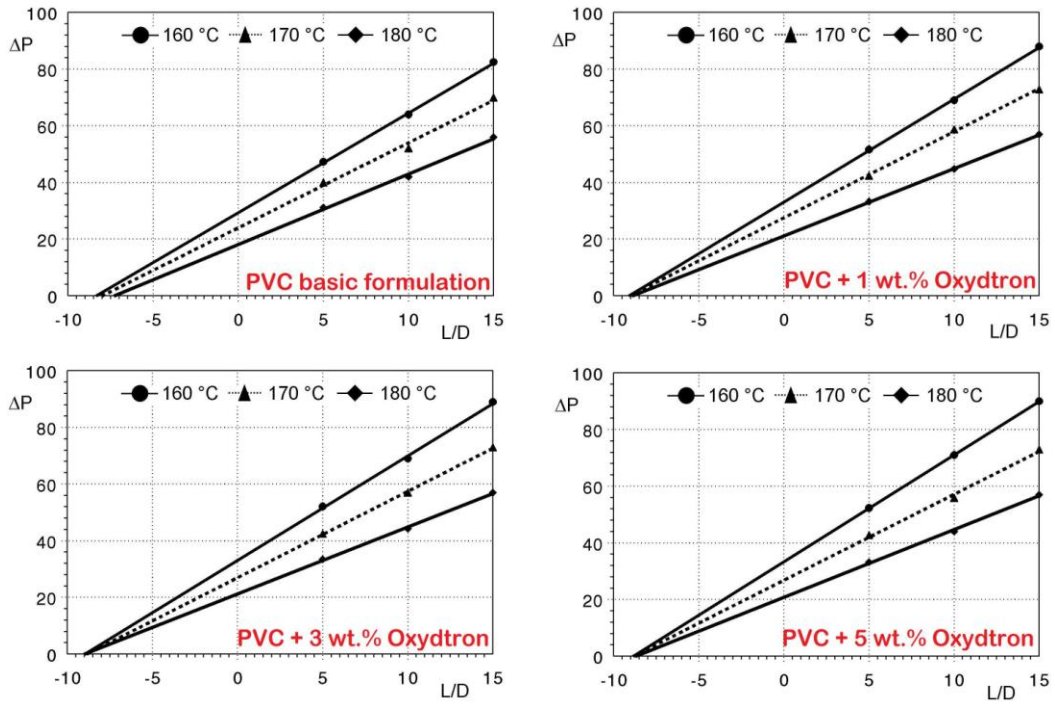


Figure 14. Length or Bagley correction for plasticized poly(vinyl chloride) containing Oxydtron at 160°C, 170°C, and 180°C respectively

Table 4. Bagley correction and slope values of plasticized poly(vinyl chloride) containing Oxydtron at 160°C, 170°C, and 180°C respectively

	Temperature, °C		
	160	170	180
Poly(vinyl chloride) basic formulation			
Bagley Correction	8.35	8.00	7.28
Slope	3.52	3.00	2.49
Poly(vinyl chloride) containing 1 wt.% Oxydtron			
Bagley Correction	9.10	9.07	8.90
Slope	3.64	3.04	2.38
Poly(vinyl chloride) containing 3 wt.% Oxydtron			
Bagley Correction	9.44	9.31	9.17
Slope	3.60	2.93	2.34
Poly(vinyl chloride) containing 5 wt.% Oxydtron			
Bagley Correction	9.57	9.45	9.26
Slope	3.62	2.92	2.31

## 5.9 Thermal Gradient Analysis for Heat Affected Zone (HAZ)

The structure of poly(vinyl chloride) will begin to release chlorine-containing compounds in the form of HCl from its internal structure at elevated temperatures, i.e., it begins to degrade in these temperatures. The structure of poly(vinyl chloride) will lose chlorine-containing compounds not just from burnt layers which directly exposed to fire, but this loss of chlorine-containing compounds extends to the under layers far from the combustion zone, which I called heat-affected zone (HAZ), as shown in Figure 15. This behavior is due to the dehydrochlorination of poly(vinyl chloride).

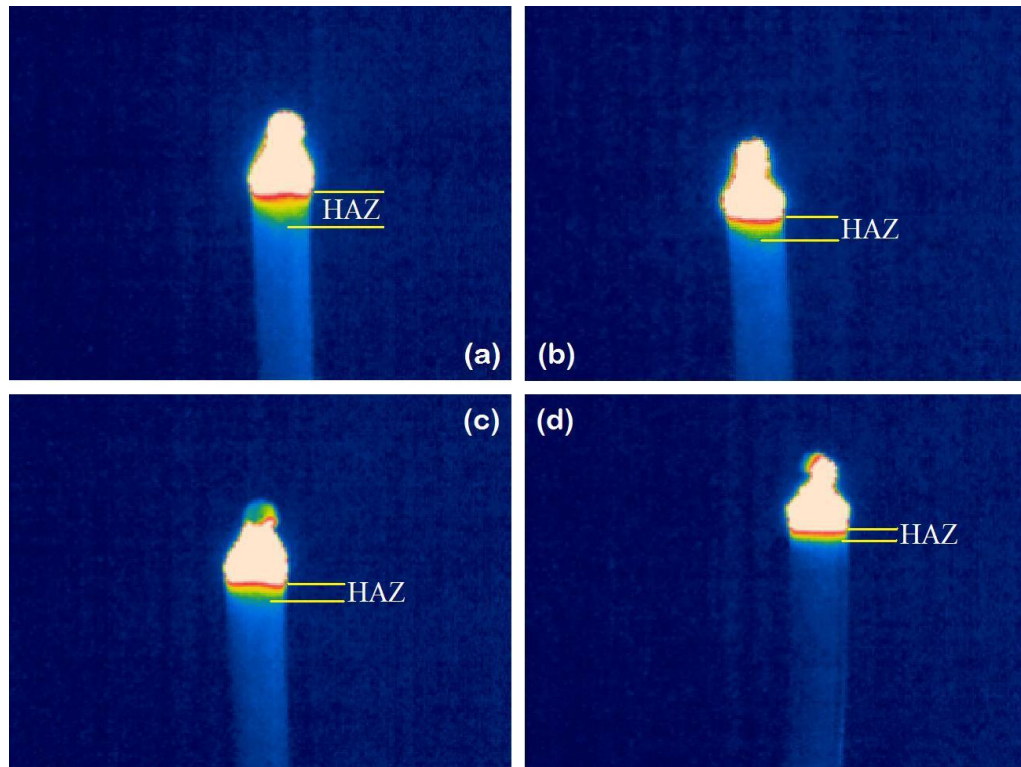


Figure 15. FLIR analysis for HAZ at (a) PVC basic formulation, (b) PVC+1% Oxydtron, (c) PVC+3% Oxydtron, and (d) PVC+5% Oxydtron

Besides, I found that when re-testing again after cutting the burned area, the under layers have been flamed faster and the heat-affected zone (HAZ) bigger as shown in Figure 16. This behavior was dissimilar to the original sample that tested for the first time, which means the heat-affected layer has low flame resistance due to less chlorine [46].

Likewise, the size of the heat-affected zone depends on the type of processing method, as it is more expansive in rolling samples than in extrusion samples, as shown in Figure 17. Since the rolling sample is exposed to processing temperatures more prolonged than the one-stage extrusion, the rolling sample is more heat stressed, accelerating its yielding and softening when exposed to fires, unlike the extrusion sample, which resists fires better. Therefore, it is necessary to pay attention to the correct selection of the processing method in applications that require a high flame resistance.

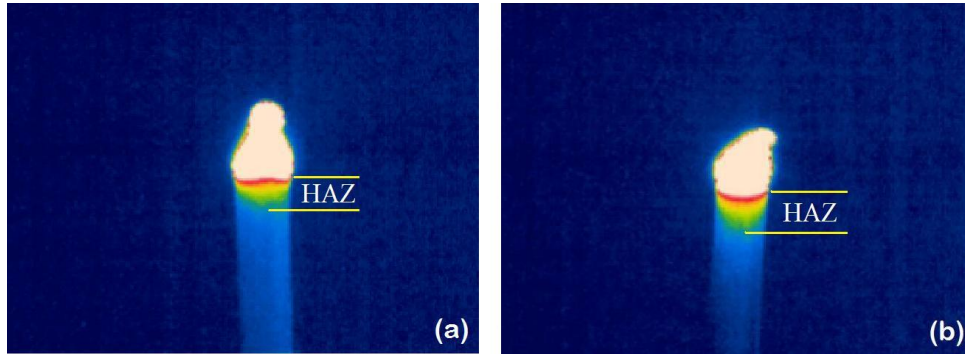


Figure 16. FLIR for extruded plasticized poly(vinyl chloride) basic formulation HAZ when (a) testing for the first time, (b) re-testing after cutting the burnt layer

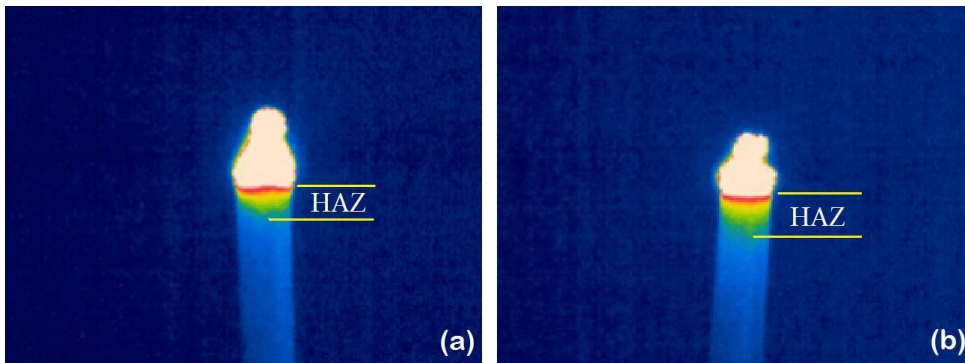


Figure 17. FLIR for HAZ of (a) extruded plasticized poly(vinyl chloride) basic formulation, (b) rolled plasticized poly(vinyl chloride) basic formulation

## 6 Conclusions

1. Oxydtron have the ability to create stabilizing-flame retarding synergistic effects which are proved by the results of thermal tests where the unique Oxydtron composition plays a major role in this characteristic and unexpected behavior for this material.
2. All the results obtained were not found in literature before.
3. All properties of plasticized poly(vinyl chloride) studied in this study were improved after the addition of Oxydtron; and the improvement ratio increases steadily with increasing the percentage of Oxydtron additives.
4. The value of L.O.I improvement after the 5% Oxydtron addition is 25.23% and 17.6% more that of poly(vinyl chloride) of basic formulation for extrusion and rolling processes.
5. The discoloration resistance of plasticized poly(vinyl chloride) increased by increasing the percentage of Oxydtron additives; where the yellowish changes have been decreased accompanied with expansion of transformation time from transparent appearance to fully dark color; also replaced the sharp reduction path of lightness changes with a gradual decreasing path after Oxydtron addition, making plasticized

poly(vinyl chloride) able to maintain a lighter appearance for longer time under the same test conditions.

6. Extended the time period between beginning and ending of the color change in congo-red test in case on plasticized poly(vinyl chloride) containing Oxydtron to 86.4% longer than poly(vinyl chloride) of basic formulation, which means the chlorine release rate has also been decreased.
7. The gelation grade decreased after adding Oxydtron where it was 8% less that of poly(vinyl chloride) of basic formulation due to the presence of calcium compounds in the Oxydtron composition, which works in two ways; first it improves the thermal stability of plasticized poly(vinyl chloride) and; second decreased the gelation grade. But the gelation temperature was shifted to a higher value than poly(vinyl chloride) of basic formulation because of the stabilizing action of Oxydtron additives.
8. FTIR analysis detected many active groups within the Oxydtron's crystalline structure which gives it more affinity with plasticized poly(vinyl chloride).
9. The degradation rate of plasticized poly(vinyl chloride) was improved by Oxydtron additives and the optimum time required for full poly(vinyl chloride) degradation were 135.2%, 88.4%, and 146.4% longer than poly(vinyl chloride) basic formulation obtained by 5% Oxydtron addition at 170°C, 180°C, and 190°C.
10. The degradation characteristic of Oxydtron containing compounds evaluated by the novel method shows better agreement with other, e.g., discoloration methods. It is worth introducing the conversion based method for all PVC compounds.
11. Although the method based on real dehydrochlorination conversion gives shorter stability times than the standard, the excellence of Oxydtron is proven.
12. Because PVC-based compounds might contain different amounts of PVC, the standard method cannot be used for comparing different compounds. 60  $\mu\text{S}/\text{cm}$  specific conductivity represents the same amount of HCl but different degradation grade. Using only this method leads to misleading results.
13. Glass transition temperature was shifted towards higher temperatures after Oxydtron addition, and this indicates that Oxydtron directly affects kinetic energy and segmental movement of plasticized poly(vinyl chloride) causing to decrease them.
14. The Oxydtron minimized the Bagley correction drop, which means the flowability of poly(vinyl chloride) was improved. Bagley correction values will decrease with increasing temperature.
15. Oxydtron additives significantly improved and increased the poly(vinyl chloride) melt elasticity.
16. The thermal degradation of poly(vinyl chloride) is not limited to the exposed flame layer but continues beyond the combustion layer, where the experiments have shown a decrease in chlorine content in the heat-affected non-burning zone. In the absence of Oxydtron, heat affected zone will ignite easily due to structural changes. But in the presence of Oxydtron, the value of the thermal gradient has been reduced, and HAZ was minimized.

17. The obvious difference in the composition of extruded and rolled poly(vinyl chloride) obtained by scanning electron microscopy proves that microstructure depends on the process and therefore this thing is what affects the properties being measured which is like a sequence and can be called process dependent structure-properties.
18. The optimum properties results were obtained with extruded polyvinyl chloride and the thermal tests L.O.I and DSC have proven that
19. The structure of poly(vinyl chloride) was more homogenous in terms of processing conditions, because it was produced in a single step (by extrusion only) so the residual stresses were less than rolled and thus less stressed.

## 7 New Scientific Results

### Claim 1

Using of Oxydtron for the first time as a poly(vinyl chloride) stabilizer and flame retardant agent with highly efficient for thermal stabilizing. Oxydtron was used first time as flame retardant agent in plasticized poly(vinyl chloride) compounds. It was discovered that Oxydtron is also a highly efficient thermal stabilizer. This stabilizing-flame retarding synergistic effect created by Oxydtron additives was unexpected behavior of a material used as a cement additive just for construction purposes. The performance of plasticized poly(vinyl chloride) at high temperatures also improved significantly using Oxydtron additive.

### Claim 2

Oxydtron increases the limiting oxygen index (L.O.I.) of plasticized poly(vinyl chloride) and can be used as flame retardant additive. By using 5 wt.% Oxydtron 25.2 % improvement was reached in case of extruded and 17.6 % in case of roll-milled PVC. This effect is comparable with the effect of the toxic antimony-trioxide, therefore it is a promising replacement of it. The Improvement percentages of L.O.I are listed in the Table 1.

Table 1. Improvement percentage of L.O.I results for plasticized poly(vinyl chloride) containing Oxydtron

	PVC	PVC+1% Oxydtron	PVC+3% Oxydtron	PVC+5% Oxydtron
Processing method	Extrusion			
L.O.I	22.2%	23.4%	25.5%	27.8%
Improvement percentage	-	5.5%	14.9%	25.23%
Processing method	Rolling			
L.O.I	21.6%	22.3%	24.8%	26.4%
Improvement percentage	-	3.24%	14.8%	17.6%

### Claim 3

The Performance of plasticized poly(vinyl chloride) during dehydrochlorination process improves significantly by 135.2%, 88.4%, and 146.4% more than poly(vinyl chloride) basic formulation after adding 5% Oxydtron addition, at 170°C, 180°C, and 190°C respectively. The Improvement percentages of DHC time are listed in the Table 2.

Table 2. Improvement percentage of DHC time for plasticised poly(vinyl chloride) containing Oxydtron

	PVC	PVC+1% Oxydtron	PVC+3% Oxydtron	PVC+5% Oxydtron
At 170°C				
DHC time, hour	2.211	4.750	4.840	5.200
Improvement percentage	-	114.8%	118.9%	135.2%
At 180°C				
DHC time, hour	1.144	1.983	2.133	2.144
Improvement percentage	-	73.3%	86.5%	88.4%
At 190°C				
DHC time, hour	0.694	1.340	1.533	1.710
Improvement percentage	-	93.1%	120.9%	146.4%

### Claim 4

I have developed a novel method for determination of level i.e. the conversion of degradation from the conductivity curve. In contrast to the standard method it describes better the process in particular in case of PVC compounds. (The computer program used in this method is shown in appendix 1). It shows a good agreement with the discoloration and initial color changes. The difference between the standard method and the Novel method in calculating the dehydrochlorination rate is shown in Figure 1.

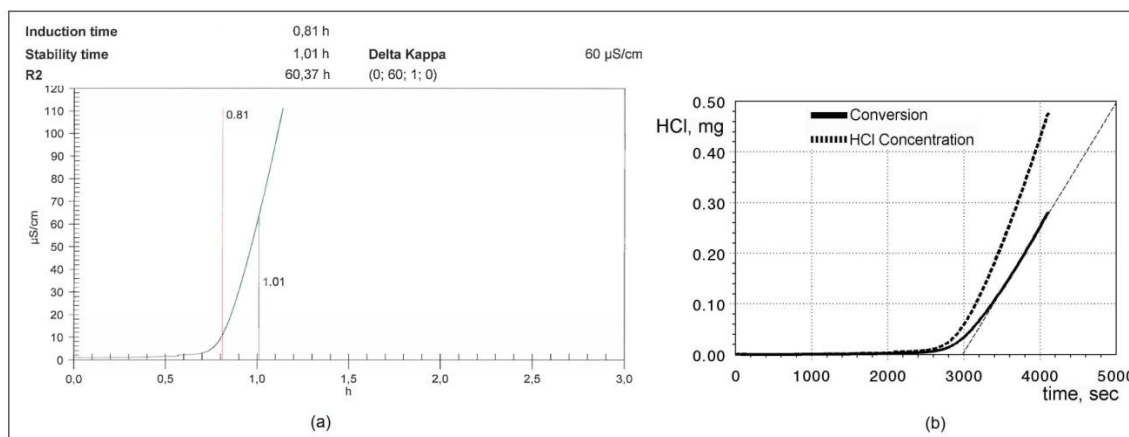


Figure 1. The standard method graph (a) is compared to the novel method graph (b)

**Claim 5**

Due to improved thermal stability of the poly(vinyl chloride), both the rate of degradation and the discoloration -expressed either in yellowing ( $\Delta b^*$ ) or in darkening ( $\Delta L^*$ )-decreased, as shown in Figure 2.

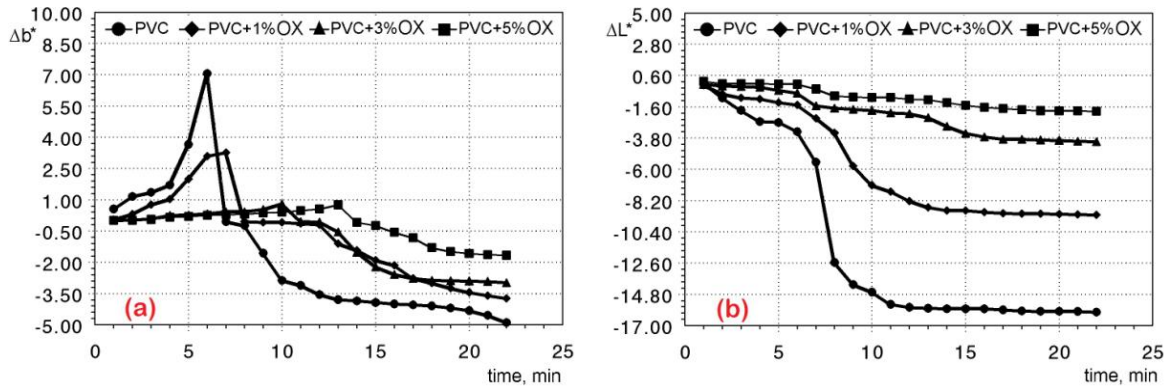


Figure 2. Reducing yellowing (a) and prolong the preservation of lightness (b) of plasticized poly(vinyl chloride) containing Oxydron (OX)

**Claim 6**

Where discoloration period has been extended after using Oxydron, and the most significant improvement was 86.8% more than poly(vinyl chloride) basic formulation when using 5 wt% Oxydron. The Improvement percentages of discoloration period are listed in the Table 3.

Table 3. Extended discoloration period for plasticized poly(vinyl chloride) containing Oxydron

Material	PVC	PVC+1% Oxydron	PVC+3% Oxydron	PVC+5% Oxydron
Beginning of discoloration, min	17.25	24.73	29.33	32.23
Improvement percentage	-	43.33%	70.03%	86.8%

**Claim 7**

It was found that the Bagley correction slightly but consequently depends on the elasticity of melt. Oxydron increases the melt's elasticity even at low concentration, e.g. 1wt.%, as shown in Figure 3.

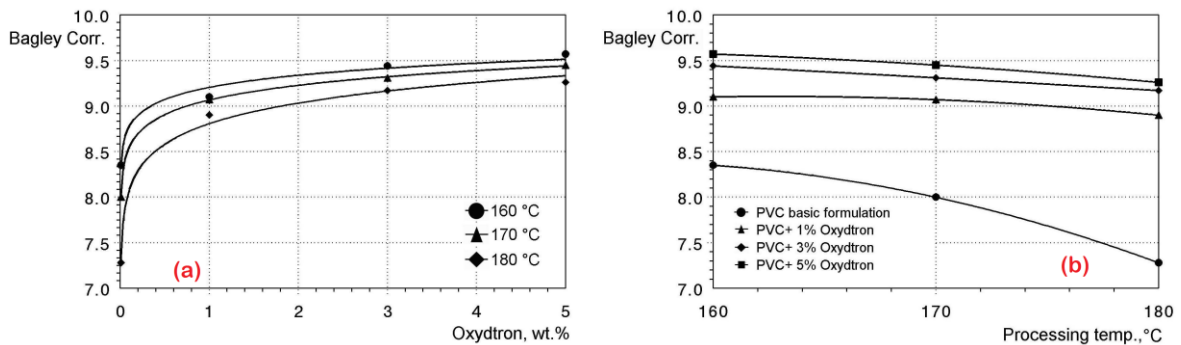


Figure 3. Bagley correction (a) as a function of Oxydron content, and (b) and as a function of processing temperature



**Claim 8**

For the first time a practical observation was supported by scientific evidence, namely, the structural changes of the layer located directly under the combustion area. I called this area heat affected zone (HAZ). This layer has not been previously studied; instead, researchers have only indicated its existence without actual study. The analysis of this zone proved to be important in assessing thermal stability, as shown in Figures 4, 5, 6 and 7.

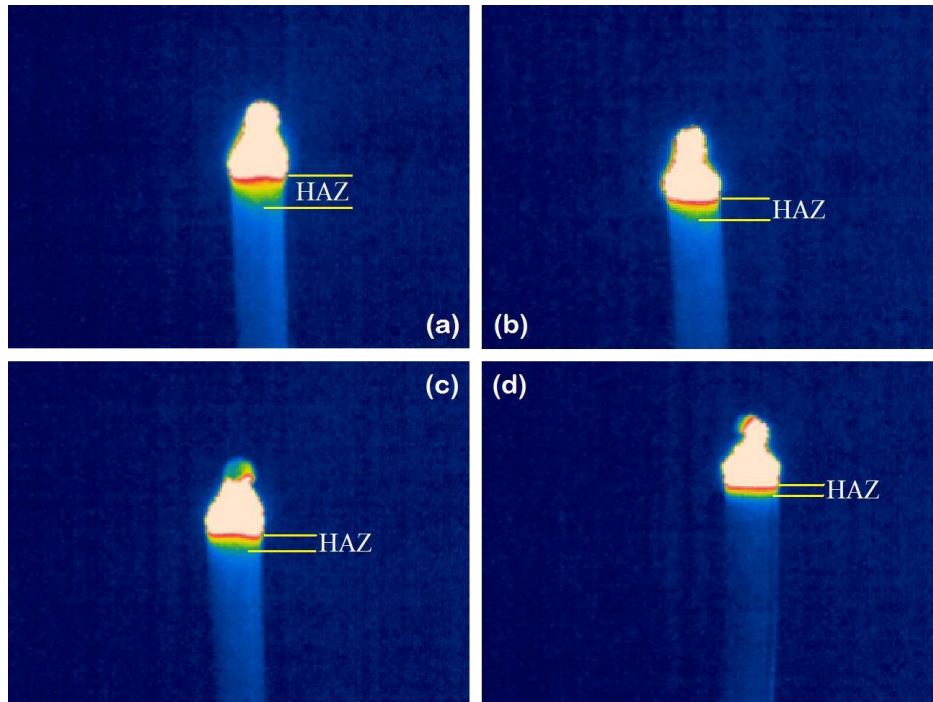


Figure 4. FLIR analysis for HAZ at (a) PVC basic formulation, (b) PVC+1% Oxydtron, (c) PVC+3% Oxydtron, and (d) PVC+5% Oxydtron

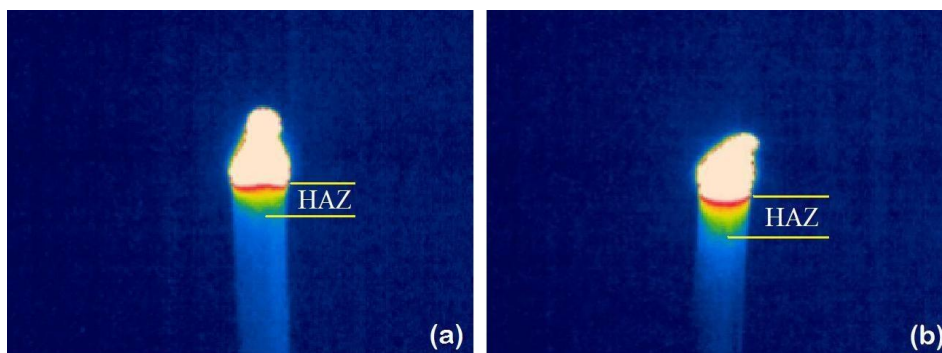


Figure 5. FLIR for extruded plasticized poly(vinyl chloride) basic formulation HAZ when (a) testing for the first time, (b) re-testing after cutting the burnt layer

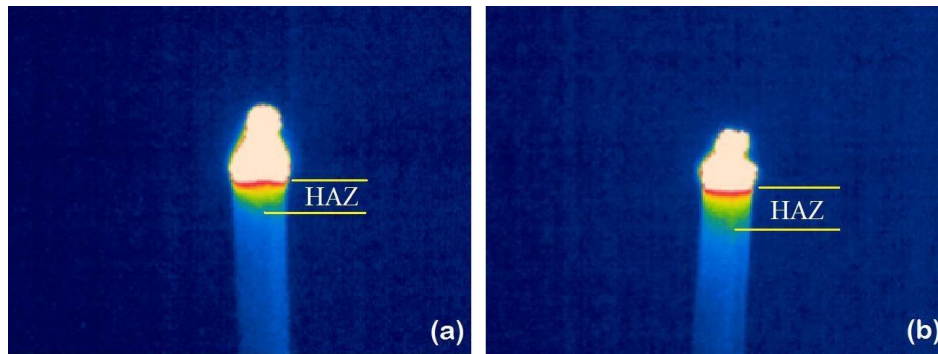


Figure 6. FLIR for HAZ of (a) extruded plasticized poly(vinyl chloride) basic formulation, (b) rolled plasticized poly(vinyl chloride) basic formulation

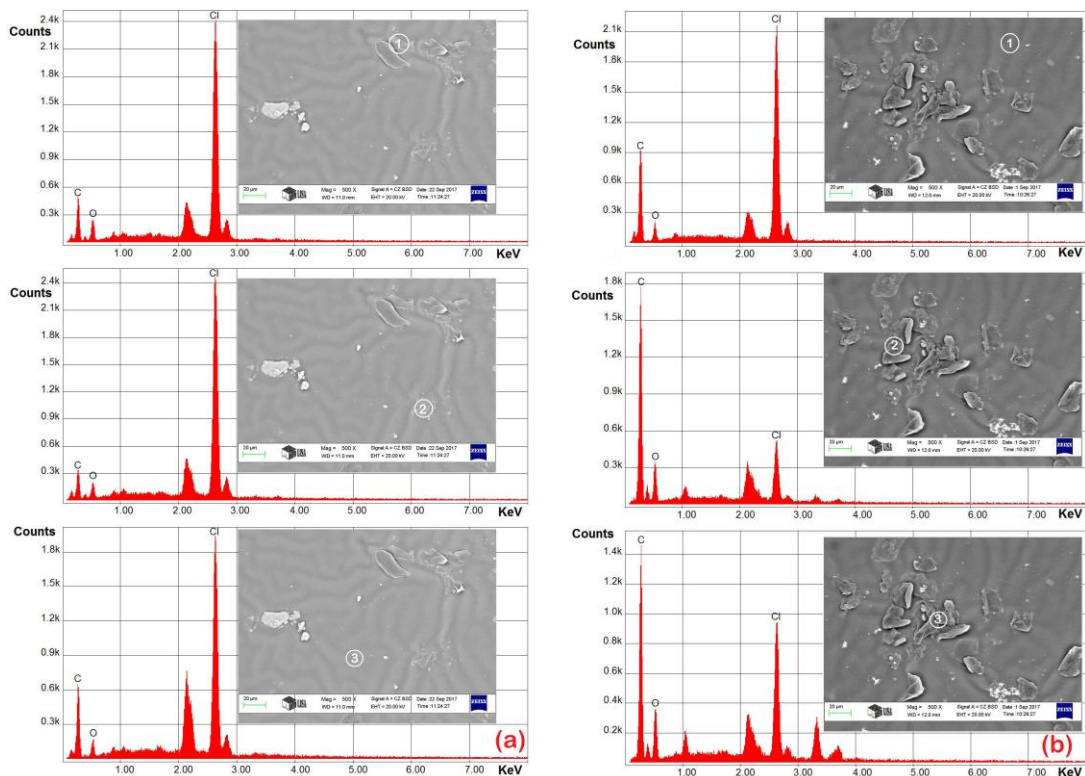


Figure 7. SEM - energy dispersive X-ray microanalysis for (a) unburned and (b) burned plasticized poly(vinyl chloride) basic formulation

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