DOI: 10.14750/ME.2021.039

Antal Kerpely Doctoral School of Materials Science and Technology

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

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree
of Doctor of Philosophy in Polymers Engineering as a Part of Stipendium
Hungaricum Scholarship in Material Science and Technology

By

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Miskolc, Hungary
2021

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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, 3rd 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).

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.

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Összefoglaló

A világegyetemben nem létezik univerzális anyag, de vannak olyan anyagok, amelyek szokatlan módon egynél több hasznos tulajdonsággal is rendelkeznek. Ezek egyike a jelen tanulmányban bemutatott Oxydtron nano cement. Az Oxydtron kiváló lángálló adaléknak bizonyult de meglepő módon kiváló hőstabilizáló hatása is van. Oxigén index (L.O.I.), statikus hőstabilitás, kongó vörös stabilitás, sósavlehasadás, kapillárviszkozimetriás és dinamikus mechanikai vizsgálatokat végeztünk.

Ezek a termikus mérések igazolták, hogy az Oxydtron jelentősen javítja a PVC magas hőmérsékleten való viselkedését, nevezetesen csökkenti az égésre való hajlamát és növeli a termikus stabilitását. Az Oxydtron így nem csupán eredeti alkalmazására, azaz a beton tulajdonságainak javítására alkalmas, hanem egyben a lágyított PVC stabilizálására és égésgátlására is alkalmas.

A PVC égésekor a közvetlenül a láng alatti zónát (HAZ, heat affected zone) hőkamera (FLIR) analízissel és pásztázó elektronmikroszköppal (SEM) vizsgáltuk. Ez a zóna égés nélkül van kitéve magas hőmérsékletnek. A FLIR és SEM analízissel készített képek azt mutatják, hogy az oxigén index mérésekor vizsgált próbatestek láng alatti zónájában a klórtartalom jelentősen csökkent míg a széntartalom viszonylag állandó maradt. Az Oxydtron tartalmú minták esetében a klórtartalom elfogadható mértékű marad.

Vizsgáltuk a PVC feldolgozástechnikai tulajdonságait is. Azt találtuk, hogy az extruziós feldolgozás után ugyanannak a keveréknek jobbak voltak az L.O.I. eredményei, mint amelyeket hengerléssel és azt követő préseléssel készítettünk. Feltételezzők, hogy az extrudált próbatestekben egyenletesebb a hőeloszlás csökkentve a termikus stresszt.

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Acknowledgement

As we walk in the darkness of the road carrying the science flame, we need someone to stand by us and offer the helping hand to keep this flame burning. Many people stood by me during my study, and I have to offer them my thanks, appreciation, and gratitude.

First of all, I'd like to thank my wife and companion, *Shaymaa*, for standing by my side, and although she was pregnant with our son *Hussein*, we used to go together to the BorsodChem, and *Hussein*, who shared the work with us, deserves part of this dissertation.

I would also like to thank my supervisor *Prof. Emeritus. Dr. Kálmán Marossy*, for the assistance, comments, and essential opinions he provided.

My gratitude and appreciation journey arrived at BorsodChem Zrt., which nurtured me for three years and provided me with the opportunity to complete my work requirements. It was difficult years, but full of energy, vitality, and fun to work. I stand with respect for PVC laboratory staff, *Csaba Kónya*, *Gabriella Szemere*, and *Krisztina Tózsa,* for their generous assistance and support throughout the three years of my work in BorsodChem. Also, I would like to thank *Irén Buzellákné Pető* at the degradation laboratory for her assistance.

My journey of gratitude and appreciation takes me back to the University of Miskolc and, in particular, to the SEM laboratory to thank the wonderful, gentlemanly, and kind-hearted *Árpád Kovach* who gave me unlimited assistance.

I go up the stairs to the polymer department to say thank you, *Assoc. Prof. Dr. Tamás Szabó* for helping me as a reviewer throughout the study period. Also, I cannot forget to extend my thanks and gratitude to *Prof. Emeritus. Dr. László Gömze* for his support.

I go to the third floor, where I find the *Assoc. Prof. Dr. Póliska Csaba*, to say thank you so much for your assistance.

Ali Ibrahim Moslem
February, 2021

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Chapter One: Introduction

1.1 Background

When Prometheus stole the fire from the Hephaestus god of blacksmiths in Mount Olympus according to the Greek mythology and gave it to humans to help them overcome the difficulties of their daily lives related to heating, lighting, and cooking; he didn't realize that fire would be useful to humans but also would bring destruction to them if they didn't use it safely. So, they have tried to find methods to extinguish the fire. Then they thought of something entirely new: creating materials that could resist fires reduce their risk and even completely stop it; thus, the concept of flame retreading appeared for the first time; and the subsequent discovery of materials "flame retardants" have the ability to break the cycle of fire [1-5]. As the concept of flame retardation developed, it became necessary to develop thinking, create new plans, and devise more modern and comprehensive strategies in this field.; now, the search for new and unconventional materials in the industry is imperative to balance environmental considerations for the safe use of non-polluting materials (or at least with limited damage) and to maintain the best possible achievement of new materials compared to traditional materials.

Many countries, including the European Union, are now seeking to restrict or even prohibit the use of environmentally harmful and persistent flame retardants. So the main aim should not use new engineering materials in the industry but to be more efficient or at least maintain the same level of performance of the traditional materials currently available, which can be termed metaphorically - the sustainability of properties - as with the sustainability of natural materials, otherwise there will be no benefit from the use of such materials [1,6-11].

1.2 Statistics on Fire Risks

Every year, fires cause significant human and financial losses in all countries, and the proportion of these losses varies from one country to another depending on the equipment and techniques used to reduce the fires risk, as shown in Table 1 and

Figure 1.1, which are represented the economic-statistical evaluation of fire costs according to the center of fire statistics report issued in the year 2016 [12].

Table 1.1. Economic-statistical evaluation of fire costs [12]

N	Country	Cost in portion of GDP, %					$\sum_{i=1}^{5} C_i$	$\frac{\text{Expenditure}}{\text{losses}}$ $\frac{C3 + C4 + C5}{C1 + C2}$
		Direct losses	Indirect losses	Cost of fire service	Fire protection in buildings	Fire insurance administrations		
		C_1	C_2	C_3	C_4	C_5		
1	Australia	0.07	-	0.17	-	-	-	-
2	Czech Republic	0.07	-	-	0.16	-	-	-
3	Finland	0.17	0.011	0.19	-	0.03	-	-
4	France	0.20	-	-	-	-	-	-
5	Germany	0.12	0.014	-	-	-	-	-
6	Hungary	0.02	-	0.13	-	-	-	-
7	Italy	0.02	-	-	0.35	0.04	-	-
8	Japan	0.12	0.060	0.26	0.12	0.09	0.650	2.61
9	Netherlands	0.15	-	0.21	0.31	-	-	-
10	New Zealand	0.12	-	0.16	0.24	-	-	-
11	Poland	0.09	-	0.16	-	-	-	-
12	Singapore	0.04	0.027	0.03	0.40	0.02	0.517	6.72
13	Spain	0.08	-	-	-	-	-	-
14	Sweden	0.18	0.060	0.13	0.20	0.05	0.620	1.58
15	UK	0.13	0.008	0.20	0.29	0.10	0.728	3.84
16	USA	0.10	0.007	0.29	0.29	0.12	0.807	6.54
Avrg.		**0.12**	**0.027**	**0.18**	**0.26**	**0.05**	**0.652**	**3.40**

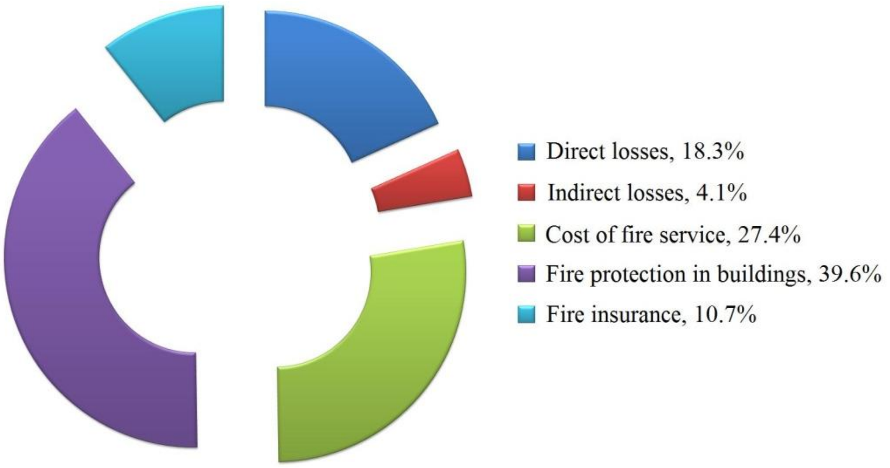

Figure 1.1. Economic-statistical evaluation graph of fire costs [12]

As shown in Table 1.1, many countries still do not pay great importance to fire protection, but at the same time spend much of their gross domestic product (GDP) to extinguish the fires after ignite, but it is best to be concerned with how to prevent the fire from happening. The government expenditure of European Union Members on fire-protection services in 2018 was 29.5 billion euro, representing just 0.5% of the government's total spending. Simultaneously, the public spending on these services is still constant at around 0.4%-0.5% since the start of the time series in 2001 as illustrated in Table 1.2 [14]. Unfortunately, no data is available for the years 2019 and 2020.

In 2018, fire safe Europe, the European association for fire safety, called for the European Union to change its building protection requirements. Despite more than 5000 fires happen in Europe every day, there is no systematic strategy for the members of the European Union. This means that European citizens do not have the same chances of survival when the building fire [15,16].

1.3 Reducing Fire Risk

The principle of fire risk reduction is generally based upon many parameters: the provision of traditional fire extinguishers; the use or enhancement of thermal resistance to materials with low inflammability ranges when highly inflammable, such as polymers where low thermal resistance of these important materials considered the primary limitation to apply these materials in such applications required high thermal resistance performance; the effective design of buildings for escaping fire supplies to mitigate the loss of people; As well as choosing appropriate furniture that meets fire safety standards and contains environmentally friendly flame retardants [6,17,18].

All the above points are relevant to the critical factor, which is the deployment of a "fire prevention culture" that is entirely dependent on people's awareness of fire hazards and the extent to which they apply safety arrangements to prevent fires or reduce it [19,20].

Table 1.2: Total government expenditure on fire-protection services in EU, 2018 [14]

Country	Million Euro	GDP	Total, %
European Union, 27 countries (from 2020)	29,516.9	0.2	0.5
European Union, 28 countries (2013-2020)	33,130.5	0.2	0.5
Belgium	893.0	0.2	0.4
Bulgaria	180.2	0.3	0.9
Czechia	590.3	0.3	0.7
Denmark	181.7	0.1	0.1
Germany	8,150.0	0.2	0.5
Estonia	63.8	0.2	0.6
Ireland	242.1	0.1	0.3
Greece	505.0	0.3	0.6
Spain	1,943.0	0.2	0.4
France	6,807.0	0.3	0.5
Croatia	123.3	0.2	0.5
Italy	3,171.0	0.2	0.4
Cyprus	36.3	0.2	0.4
Latvia	63.4	0.2	0.6
Lithuania	100.3	0.2	0.7
Luxembourg	100.3	0.2	0.4
Hungary	289.4	0.2	0.5
Malta	9.1	0.1	0.2
Netherlands	1,740.0	0.2	0.5
Austria	654.6	0.2	0.3
Poland	999.2	0.2	0.5
Portugal	291.2	0.1	0.3
Romania	584.4	0.3	0.8
Slovenia	65.4	0.1	0.3
Slovakia	194.6	0.2	0.5
Finland	576.0	0.2	0.5
Sweden	962.3	0.2	0.4
United Kingdom	3,613.6	0.1	0.4
Iceland	20.3	0.1	0.2
Norway	942.4	0.3	0.5
Switzerland	725.4	0.1	0.4

Chapter Two: Flame Retardants

Flame retardants are defined as chemical agents that can withstand direct flame by stopping flame entry into the material, controlling its spread, and even extinguishing utterly. These materials can be added during or after the products' fabrication for burning protection. The development of flame retardants allowed the safe usage of fabrics that cause flammable behaviour by reducing flammability and reduce the rate of burning. The compounds of phosphorus, nitrogen, chlorine, bromine, boron, and antimony are ones of the most widely used for flame retarding [3,20-26].

2.1 Historical Overview of Flame Retardants

Many materials with flame retardant properties have been known for many centuries, as shown in Table 2.1. Where about 3000 years ago, the ancient Egyptians were soaking grass and reed in seawater before they used it for roofing, so when these grass and reed dry, the mineral salts will crystallize and act as a fire retardant. The Egyptians and Chinese also used alum and vinegar to paint timbers in temples to protect them from the fire [27-30]. Although the ancient civilizations did not have the necessary equipment to analyze these materials' components, they pay attention to the nature of these substances acting as retardants. The discovery of the flame retardancy properties of these materials was through coincidence. Still, they inevitably conducted some practical experiments, even if primitive, to prove these materials' effectiveness in fire protection, in addition to searching for other materials with the same properties. Indeed, this led to the development of testing devices to detect these materials [31].

With the development of human lifestyle, the needs to discover new materials that reduce the risk of fires have increased. This calls for relying on a scientific and practical basis and not to depend on chance only. So the first practical experiments to reduce fire risk began to appear. As a scientific procedure recorded, the first fire testing experiments can be traced to London's 1790s done by the Associated Architects. There was Quantitative work in Germany beginning in the 1880s, and in the U.S. and England in the 1890s. The growing interest in these tests led to establishing unified test standards in the early twentieth century. Where the first standard about fire testing methods was ASTM C19 (later called E 199) [31,34-37].

Table 2.1. A historical overview for early use of flame retardants [28,29,30,32]

Material	Used by	Date
Potassium Aluminium Sulphate (Alum)	The Egyptians have used Alum and Vinegar to reduce wood flammability	450 B.C.
Vinegar	The Egyptians and Chinese used painted timbers by vinegar to increase their resistance to burning	360 B.C.
Alum, Vinegar, and clay	The Roman army painted the wooden siege towers with alum, vinegar, and clay to protect them from burning when they besieged Piraeus	87-86 B.C.
Clay-Gypsum Mixture	Had been used by Nicola Sabbatini in France for reducing painted canvas inflammation at Parisian theatres	1638
Alum- Ferrous Sulfate-Borax Mixture	It was discovered by Obadiah Wyld and used in Britain for preventing paper, linen, canvas, & c., from flaming or retaining fire, & c. Wyld received the first patent for fire retardants No.551 [33]	1735
Potassium Aluminium Sulphate (Alum)	Used by the French brothers Montgolfier to reduce flammability of hot air balloons	1783
$(NH_4)_3PO_4$ - NH_4Cl - Borax Mixture	Used by the French chemist Gay-Lussac for linen and hemp fabrics [34]	1821

2.2 Categorization of Flame Retardants

Flame retardants are typically categorized into four major categories: Inorganic FRs; Phosphorus-containing FRs; Nitrogen-containing FRs; and Halogenated organic.

2.2.1 Inorganic Flame Retardants

The most significant types of this category are antimony trioxide containing halogen, magnesium hydroxide, zinc borate, aluminum hydroxide, and zinc sulfide. If this category of flame retardant is exposed to heat, it does not evaporate. Instead, it decomposes and released non-flammable gases, such as water vapour, carbon dioxide, sulfur dioxide, hydrogen chloride, and other gases. Most of these compounds produce endothermic reactions. These flame retardants' mechanism of action depends on its disintegration at high temperatures and causing the release of non-flammable gases, which minimize the mixture of flammable gases. Then, it separates the plastic's surface by forming a glassy protective layer on the surface of the plastic that prevents oxygen and heat access [5,38-43].

2.2.2 Phosphorus-Containing Flame Retardants

This category typically includes phosphate esters, red phosphorus, ammonium polyphosphates, and ammonium orthophosphates. Its principle of action is based on its oxidation during combustion to phosphorus oxide, which converted into phosphoric acid when interacting with water. This acid induces the release of water and removes it from the substrate layer of the thermal decomposing material, which contributes to its decomposition and thereby increases the formation of carbonaceous waste and decreases the emission of combustible gases [44-47].

2.2.3 Nitrogen-Containing Flame Retardants

Nitrogen-containing flame retardants: Often referred to as organic flame retardants. Melamine and its derivatives are the essential compounds in this category. These retardants' principle of action depends on the formation of an insulating surface layer by gases released from these retardants during combustion cause the material to swell [48-53].

2.2.4 Halogenated Organic Flame Retardants

This category contains primary bromine and chlorine in particular. Its principle working action depends on chemical interference with the root chain mechanism, which occurs in the gaseous phase during combustion. Halogen flame retardants eliminate the high-energy hydrogen and hydroxide generated during the combustion process by combining them, so the flame is poisoned by the halogen radicals released during combustion [5,6,54-56].

2.3 Classification of Flame Retardants

Flame retardants can be classified into three primary groups, depending on how they are applied to the polymer, and these two groups are: Additive FRs; Reactive FRs.; and Additive- Reactive FRs

2.3.1 Additive Flame Retardants

This type is used for thermoplastics in particular. Additive flame retardants can be added to plastics in three ways: (1) before polymerization, (2) during the process, or (3) after polymerization, and it is the most common way to add them. In addition to its direct action as flame retardants, it can be a plasticizer if they are compatible with the plastic or as fillers if they aren't compatible with it. The main disadvantage of these retardants, is their instability, where they sometimes can be volatile or even bled from the plastic, especially from the layers near the surface, causing plastic to lose its ability to resist burning, which is very dangerous because this state can only be realized when combustion occurs [57-59].

2.3.2 Reactive Flame Retardants

This type of flame retardant is binding to the polymer molecule with the other components. This chemical bonding prevents it from evaporating and bleeding from the polymer over time. It happens with additive flame retardants, enabling the polymer to maintain flame retardant properties as long as possible. Although they are chemically binding to the polymer molecules, they have no plasticizing effect and are non-affecting the polymer's thermal stability. The practical and widespread use of reactive flame retardants is with thermosets [56-59].

2.3.3 Additive- Reactive Flame Retardants

Several materials are not classified as stand-alone flame retardants, which will often work as fillers if used alone. Still, they have a special synergistic effect if they are added to other retardants, where the effectiveness and efficiency of these retardants increase to resist fire. An example of such materials is antimony compounds, especially antimony trioxide. The main purpose of this combination is to reduce the cost and, as mentioned, increase the effectiveness of the primary flame retardant [5,57,58,60,61].

2.4 Working Mechanism of Flame Retardants

The method of slowing or even stopping the flame depends on the nature of the flame retardant, as the flame retardant can act chemically or physically in the solid, liquid, and gas state, where the flame retardant is interpenetrating with the combustion process during the various stages of this process, i.e., heating, decomposition, ignition, or flame propagation [5,62,63]. In general, there are two standard methods of flame retardation. The first method is based on preventing oxygen from accessing the flame area by generating non-combustible gases, where these gases can poison and extinguish the flame with free radicals. The second method is based on the thermal flame theory, which states that flame retardants require thermal energy for decomposition, leading to a decrease in the material's surface temperature to a temperature lower than its burning point, and the combustion breaks down [64].

2.4.1 Physical Mode

This working mode can be achieved in three ways [62,65,66]:

2.4.1.1 Cooling

Additives cause endothermic processes that cool the substrate of the material to a temperature lower than the level of combustion. An example of flame retardants behaving like this is aluminum hydroxide.

2.4.1.2 Formation of Insulation Layer

The insulating semi-glass layer is created by a flame retardant that expels the oxygen needed to begin the combustion process, preventing heat transfer. Inorganic phosphorous compounds and boron are behaving like this mode.

2.4.1.3 Dilution

The incorporation of inert materials (fillers) and additives that release inert gases after their thermal decomposition dilute the fuel in both the solid and gaseous states in such a way that the minimum ignition limits for the gas mixture are not exceeded. Phosphorous and boron compounds work this way.

2.4.2 Chemical Mode

Can be achieved in two ways:

2.4.2.1 Gaseous Phase Reaction

The free radical mechanism is stopped by the flame-retardant materials, causing eliminating the exothermic processes and, so the system will cool down. The percentage of flammable gases is reduced and even wholly prohibited as shown in Figure 2.1. The flame retardant which exhibits this behavior is halogen compounds [5,66].

2.4.2.2 Solid Phase Reaction

A carbon film is formed on the surface of the polymer by the dehydrating action of flame retardant, forming double bonds in the polymer (see Figure 2.2). These double bonds will create a carbon film by cross-linking. An example of these retardants is phosphorous compounds. In the case of phosphorous compounds addition, their mode of action depends on substituting the hydroxyl and hydrogen radicals in the combustion cycle by low-potency radicals, eliminating their damage as shown in the equations below, which represents the combustion reaction (Chain reaction equations), and the hinderation reaction (Chain hinderation equations). This mechanism is similar to that of the halogen compounds. The change in the combustion cycle's radical composition in the gaseous phase leads to flame suppression and reduced heat production, which cools the combustion zone. The combustion process activated several sequential reactions, which include: chemical chain-branching, chain-propagating, and chain-breaking reactions. These chemical processes help preserve the flame by changing the quantity, form, and mole ratio of the radicals present in the gas phase. Therefore, in order to change this state, Lower energy radicals are required to remove the unstable radicals of OH· and H·. Replacing the unstable OH· and H· radicals with less reactive and more stable radicals works to inhibit the combustion chain reaction and lead to cut this reaction. Thus the self-extinguishing process of the system will occur [5,67-69].

Chain reaction equations [69]:

$$\mathrm{OH^{\cdot} + CO \rightarrow CO_2 + H^{\cdot}} \qquad (1)$$

$$\mathrm{CH_4 + O_2 \rightarrow CH_3^{\cdot} + H^{\cdot} + O_2} \qquad (2)$$

$$\mathrm{H^{\cdot} + O_2 \rightarrow OH^{\cdot} + 0.5O_2} \qquad (3)$$

$$\mathrm{OH^{\cdot} + CH_4 \rightarrow H_2O + CH_3^{\cdot}} \qquad (4)$$

$$\mathrm{CH_3^{\cdot} + O_2 \rightarrow CH_2O + HO^{\cdot}} \qquad (5)$$

$$\mathrm{CH_2O + HO^{\cdot} \rightarrow CHO^{\cdot} + H_2O} \qquad (6)$$

$$\mathrm{CHO^{\cdot} + O_2 \rightarrow CO^{\cdot} + H^{\cdot} + O_2} \qquad (7)$$

Chain hinderation equations [69]:

$$\mathrm{PO^{\cdot} + H^{\cdot} \rightarrow HPO} \qquad (8)$$

$$\mathrm{PO^{\cdot} + OH^{\cdot} \rightarrow HPO_2} \qquad (9)$$

$$\mathrm{HPO + H^{\cdot} \rightarrow H_2 + PO^{\cdot}} \qquad (10)$$

$$\mathrm{HPO + CH_3^{\cdot} \rightarrow H_2 + PO^{\cdot}} \qquad (11)$$

$$\mathrm{HPO_2^{\cdot} + H^{\cdot} \rightarrow H_2O + PO} \qquad (12)$$

$$\mathrm{HPO_2^{\cdot} + H^{\cdot} \rightarrow H_2 + PO_2} \qquad (13)$$

$$\mathrm{HPO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + PO_2} \qquad (14)$$

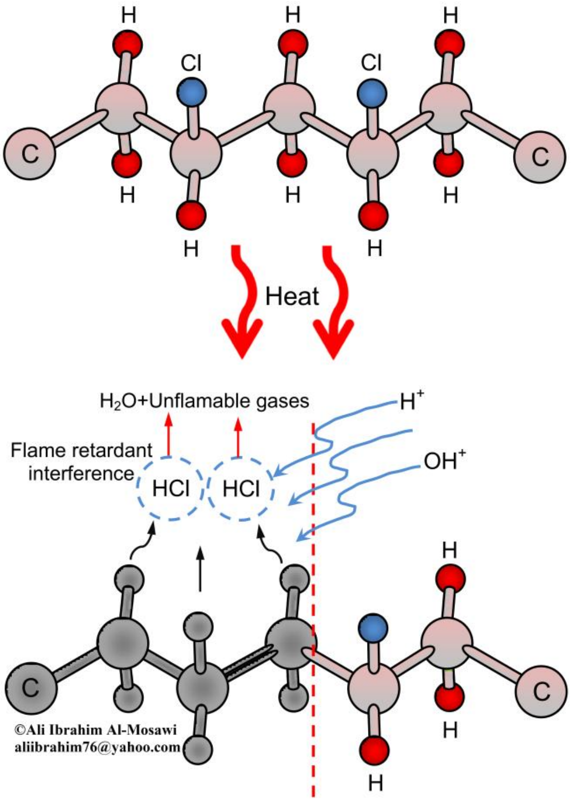

Figure 2.1. Gaseous phase reaction

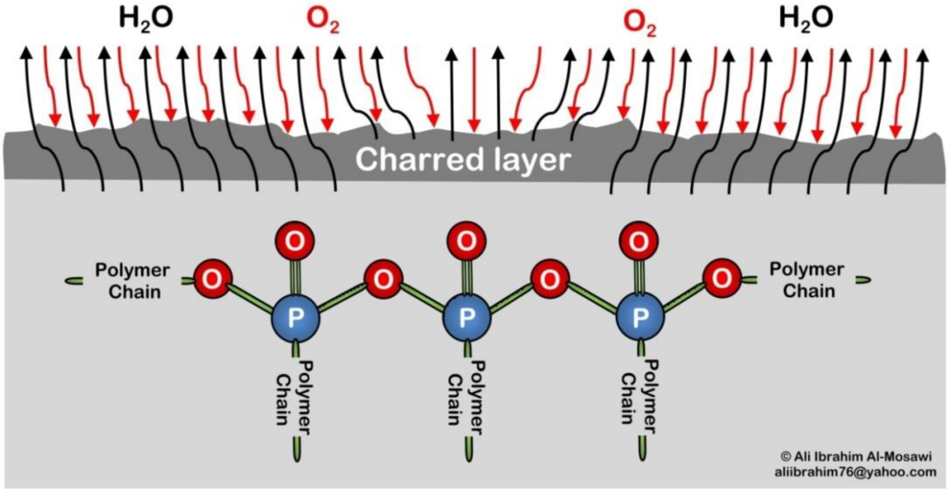

Figure 2.2. Solid phase reaction

2.5 Flammability and Combustibility

Many people think that flammability or ignitability and combustibility is similar in denoting the same characteristic. Still, the truth is that they are different, so I will explain what these two terms refer to in this paragraph. The flammability or ignitability is defined as a material's ability to catch fire (ignite), causing a fire, combustion, or even an explosion if the material is unstable. Whereas combustibility is defined as how easily a material burns to cause a fire or combustion [70]. The main criterion by which materials are classified as flammable or combustible is the flash point, where flammable materials have a lower flash point than combustible materials. The flash point of flammable materials is less than 37.8 °C, while in the case of combustible materials; its value is higher than 37.8°C and less than 93.3°C [70-73]. Table 2.2 represents the flash-ignition and self-ignition temperatures for various polymers.

Table 2.2. Flash and self ignition temperatures for various polymers [73,74]

Polymer	Flash-ignition Temperature, °C	Self-ignition temperature, °C
Poly(methyl methacrylate)	300	430
Polypropylene	320	350
Polyethylene	340	350
Polystyrene	350	490
Rigid Poly(vinyl chloride)	390	450
Plasticized Poly(vinyl chloride) (Insulation)	330	385
Plasticized Poly(vinyl chloride) (Fire resistant, low acid emission)	400	410
Poly(acrylonitrile)	480	560
Polyamide 6’6	490	530
Poly(tetrafluoroethylene)	560	580

2.6 Flame Retardants and the Environment

Most of conventional flame retardants and stabilizers for plastics contain heavy metals or other ingredients e.g., bromine being potentially harmful to the environment or health. The accumulation of 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 have been 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 [75-84]. Therefore, in light of 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 [85-87]. 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 [88]. There are heavy metal-free flame retardants (earth metal hydroxides), but it must be used in high concentrations (40- 60 phr), which in turn will reduce the mechanical properties and wear resistance of the plastic [75].

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 [25,75, 88-90]. 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 [91]. With the tendency to replace traditional flame retardants with environmentally friendly ones, the environmental conditions surrounding the product containing this type of 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 [92]. 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. Whereas the chemical stability of environmentally friendly flame retardants in different conditions is of critical importance to increase safety level when using these retardants.

Chapter Three: Poly(vinyl chloride)

3.1 Characteristics of Poly(vinyl chloride)

Poly(vinyl chloride) or PVC for short is an essential and widely used plastic in many applications where it can be used as rigid or plasticized depending on the type of application. Poly(vinyl chloride) has a high molecular weight; therefore, many organic compounds do not affect it at average temperatures. Some chemical compounds can attack poly(vinyl chloride): chloro-hydrocarbons and certain esters [93-96]. Poly(vinyl chloride) is primarily a rigid polymer at low temperatures due to the firm, attractive forces between the molecules resulting from a small distance between the molecules. These distances begin to widen when poly(vinyl chloride) is heated, causing its structure to soften, but the softness quickly disappears when it cools. Thus, to preserve this softness in the poly(vinyl chloride) structure even at room temperature, the addition of plasticisers that prevent polymer molecules from approaching each other can keep polymer softness due to the vast distance between molecules[97]. The bonding mechanism of plasticiser-poly(vinyl chloride) shown in Figure 3.1.

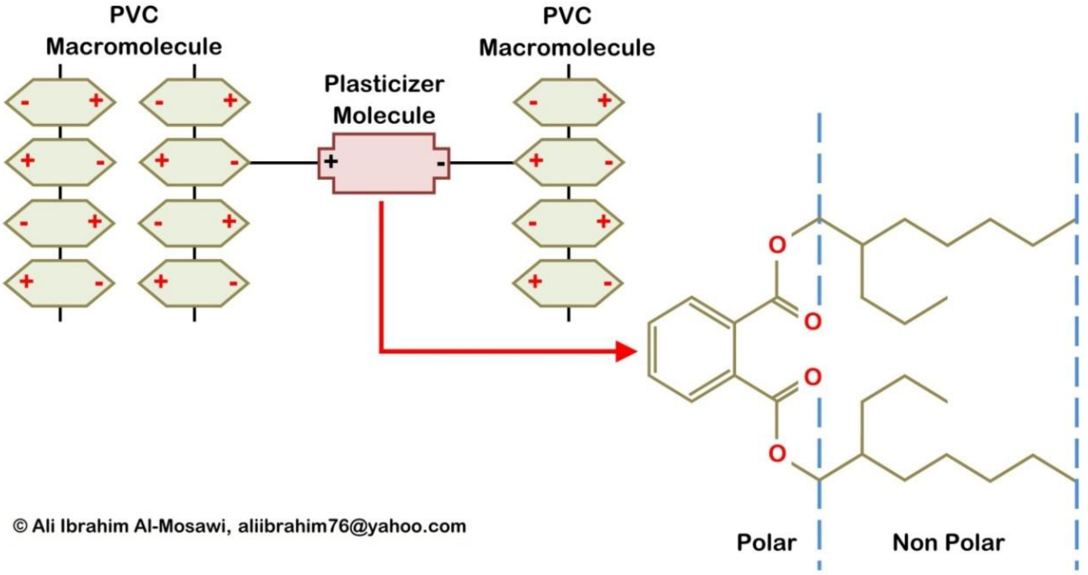

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Figure 3.1. Plasticiser-poly(vinyl chloride) bonding mechanism (Re-drawing depending on the reference [98])

When poly(vinyl chloride) is heated to the range temperatures between 170 and 180°C, the chlorine and hydrogen will be removed from the molecules, and the hydrogen chloride is released. The emergence of this decomposition will cause instability of molecules structure, which will lead to the removal of hydrogen chloride rapidly and significantly. Since poly(vinyl chloride) is heated to soften phase during processing, like extrusion or rolling, limiting the release of hydrogen chloride is one of the priorities that must be considered. This thing can only be done by stopping the decomposition or reducing its effects. So, the release of hydrogen chloride from poly(vinyl chloride) would be avoided by the presence of a stabilizer [99]. The main types of poly(vinyl chloride) stabilizers are listed in Table 3.1.

Table 3.1. Types of stabiliser added to poly(vinyl chloride) [99]

Stabiliser type	Principal metal	Metal content (%) packaging	In PVC formulation other
Lead compounds	Lead	Not used	-
Organotins	Tin	0.1-0.2	0.3-1.0
Barium-Zinc compounds (only for plasticized applications)	Barium zinc	Not used	~0.1 <0.2
Calcium-Zinc compounds	Calcium zinc	0.1 <0.2	<0.5

Poly(vinyl chloride) can be produced in more than one state, so, the primary classification key of poly(vinyl chloride) is its elasticity, where it is classified as rigid or plasticized. The important thing is that changing poly(vinyl chloride) from rigid to plasticized state there's no need to change its chemical formula through polymerization but through additives only, which is not available in the majority of other polymers [100]. In general, poly(vinyl chloride) is considered not chemically reacted for both types. The rigid type is stiff, strong, and has significant chemical and UV resistance. It also has a reasonable machinability rate. Plasticized poly(vinyl chloride) has better tensile strength and flammability than rigid form [101,102]. Properties of plasticized and rigid poly(vinyl chloride) shown in Table 3.2.

Table 3.2. Properties of plasticized and rigid poly(vinyl chloride) [101]

Properties	Plasticized PVC	Rigid PVC
Physical properties		
Density, g/cm^3	1.3 – 1.7	1.35 – 1.5
Glass Transition Temperature, °C	-5 – -5	60 – 100
Mechanical properties		
Young’s Modulus, GPa	0.001 – 1.8	2.4 – 4
Flexural Modulus, GPa	0.001 – 1.8	2.1 – 3.5
Elongation at Break, %	100 – 400	25 – 80
Service temperature		
Max. Continuous Service Temperature, °C	50 – 80	50 – 80
Min. Continuous Service Temperature, °C	-40 – -5	-10 – 1
Other properties		
Dielectric Strength, kV/mm	10 – 30	10 – 40
Transparency, %	75 – 85	80
Thermal Insulation (Thermal Conductivity) W/m.K	0.16	0.16

3.2 Degradation of Poly(vinyl chloride)

It is known to everyone that one of the main disadvantages of poly(vinyl chloride) despite the many advantages which is the release of chlorine containing compounds (HCl) from its internal structure after exposure to high temperatures as shown in Figure 3.2, and this process is called dehydrochlorination. When poly(vinyl chloride) reaches this stage of releasing HCl, it actually begins to degrade, which is dangerous not only because it has started to lose its properties, but because degradation products "chlorine compounds" are toxic, which is a danger to human health and leads to environmental pollution although the poly(vinyl chloride) fires are not so huge to consider as an environmental disaster but it is a danger that can't be overlooked [103].

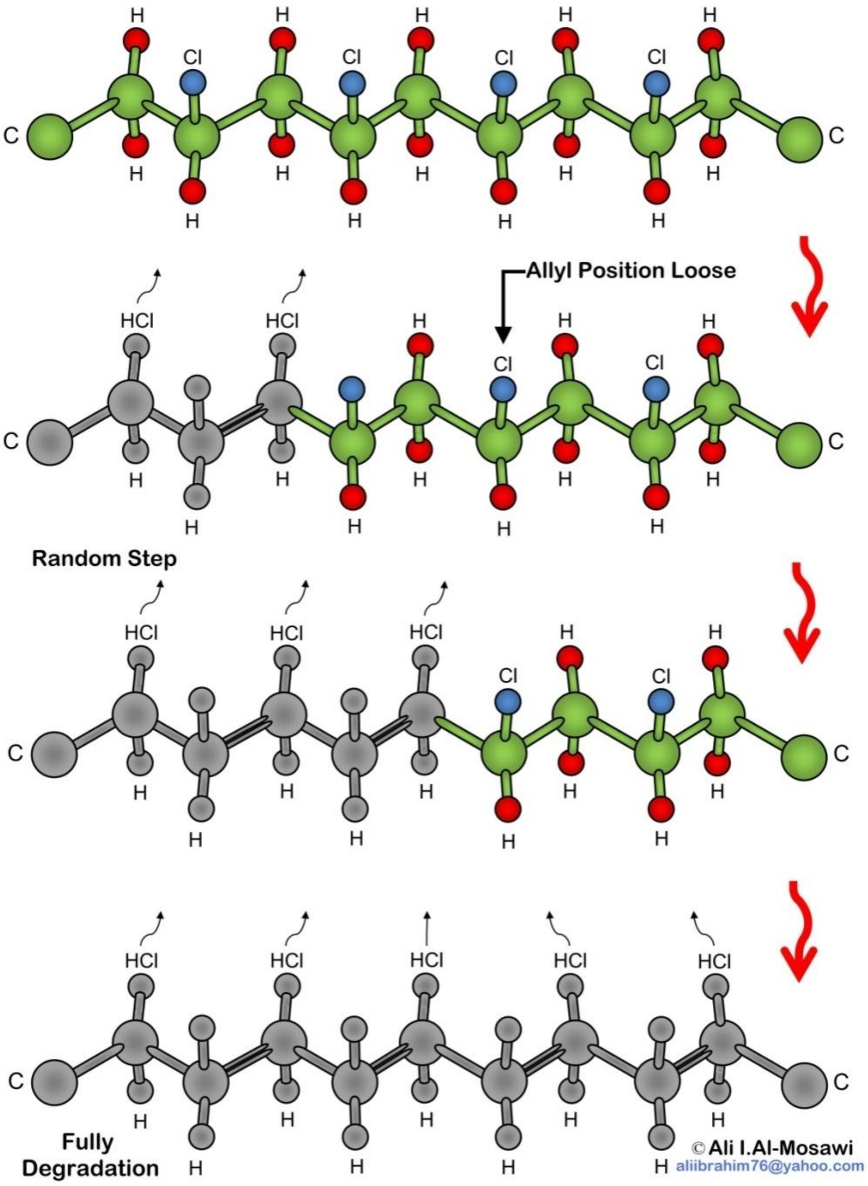

Figure 3.2. Mechanism of degradation for poly(vinyl chloride) [96]

The initiation of poly(vinyl chloride) degradation occurs at the defects created during the polymerization. The most common and important types of polymerization defects are: tertiary chlorine atoms resulting from branch formation during polymerization, and allylic chlorine atoms formed by termination of the polymerization reaction as shown in Figure 3.3 [104,105]. As mentioned, hydrogen chloride is released during the process, which will generate new defects associated with the existing defects arising mainly from polymerization. The releasing of HCl will continue in a zipper-like fashion when no stabilizer interferes to stop it. After forming HCl and conjugated double bonds (polyene sequences), a pale yellow color appears when six to seven conjugated double bonds are produced. This pale yellow appearance can turn darker with a growing conjugation length, changing from red to brown and eventually to black [104-111].

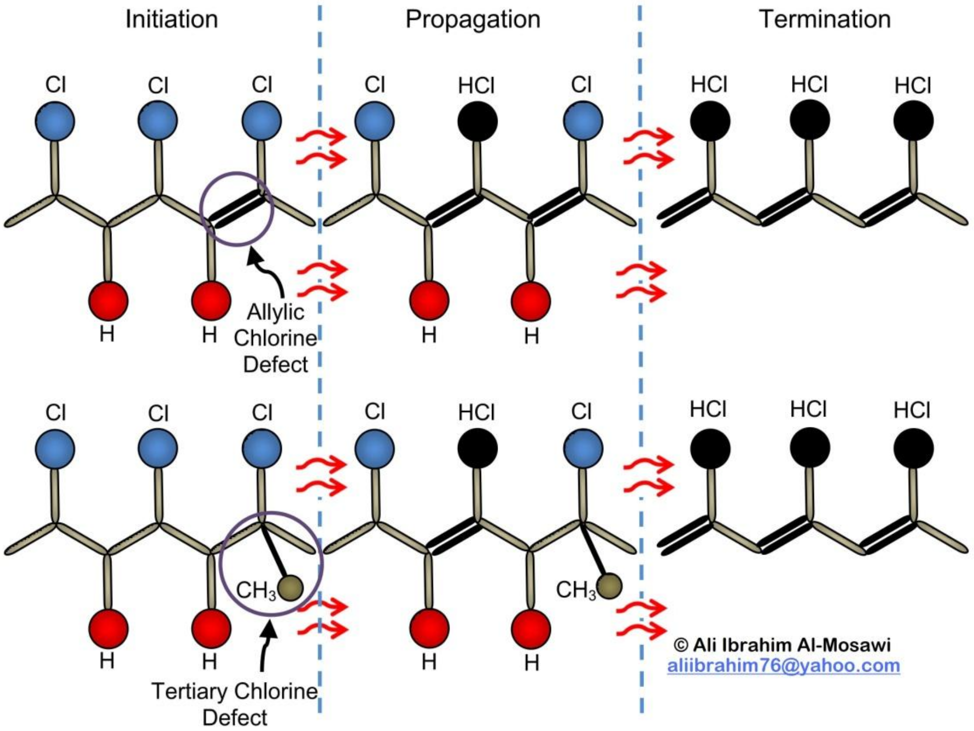

Figure 3.3. Degradation of poly(vinyl chloride) due to heat or shearing at allylic and tertiary chlorine atoms (depending on the data of reference [106])

3.3 Flammability Performance of Poly(vinyl chloride)

The flammability efficiency and thermal resistance of poly(vinyl chloride) are considered the essential criteria in choosing this polymer for such applications that required high thermal resistance. The high percentage of chlorine (56.8%) makes poly(vinyl chloride) intrinsically fire-resistant, even with no flame retardants as shown in Figure 3.4 and Table 3.3 [112-115]. However, for many applications, especially thermal ones, the poly(vinyl chloride)'s natural flame retardancy is unreliable, because polyvinylchloride loses a high percentage of chlorine while combustion. As an example, it has been found that the plasticized poly(vinyl chloride) will reduce about 20% chlorine by mass during burning [91].

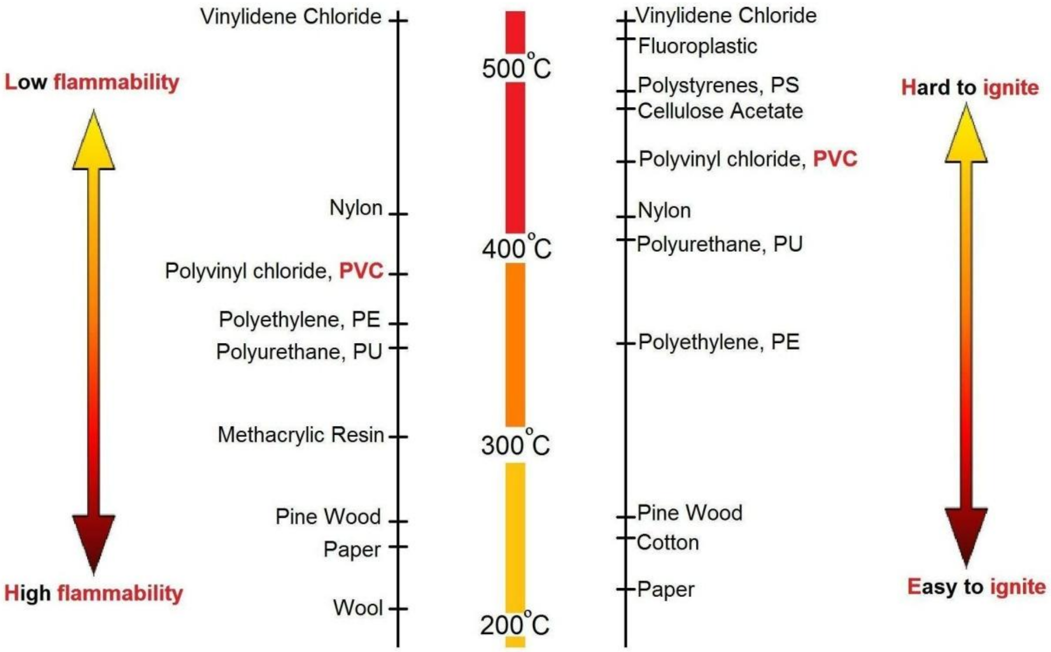

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Figure 3.4. Flammability ranges of non metallic materials including poly(vinyl chloride) (Re-drawing depending on results of reference [112])

Table 3.3: Limited oxygen indices of unmodified thermoplastics [113]

Material	L.O.I, %
Chlorinated PVC	60-70
Rigid PVC	45-49
Polycarbonate	26-28
Nylon 6, 6	24-29
ABS	18.3-18.8
cellulose	19.0
Polyacrylonitrile	18.0
Polystyrene	17.6
Polyethylene & Polypropylene	17.4
Polymethylmethacrylate	17.4

The high chlorine content makes poly(vinyl chloride) compatible with a wide variety of flame retardants. Some flame retardants additives such as antimony trioxide have a synergistic action with chlorine to create free-radical scavengers that serve as flame poisons. In contrast, some flame retardants and smoke suppressants convert the products of the degradation process of poly(vinyl chloride) into more aliphatic and less aromatic products in the fire. Also, some smoke suppressant additives convert aromatic products from poly(vinyl chloride) degradation into char instead of smoke. Comparative combustion heat of methane gas, PVC, and some other thermoplastics is shown in Table 3.4 [112-114]. As is evident from this table, the low heat of combustion of poly(vinyl chloride) qualifies it to be among the best options for industrialists to meet flame resistance requirements and prevent its spread [106].

Table 3.4. Heat of combustion for thermoplastics [113]

Material	ΔH_c, kJ/g
Methane Gas	50.0
Polyethylene, PE	43.3
Polypropylene, PP	43.3
Polystyrene, PS	39.9
Polyacrylonitrile, PAN	30.8
Polycarbonate	29.7
Nylon 6, 6	29.6
Polymethylmethacrylate	24.9
Polyvinylchloride, PVC	16.4

3.4 Environmental Considerations

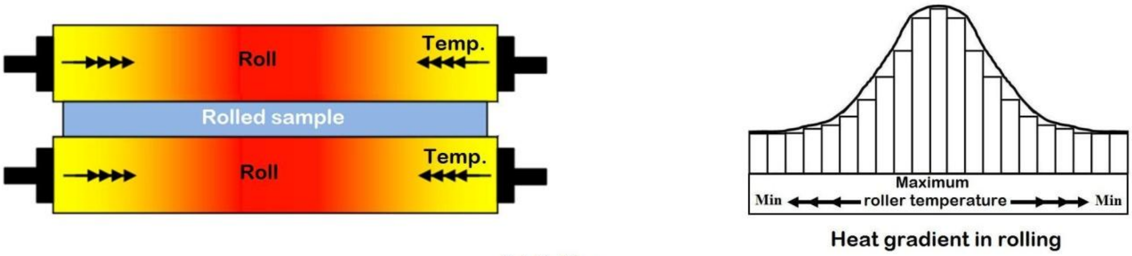
Most of conventional flame retardants and stabilizers for poly(vinyl chloride) contain heavy metals or other ingredients e.g. bromine, being potentially harmful to the environment or health, although they increase the efficiency of the performance of poly(vinyl chloride) at high temperatures and make its structure more stable. So it must (as much as possible) that these stabilizers and other additives are environmentally friendly and at the same time have the ability to improve the thermal resistance of the poly(vinyl chloride) [75,103,116-118]. 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 occupy the place of these stabilizers, such as calcium/zinc, organotin, and barium/zinc systems, but there are still disadvantages for the plasticized vinyl formulator. Therefore, a complete switch to environmentally friendly stabilizers needs more research in this field [119,120].

3.5 Selection of Proper Processing Method

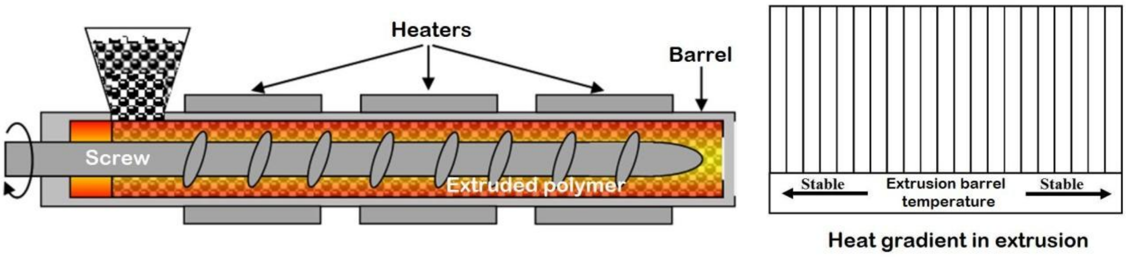
Polymers in general, are known to be highly sensitive to heat due to their low melting points; therefore, any change in temperature will change its structural phases, and thus will change its qualities and properties. This change depends on the thermal range and the time period of heat exposure. Poly(vinyl chloride) is one of these thermally sensitive polymers; where its properties depending on the operational history so it is very sensitive to any change or irregularity in processing temperature. Therefore, the processing method must be carefully selected. Every processing method has its characteristics and limitations, which are affected by the conditions surrounding the process. These conditions control the processing method's efficiency to achieve an individual work of high quality compared to other processes [121-125].

There are several critical parameters (constant or variable) that control any of the forming process. These parameters are: temperature, time, speed and pressure. These critical parameters are closely related, and directly affect the properties of the product, the economic feasibility of the forming process, and its technical relevance to the formed material, in order to obtain the best properties, whether mechanical, thermal, chemical, etc. In addition to the above parameters, there is a parameter of no less importance, which is the human factor (worker), and the extent of its intervention in the forming process, and whether the process depends on it completely or not. Therefore, the worker efficiency will be also a critical parameter the properties of the final product. All these parameters must be taken into consideration in order for the forming process to be successful [121]. In the forming processes of polymers, high temperatures are required, in order to increase their flowability and reduce the viscosity, thus, the shear stress will decrease. In addition, the forming processes differ in terms of the homogeneous thermal distribution on all formed area, and the stability of the heating and not affected by the surrounding environment, which improves the quality of the product and reduces the deformations resulting from different temperatures between the parts of the same product [121].

The poly(vinyl chloride) can be processed by rolling or extrusion, where the regularity of temperature is different due to the machine specifications. In the rolling process, the heat distribution is not symmetrical and varies along the length of the roll, where the temperature of the roll will be the highest value in the centre and decreases in the direction of the sides, which negatively affects the properties and structure of the polymer processed in this method (see Figure 3.5, a). On the other hand, the heat is distributed regularly along the extruder barrel in the extrusion process, thus providing a balanced and suitable thermal environment in which the polymer can retain its properties during the processing resulting inhomogeneous products in terms of structure and properties, as shown in Figure 3.5,b [121-128].



(a) Rolling



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(b) Screw-extrusion

Figure 3.5. Heat distribution in (a) Rolling, (b) Screw-extrusion [121,124]

Chapter Four: Oxydtron

4.1 What is Oxydtron?

Oxydtron is one of the non-traditional polymer additive materials that I used in this study. According to its technical data sheet Oxydtron is a nano cement mineral admixture which is added to the concrete mixture to increase the water leakage-, freezing-, heat- and acid /alkali resistance. Those who hear about Oxydtron for the first time assume it to contain nano particles as indicated by the term "nano cement" but this is not true because Oxydtron is a micro particles powder and just the particle's coating layer is consisting modifier materials of nano size (10 to 100 nm); which gives this material special characteristics in addition to its low cost.

4.2 Chemical Composition of Oxydtron

Nano cement in general, and Oxydtron is one of its types containing many nano oxides and nano carbides compounds, like Al_2O_3; TiO_2; Fe_2O_3; $CaCO_3$ and nanotubes or fiber, and copolymers such as styrene-butadiene; Vinyl acetate. The percentage of the copolymer is 10-20%. These ingredients depend on the type of nano cement [75,129]. The chemical composition of the Oxydtron used in this study is shown in Figure 4.1.

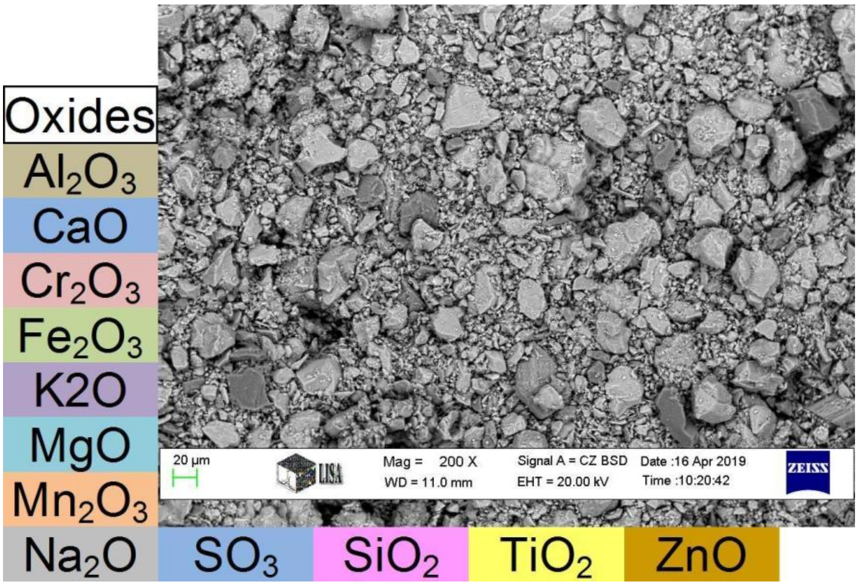


Figure 4.1. The chemical and granular composition of Oxydtron [75]

4.3 Appearance of Oxydtron

Oxydtron has a dark gray appearance due to contaminated silicate raw materials because its primary use is an additive to cement mixtures, as mentioned. The grey color and dark appearance of Oxydtron are not considered a limitation for use in the industry because most of the present additives change the appearance of the poly(vinyl chloride). Also, when comparing the dark appearance of the poly(vinyl chloride) containing Oxydtron with its high performance and environmental friendly effect, the demand for it will be high and growing. In my opinion, the producing company of Oxydtron could change the production technology by using less contaminated silicate raw materials, but it depends on the company's intention.

4.4 The Uses of Oxydtron

Unfortunately, all that I found through my search for Oxydtron references are using this material to improve concrete properties. I did not find anyone who used this nanocement as an additive for polymers, especially in enhancing flame retardation and thermal stability. For further clarification, many nano admixtures are added to the concrete mixture along with basic components (cement, water, aggregates) which can be added during the mixing process of the basic components in order to improve the properties of the concrete mixture. The improved properties vary according to the type of the admixture, where there are admixtures that improve the workability of the concrete and its durability, accelerate or slow the cohesion of concrete, another admixture type works on increasing the wear resistance of the concrete surface, and there are admixtures minimizing the amount of water needed ...etc. Oxydtron contains high-temperature oxides and carbonates that make it one of the alternative options for conventional flame retardants used today [75,129,131-133].

Chapter Five: Literature Survey

Poly(vinyl chloride) has a long and eventful history with many additives, starting with additives that transformed it into poly form polymers through additives that made it a flexible material, and additives that raised its heat and fire resistance value. As for the future perspective, the additives aim to reduce the risk of the poly(vinyl chloride) upon ignition by combining the additives with the combustion products, which are hydrogen chloride, and making this polymer safer. Millions of published studies have been done to improve poly(vinyl chloride) properties, which cannot be summarized in a short paragraph, so I will have to contend by mentioning the historical pathway of additives that have improved the properties of this polymer.

5.1 Traditional Additives

1872: Poly(vinyl chloride) was discovered by German chemist Eugen Baumann by accident after a long experimentation procedure, and published his work at Annals of chemistry and pharmacy [134].

1926: American chemist Waldo Lonsbury Semon who worked for the B.F. Goodrich Company mixed some additives to PVC to eliminate chlorine in order to obtain a polymer that could bind rubber to metal. But instead, he discovered plasticized poly(vinyl chloride) [135].

1929: I.G. Farben received a patent for using Amines as a stabilizer for poly(vinyl chloride) [136].

1933: Waldo Lonsbury Semon was awarded a patent for the use of phosphate and phthalate compounds to create a flexible, adaptable PVC adhesive compositions. Waldo used white lead and sodium silicate as heat stabilizers [137].

1934: Groff Frazier received first patent No. CA 346164 for using metal soaps as a stabilizer for poly(vinyl chloride) [138,137].

1937: Marion C.Reed and Groff Frasier received first patent No. US 2075543Afor using Cadmium laurate and other soaps as a heat stabilizer for poly(vinyl chloride) [139].

1939: Antimony oxide as a heat stabilizer was used by Arthur K. Doolittle according to the American parent No. US 2161026A [140]

1940: Yngve Victor received first patent No. US 2219463A for using Alkyl or aryl tin or lead as a stabilizer for poly(vinyl chloride) [141].

1941: Arthur K. Doolittle was used Sodium and calcium as heat stabilizer for poly(vinyl chloride) and received a patent No. US 2258243A [142].

1943: Yngve Victor received patent No. US 2307090A for using Organo lead compounds as a stabilizer for poly(vinyl chloride) [143].

1966: Robert A Buckley and Russo Nadine used a mixture of calcium salt, zinc salt, phosphorus compound, and sulphate or saccharin as a heat stabilizer for plasticized poly(vinyl chloride) [144]

1976: Robert G. Elcik prepared a fire retardant poly(vinyl chloride) film using a combination of magnesium hydroxide, zinc borate and antimony trioxide. The films extracted are especially useful in the preparation of vapor barrier constructions for use in the building trade [145].

5.2 Environmentally Friendly Additives

The discovery and use of new flame retardants and stabilizers containing heavy metals continued during the whole of the twentieth century, which led to environmental pollution, as this was not important to many manufacturers of these materials as much as it was essential to technological development and increased the financial resources of companies. But at the beginning of the twenty-first century, there was a revolution in environmental awareness all over the world, and calls increased to prevent the use of these environmentally harmful substances. Therefore, many studies have been published aimed to provide environmentally friendly alternatives.

2014: Li Nie presented an alternative environmentally friendly technology that provides a stabilized halogenated polymer, such as chlorinated polyvinyl chloride (CPVC), composition. This alternative technology consists of zeolite, C6 to C12 and metal carboxylate, as a heat stabilizer [146].

2014: Ugo Zucchelli presented an invention using Hypophosphites (aluminum hypophosphite, calcium hypophosphite, manganese hypophosphite, magnesium hypophosphite, zinc hypophosphite, barium hypophosphite) as a flame retardant for plasticized poly(vinyl chloride) that can fully substitute antimony trioxide or any other antimony-based compound in the same formulations. Ugo Zucchelli received a patent No. WO 2014013284A1 for his work [147].

2017: The effect of organic heat stabilizers such as uracil derivative (1,3-dimethyl-6-ami-nouracil; DAU) and eugenol has been investigated by Aran Asawakosinchai, Chanchira Jubsilp, Phattarin Mora, and Sarawut Rimdusit. The researchers compared the results of organic stabilizers with those made from lead, Ca/Zn. The results of thermal and mechanical properties of poly(vinyl chloride) with organic stabilizers addition were better than the properties in case of commercial stabilizers for the same addition percentages [148].

2020: The study of Korkusuz and Demir has been focused on a systematic comparison of the natural and non-toxic hydrothalcite thermal stabilization actions with high stabilizing performance organic stabilizers (mixed metal salts, maleimide and tri-nonyl phenyl phosphite). The results of the thermal tests showed a higher stabilizing performance of hydrotalcite compared to that of the thermal stabilizers in terms of the number of double bond conjugates, the concentration of polyene, the rate of formation of polyene and the change in color. The results are believed to contribute to the thermal stability of PVC by different stabilizers and blends, and an attempt has been made in this article to shed light on this issue [149].

2020: The researchers Bing Wang, Yi-heng Lu, and Yu-wei Lu modified the nanosized titanium dioxide (NT), calcium–zinc (Ca-Zn)*, dipentaerythritol (Dip) and organotin (OT) with butyl titanate (BT), coupling agent to synthesize a composite material and used as the strengthening agent for PVC. The results showed that, as a result of the BT relation which had a synergical impact on PVC, not only preserved the basic configuration of NT particles, the shaped PVC film also showed excellent thermal stability. They also noted that pentaerythritol has a stimulating effect on the release of CH_4 from PVC, and that the peak intensity of CO_2 is transferred to a high temperature zone, and there is no formation of hydroxyl or water, which means that the pathway of thermal degradation of PVC has changed and it is possible to inhibit the generation of aromatic hydrocarbons and dioxins [150].

Chapter Six: Knowledge Gap and Objectives

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.

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.

Chapter Seven: Experimental Procedure

This section includes the materials that were used and their specifications, the methods for preparing the samples, as well as the thermal tests performed on them, the standards that were used in the preparation and testing of these samples. Finally, the selection of the proper processing method which gives the best product.

7.1 Materials

The percentages of following primary materials used in this study illustrated in Table 7.1. The description of these materials as follows:

1. PVC suspension type S-5070 (under trademark Ongrovil®) produced and supplied by BorsodChemZrt., Hungary, with specifications shown in Table 7.2.
2. DOP (or DEHP), Bis(2-ethylhexyl- phthalate) plasticizer (ortho-structure) supplied by DEZA, a. s. CO., Valašské Meziříčí, Czech Republic. The specifications of this material is shown in Table 7.3.
3. Calcium-Zinc-based stabilizer (under trademark Newstab-50), which supplied by Betaquímica CO., Barcelona, Spain, with general specifications illustrated in Table 7.4.
4. Wax-E external lubricant (under trademark Licowax®E) supplied by Clariant International Ltd, Muttenz Switzerland, with general specifications shown in Table 7.5.
5. Oxydtron (type A) supplied by Bioekotech Hungary Kft. There is no official data available about Oxydtron specifications from the producer and supplier. Therefore, I will review the specifications of this material that I obtained through the tests that I have performed in later paragraphs mentions in the tests section.

Table 7.1. Materials used and their ratios

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

Table 7.2. Specifications of PVC type S-5070 (Ongrovil®) [151]

Parameters		Value
K-value		69-71
Volatile content (max.), %		0.3
Apparent density, kg/m^3		470-530
Particle size distribution, %	Above 0.250 mm (max.)	1
	Below 0.063 mm (max.)	5
Plasticizer absorption, % (min.)		30
Fish-eyes, pcs/dm^2 (max.)		10
Number of impurities, pcs/9dm^2 (max.)		20
Residual vinyl-chloride content, mg/kg (max.)		1
Specific vol. resistance at 23°C, Ω x cm (min.)		5×10^{13}
Glass transition temperature, °C		75-85
Density of melted solid PVC resin, g/cm^3		1.41
Flow temperature, °C		140

Table 7.3. Specifications of Dioctyl Phthalate (DOP) plasticizer [152]

Parameters	Value
Melting temperature, °C	-50
Boiling temperature, °C	384
Flash point, °C	207
Flame point, °C	233
State at 20 °C	Viscous liquid

Table 7.4. Specifications of Newstab-50 stabilizer [153]

Properties	Value		
Viscosity at 20°C, cps	Minimum	Maximum	Average
	220	280	250
Density at 20°C, g/cm^3	0.89	0.99	0.94
Ca content, %	0.81-0.83		
Zn content, %	0.64-0.66		
Appearance	White powder		

Table 7.5. Specifications and general properties of Wax-E lubricant [154]

Characteristics	Value	Test method
Drop point, °C	80	DGF-M-III 3
Flash point, °C	160	DIN 51758
Viscosity, mPa·s	30	DGF-M-III 8 at 100°C
Density, g/cm³	1.01-1,03	DIN 53479 at 20°C
Appearance	Light yellow flakes	QM-AA-634

7.2 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.

7.3 Mixing Procedure

There are two types of mixing processes used in this study: primary and secondary mixing as shown in Figure 7.1.

7.3.1 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 9 (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.

7.3.2 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 5wt.%). This new mixture is mixed by a small electrical mixer for one minute to uniformly dispersed and homogenized Oxydtron into the mixture.

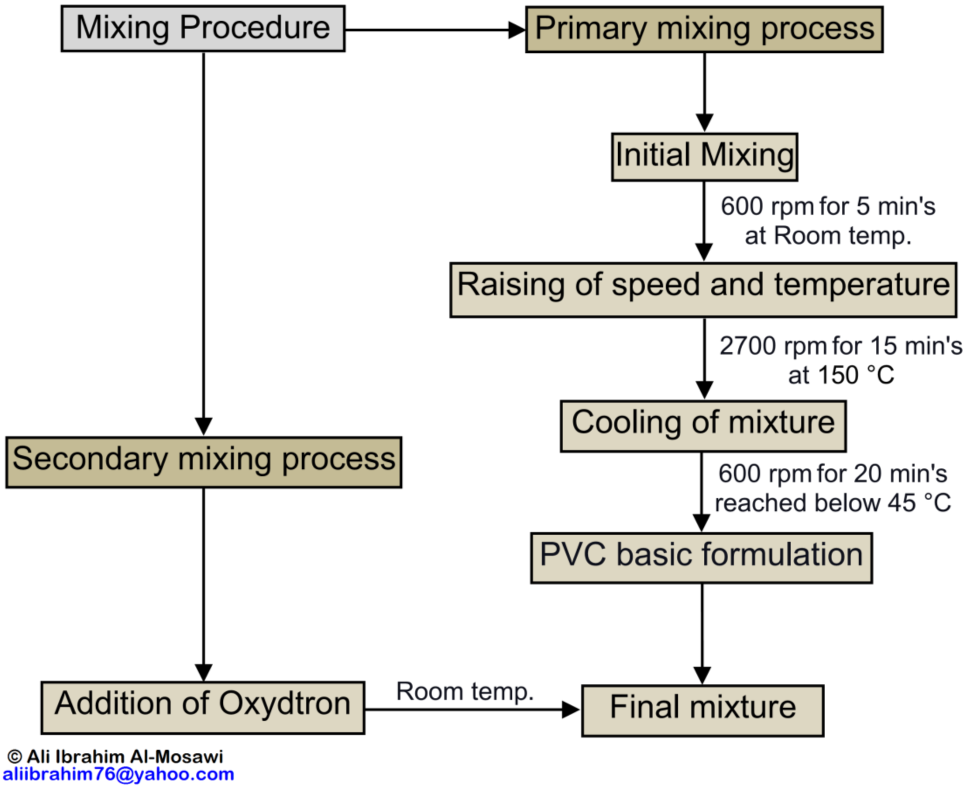


Figure 7.1. Scheme of Mixing Procedure

7.4 Samples Preparation

In all tests, four blends of plasticized poly(vinyl chloride) had been made as shown in Table 7.6.

Table 7.6. Components of test samples

Sample No.	Content
Sample 1	Poly(vinyl chloride) basic formulation
Sample 2	Poly(vinyl chloride) + 1wt.% Oxydtron
Sample 3	Poly(vinyl chloride) + 3wt.% Oxydtron
Sample 4	Poly(vinyl chloride) + 5wt.% Oxydtron

All samples have been prepared according to ISO standards, and all preparation steps have been completed at BorsodChem Zrt., Hungary as follows:

1. Static Heat Stability Samples: 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 as shown in Figure 7.2.

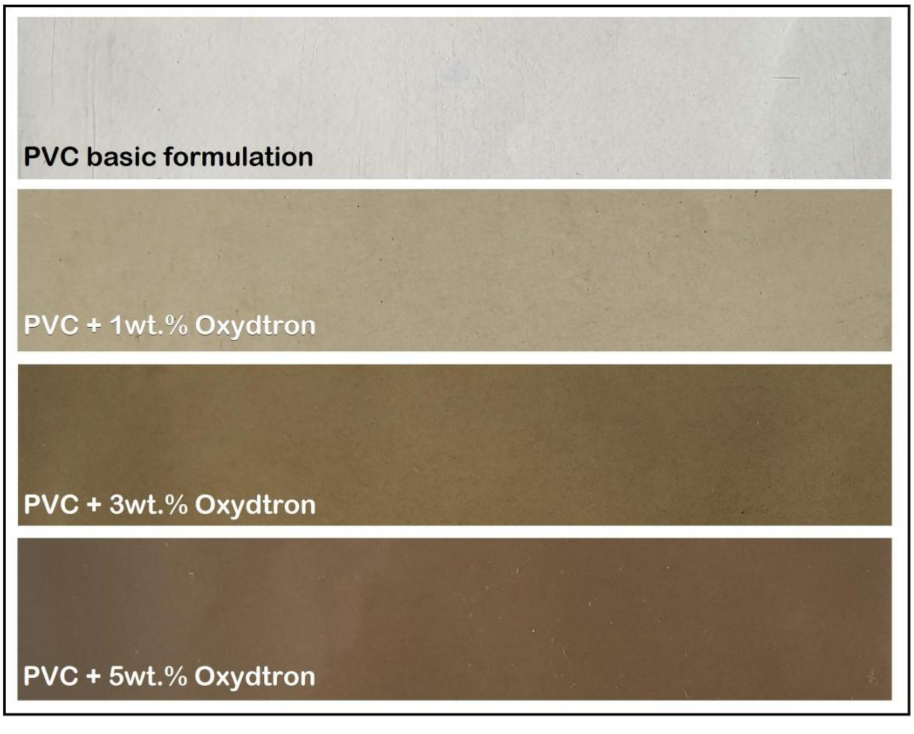


Figure 7.2. Samples of static heat stability test

2. Limiting Oxygen Index Samples (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 ºC temperature and 60 rpm speed at uniform conditions (pressure, temperature, and compression). L.O.I samples are shown in Figure 7.3.
3. Differential Scanning Calorimetry Test Samples (DSC): A 10 milligrams weight sample from poly(vinyl chloride) containing Oxydtron additives. These 10 milligrams have been cut from L.O.I test samples.
4. Color Change Test Samples: Samples of static heat stability test where used.

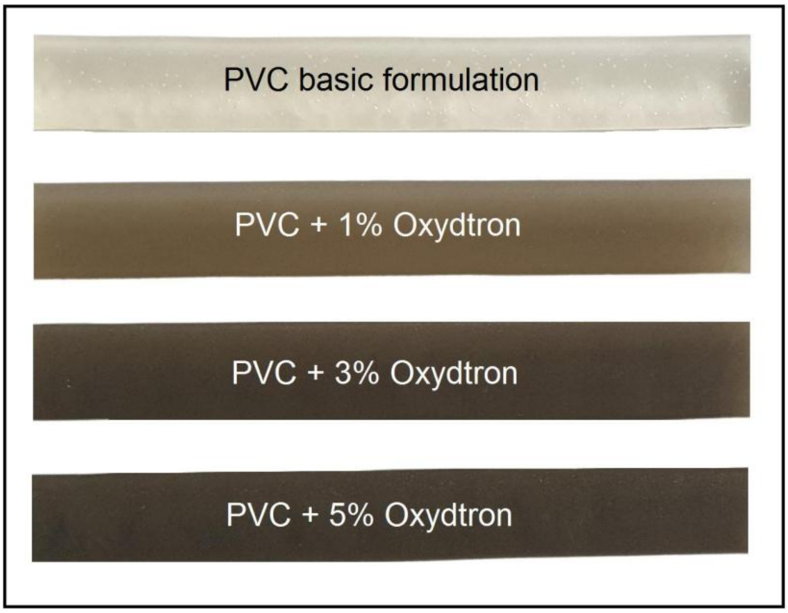


Figure 7.3. Samples for Limiting Oxygen Index test

5. Dynamic Mechanical Analysis Test Samples (DMA): The DMA test samples were a strips (see Figure 7.4) fabricated by using extrusion machine type GÖTTFERT at 170 ºC temperature and 60 rpm speed at uniform conditions (pressure, temperature).

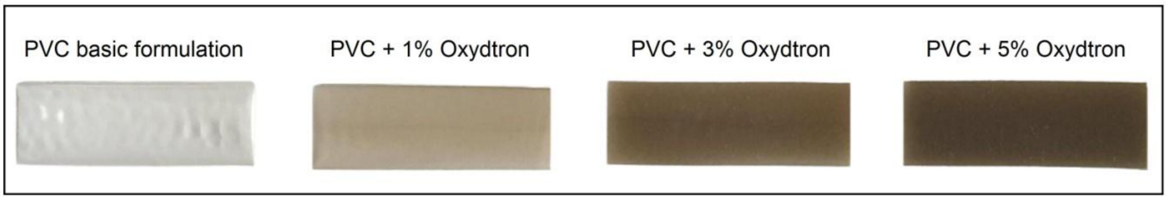


Figure 7.4. Samples of DMA test

6. **6.** Congo-Red Test Samples: 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 shown in Figure 7.5 at uniform conditions, as listed in Table 7.7.
7. **7.** Capillary Rheometry Analysis Samples: the samples were produced as pellets with the same procedure, dimensions, and conditions of congo-red test samples.
8. **8.** Dehydrochlorination Test Samples: 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.

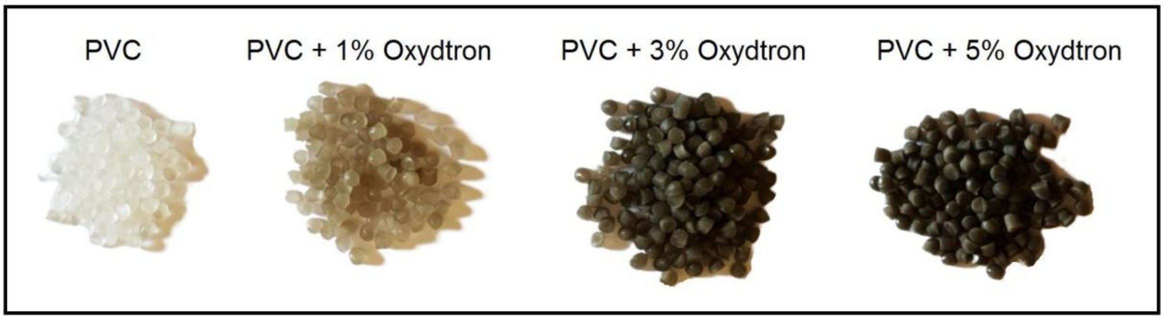


Figure 7.5. Samples of congo-red, capillary rheometry, and dehydrochlorination

Table 7.7. Processing conditions of congo-red, capillary rheometry, and dehydrochlorination test samples

Processing temperature, ºC				Pressure, bar	Speed, rpm
Zone 1	Zone 2	Zone 3	Zone 4		
125	130	135	140	100	60

7.5 The Tests

The tests were completed at BorsodChem Zrt. are: Static heat stability, L.O.I, congo-red, DSC, DMA, dehydrochlorination, capillary rheometry analysis, color change, FLIR analysis, and FTIR. The tests completed at the University of Miskolc are: SEM, Oxides analysis, and particle size distribution analysis. The devices used are periodically calibrated by the company and the university to provide maximum test accuracy.

7.5.1 Static Heat Stability Test

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 305:2019 standard [155]. This test finished within 2 hrs at 190°C, where the samples move out of the device with velocity 2 mm/min. This test's principle is based on the gradual and sustained exposure of polymer strips at a constant temperature tunnel oven maintained at a constant temperature. The gradual color change occurring over time in the test samples (see Figure 7.6) provides an evaluation of the products' long-term thermal stability [156].

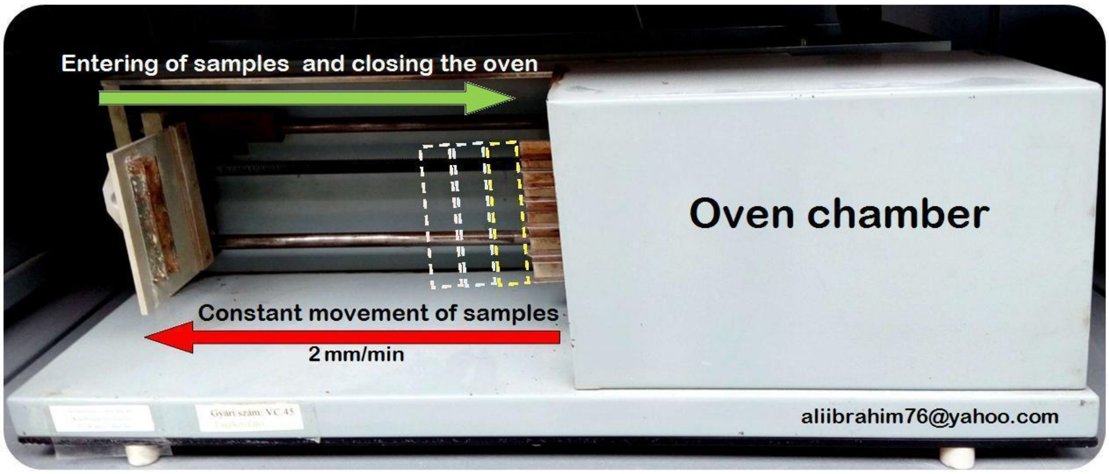


Figure 7.6. Heat stability testing oven (Stabilimetr device)

7.5.2 Limiting Oxygen Index Test

L.O.I test was done according to ISO 4589-2 standard [157] by using a Stanton Redcroft FTA flammability unit at BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology. L.O.I unit shown in Figure 7.7. In L.O.I test; the poly(vinyl chloride) sample is placed into a glass cylinder opened from the top and connected from the bottom by the device's air tunnel. When the test begins, the device injects a mixture of oxygen and nitrogen gas into glass cylinder containing the poly(vinyl chloride) sample for developing and speeding up the ignition process. The time required to complete this test is 3 minutes, and if the burning sample extinguishes before this time, the test is repeated, where the percentage of oxygen is increased. However, if the opposite thing happens, where the test is in its early stages, and the ignition continues and exceeds a period of 3 minutes, then in this case, the test is repeated with the reduction of the oxygen level. This adjusts the oxygen concentration until the sample supports combustion. The reported oxygen concentration is the volume percentage, mostly 0.1% O_2 repeatability. Downward flaming discharge can be deemed the safest case for a substance with L.O.I. of less than 21 percent. Still, materials with L.O.I. percentage exceed 21 percent also need to be considered flammable [150]. The limiting oxygen index can be determined by using the following formula:

$$L.O.I = \frac{O_2}{O_2 + N_2} \times 100 \tag{15}$$

Where O_2 and N_2 represent the minimum concentrations of inflow oxygen and nitrogen, respectively.

Figure 7.7. Stanton Redcroft FTA flammability unit

7.5.3 Congo-Red Test

Congo-red test: was done by using a Julabo MC-12 circulator oil bath at 200°C shown in Figure 7.8 according to ISO 182-1:1990(E) standard [159], and found also at BorsodChem Zrt., Hungary; Laboratory of Vinyl Technology. In congo-red test, the poly(vinyl chloride) sample in particle form is placed into glass test tube with a quantity reached to 50mm. Then the glass tube is placed inside the device; and the poly(vinyl chloride) sample is completely immersed in the oil bath (50mm). The test begins at a uniform and stable temperature (200°C) as mentioned, until the color of the paper changes due to increased poly(vinyl chloride) degradation and HCl release, where the beginning and ending time of discoloration is recorded.

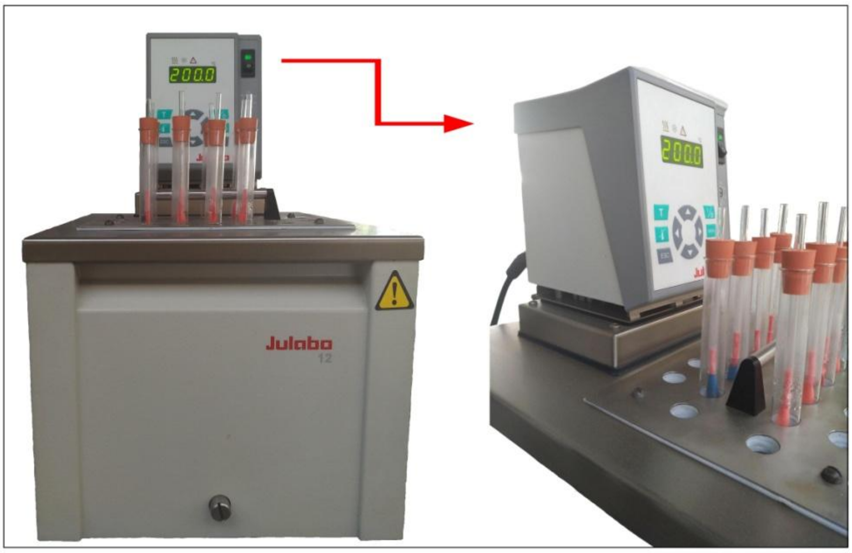
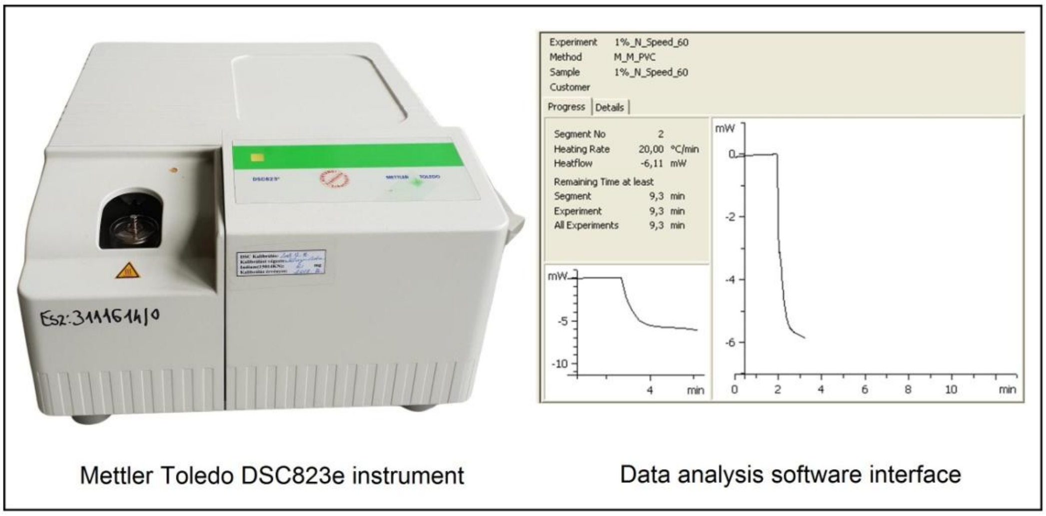


Figure 7.8. Julabo MC-12 circulator oil bath, and the test paper appears in orange and blue color

7.5.4 Differential Scanning Calorimetry Test (DSC)

The Mettler Toledo DSC823^e instrument was used to complete the DSC test to measure the gelation or fusion grade (G.G) by following the ISO 11357-2 standard [160] and using a heating profile of 30 °C to 240 °C with a heating rate 20°C/min. The instrument found at BorsodChem Zrt., Hungary. DSC is used to quantify thermal effects, and analyze thermal processes in order to classify, recognize and simplify the comparison between different materials' thermal behaviors. The transition measurements such as crystallization, glass transition, and melting can be made by DSC. In addition to what has been mentioned, the chemical reactions likes specific heat capacity, heat history, purity analysis, and thermal curing are observable and can be analyzed [161]. Figure 7.9 represent the Mettler Toledo DSC823^e instrument and data analysis software interface.



Experiment 1%_N_Speed_60
Method M_M_PVC
Sample 1%_N_Speed_60
Customer

Segment No 2
Heating Rate 20,00 °C/min
Heatflow -6,11 mW
Remaining Time at least
Segment 9,3 min
Experiment 9,3 min
All Experiments 9,3 min

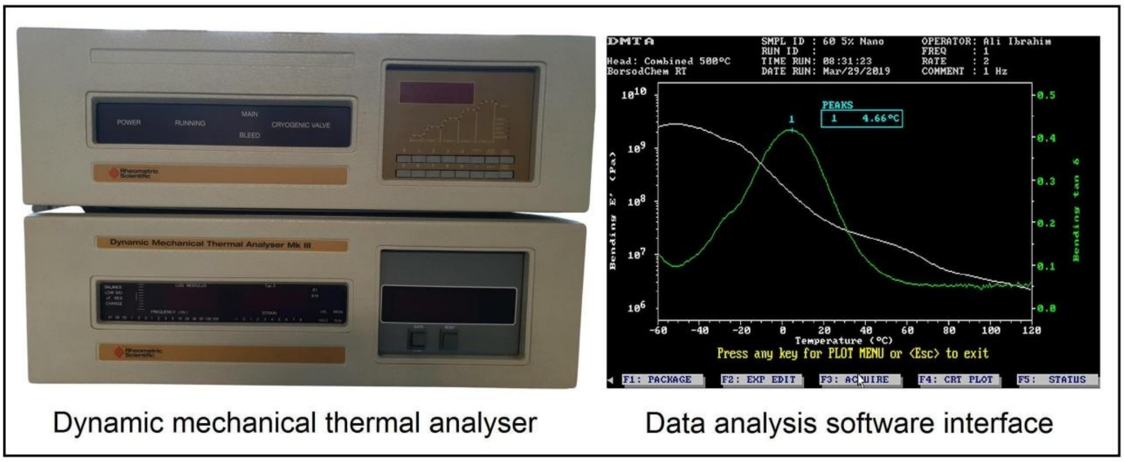
Mettler Toledo DSC823e instrument

Data analysis software interface

Figure 7.9. Mettler Toledo DSC823^{e} instrument and data analysis software interface

7.5.5 Dynamic Mechanical Analysis Test

This test was done according to ISO 6721-11:2012 standard [162] by using dynamic mechanical thermal analyser MK III manufactured by Rheometric Scientific, Inc. and found at BorsodChem Zrt., Hungary, used for testing the samples. The temperature range is -60°C to 120°C with heating rate 2°C per min and the test finished within 2 hrs. The DMA analyser shown in Figure 7.10.



```
Head: Combined 500°C   SMPL ID  : 60 5% Nano     OPERATOR: Ali Ibrahim
BorsodChem RT          RUN ID   :                FREQ    : 1
                       TIME RUN: 08:31:23        RATE    : 2
                       DATE RUN: Mar/29/2019     COMMENT : 1 Hz
PEAKS
 1    4.66°C
Press any key for PLOT MENU or <Esc> to exit
```

Dynamic mechanical thermal analyser

Data analysis software interface

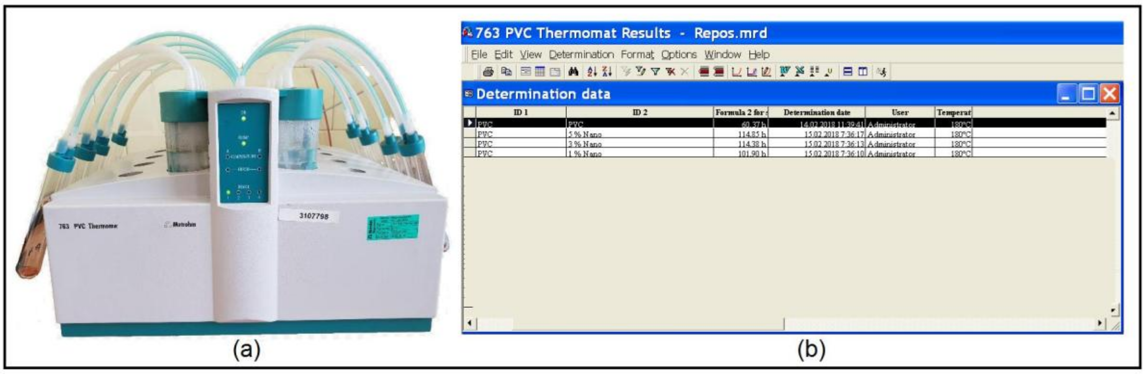
Figure 7.10. Dynamic mechanical thermal analyser MK III

7.5.6 Dehydrochlorination Test

Two methods were used to calculate the dehydrochlorination rates as follows:

7.5.6.1 Standard Method

Dehydrochlorination rates have been measured by Metrohm 763 Thermomat (see Figure 7.11, a) found also at BorsodChem Zrt., Hungary. This test was carried out according to ISO 182-3:1993 standard [163] at three different temperatures, which are: 170 ºC, 180 ºC, and 190 ºC. This method involves exposing the poly(vinyl chloride) samples inside device to high temperatures to measure the stability time (the time until poly(vinyl chloride) begins to release HCl) [164]. Stability time determined as time to 60 µS/cm conductivity, which means about 0.9% conversion of dehydrochlorination. Time axis intercept is the induction time.



ID 1	ID 2	Formula 2 for	Determination date	User	Temperat
PVC	PVC	60.37 h	14.02.2018 11:39:41	Administrator	180°C
PVC	5 % Nano	114.85 h	15.02.2018 7:36:17	Administrator	180°C
PVC	3 % Nano	114.38 h	15.02.2018 7:36:13	Administrator	180°C
PVC	1 % Nano	101.90 h	15.02.2018 7:36:10	Administrator	180°C

Figure 7.11. (a) Metrohm 763 Thermomat, and (b) determination data of dehydrochlorination

7.5.6.2 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 (see Figure 7.11, b). 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:

$$\lg(c) = -1.05788 + 0.9882 \times \lg(k) + 0.003988 \times (\lg(k))^2 \qquad (16)$$

Where:
c: HCl concentration in mg/l.

k: Specific conductivity in µS/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:

$$\mathrm{k} = \mathrm{m}_{\mathrm{HCl}} / 0.584 \times \mathrm{m}_{\mathrm{PVC}} \qquad (17)$$

The four columns of the result files in the data conversion program are:

1. Time in seconds in steps given by the program (20 or 30 sec.).
2. Interpolated conductivity in µS/cm.
3. HCl evolved in mg, not the concentration but in the 50ml water.
4. Conversion in percent (after inputting the PVC in mg for the program).

The difference between the standard method and the Novel method in calculating the dehydrochlorination rate is shown in Figure 7.12.

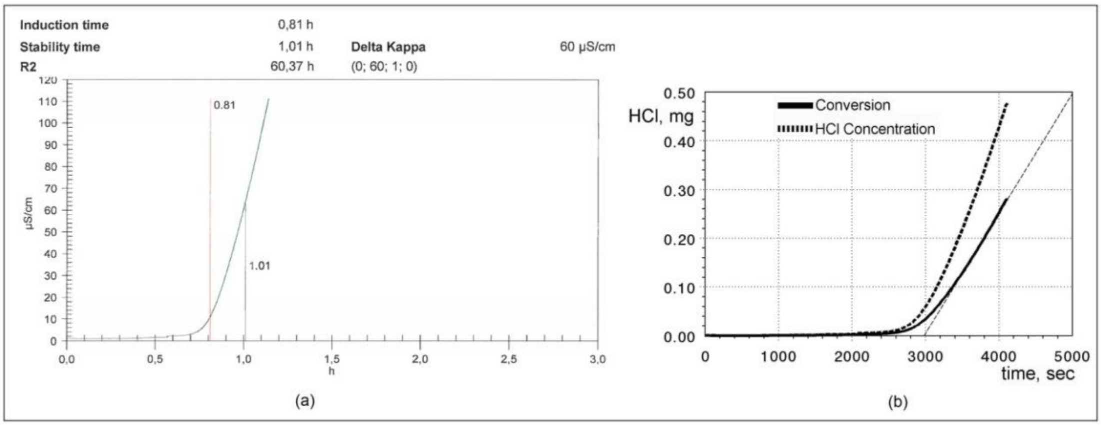


Figure 7.12. The standard method (a) is compared to the novel method (b) to calculate the dehydrochlorination rate

7.5.7 Color Change Measurement

Datacolor spectraflash SF 300 spectrophotometer was used to analyze the color change for the samples of static heat stability test. The spectrophotometer is found at BorsodChem Zrt., Hungary. This test was done according to ISO 11664-1 standard [165]. This test's working principle depends on measuring the transmitting or reflecting percentage of the light for a specific wavelength within the ranges

DOI: 10.14750/ME.2021.039

(360-740 nm) in the visible spectrum. The Color recordings will appear as L*A*B* coordinates [166]. Datacolor spectraflash SF 300 shown in Figure 7.13.

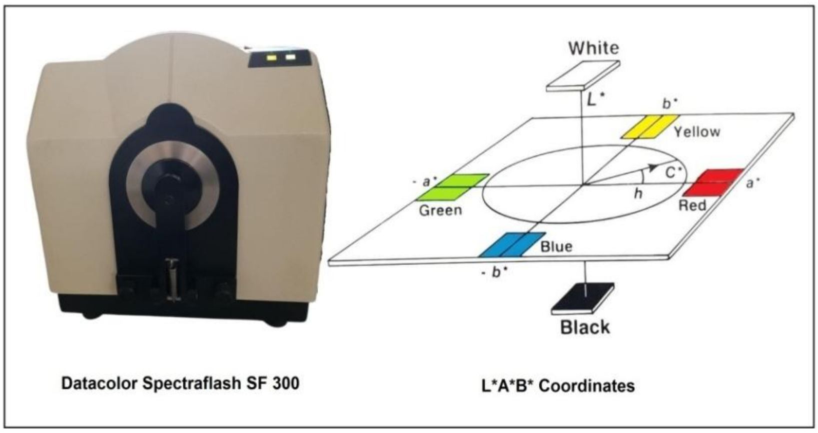


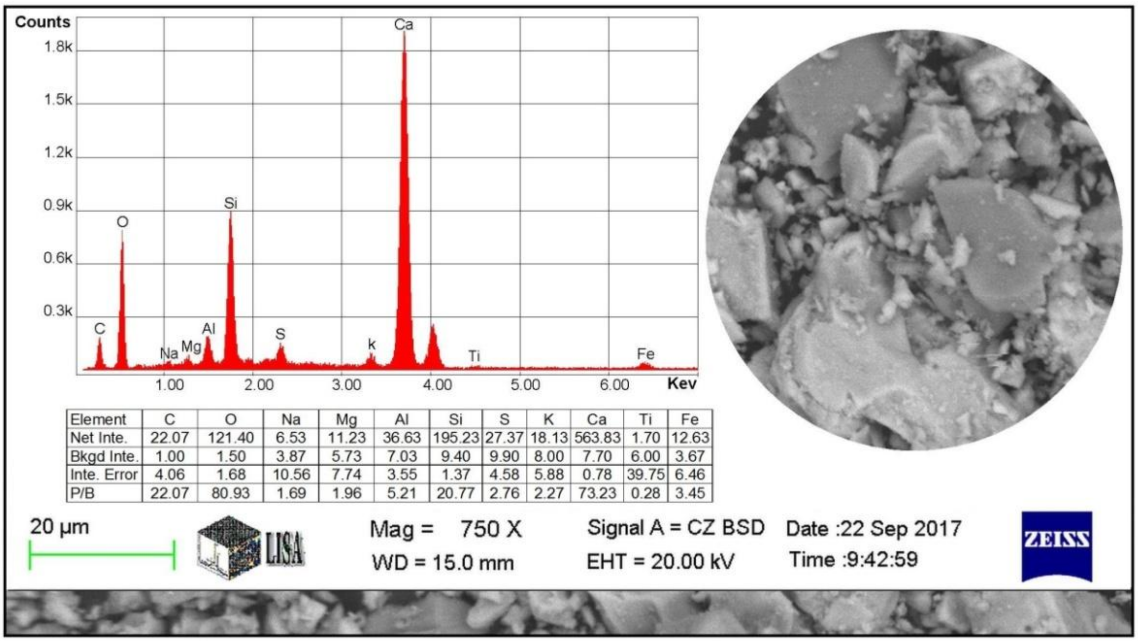
Figure 7.13. Datacolor spectraflash SF 300 and L*A*B* coordinates

7.5.8 Capillary Rheometry Analysis

This test was done according to ISO 11443:2014 standard [167] at different temperatures rang (160 ºC, 170 ºC, and 180 ºC) and different dies lengths (15, 30, and 45mm) with (3mm) die hole diameter for all lengths. Laboratory extruder type Göttfert Extrusiometer G20 was used to complete this test with processing speed 60 rpm. Capillaries rheometer tests are often achieved by applying pressure above the capillary inlet. Therefore, an additional pressure drop at the entrance of the die hides the true pressure drop along the capillary, where the flowing material goes from a wide reservoir (the main cylinder or barrel) to a narrow capillary, possibly also generating turbulence. Assuming that the same extra pressure drop occurs with different capillary lengths (but maintaining a constant barrel and capillary diameter and inlet shape), the pressure reading can be corrected and the true pressure drop can be estimated much more accurately. The state called Bagley correction.

7.5.9 Scanning Electron Microscopy

SEM was used to analyze the chemical composition and structure analysis of Oxydtron as shown in Figure 7.14. 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, Hungary.



Element	C	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
Net Inte.	22.07	121.40	6.53	11.23	36.63	195.23	27.37	18.13	563.83	1.70	12.63
Bkgd Inte.	1.00	1.50	3.87	5.73	7.03	9.40	9.90	8.00	7.70	6.00	3.67
Inte. Error	4.06	1.68	10.56	7.74	3.55	1.37	4.58	5.88	0.78	39.75	6.46
P/B	22.07	80.93	1.69	1.96	5.21	20.77	2.76	2.27	73.23	0.28	3.45

Mag = 750 X
WD = 15.0 mm
Signal A = CZ BSD
EHT = 20.00 kV
Date :22 Sep 2017
Time :9:42:59

Figure 7.14. SEM- EDAX analysis for Oxydtron

7.5.10 Fourier Transform Infrared Analysis (FTIR)

FTIR analysis was completed by using A Shimadzu IRTracer-100 device found at BorsodChem Zrt., Hungary. The analysis of chemical compounds of the Oxydtron shown in Figure 7.15 and Table 7.8. There are many active groups in this analysis which represents aldehyde compounds, ketone, amines, polyamides, and alcohols or aromatic or phenolic compounds. All of these compounds can form double and tie triple bonds and aromatic rings with PVC causing a stronger material.

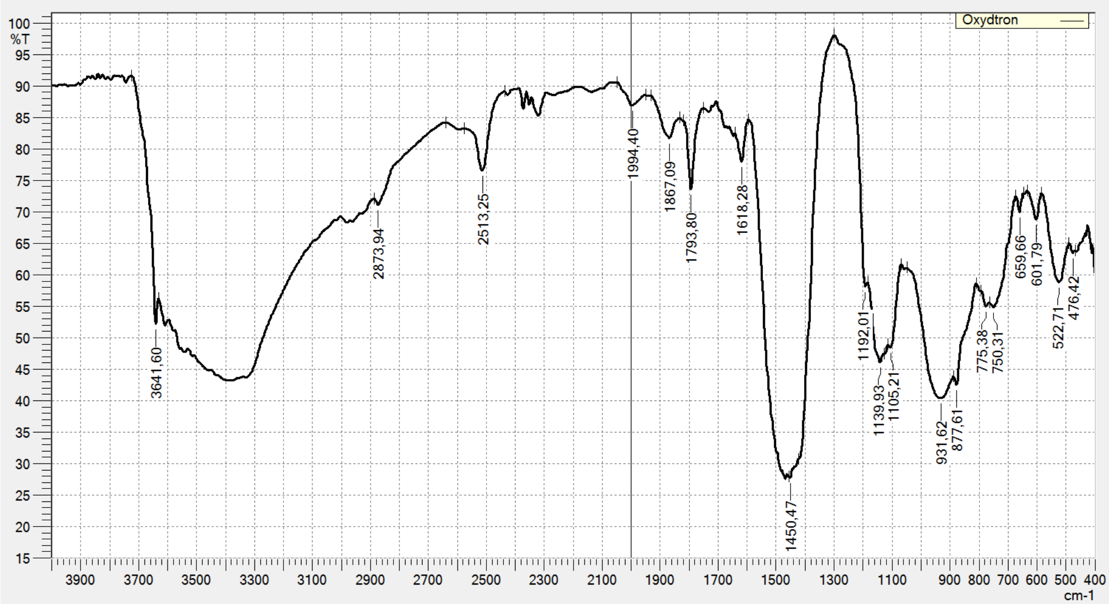


Figure 7.15. FTIR analysis for Oxydtron

Table 7.8. The IR active groups and positive numbers for Oxydtron powder

Wave number	Active group
(3641.60) cm^{-1}	OH
(2873.94) cm^{-1}	CH
(2513.25) cm^{-1}	C-H
(1994.40-1793.80) cm^{-1}	C = O
(1618.28) cm^{-1}	C = C
(1450.47) cm^{-1}	$-CH_2$
(1192.01-1105.21) cm^{-1}	C–O-H or C–O-R
(931.62-659.66) cm^{-1}	= CH

7.5.11 Oxides Analysis

During the experiments an axially viewed ICP-AES spectrometer, made by Varian Inc. was used. The results of the analysis are listed in Table 7.9. From this analysis we can see that Oxydtron consists of some mineral components such as calcium oxide, silicates and aluminates; so these components play important roles during the preparation processing of poly(vinyl chloride). ICP-OES spectrometer is at the institute of chemistry, University of Miskolc, Hungary.

Table 7.9. ICP-OES chemical composition analysis of Oxydtron

Oxide	Ratio, wt%	Element	Ratio, wt%
Al_2O_3	4.47	Al	2.37
CaO	58.0	Ca	41.4
Cr_2O_3	0.006	Cr	0.004
Fe_2O_3	2.67	Fe	1.87
K_2O	0.78	K	0.65
MgO	1.20	Mg	0.72
Mn_2O_3	0.05	Mn	0.04
Na_2O	0.31	Na	0.23
SO_3	2.50	S	1.00
SiO_2	21.44	Si	10.0
SrO	0.093	Sr	0.079
TiO_2	0.274	Ti	0.164
ZnO	0.138	Zn	0.111

7.5.12 Particle Size Distribution Analysis (PSD)

HORIBA LA-950V2 laser particle size analyzer was used for analyze particle size distribution gradient as shown in Figure 7.16.

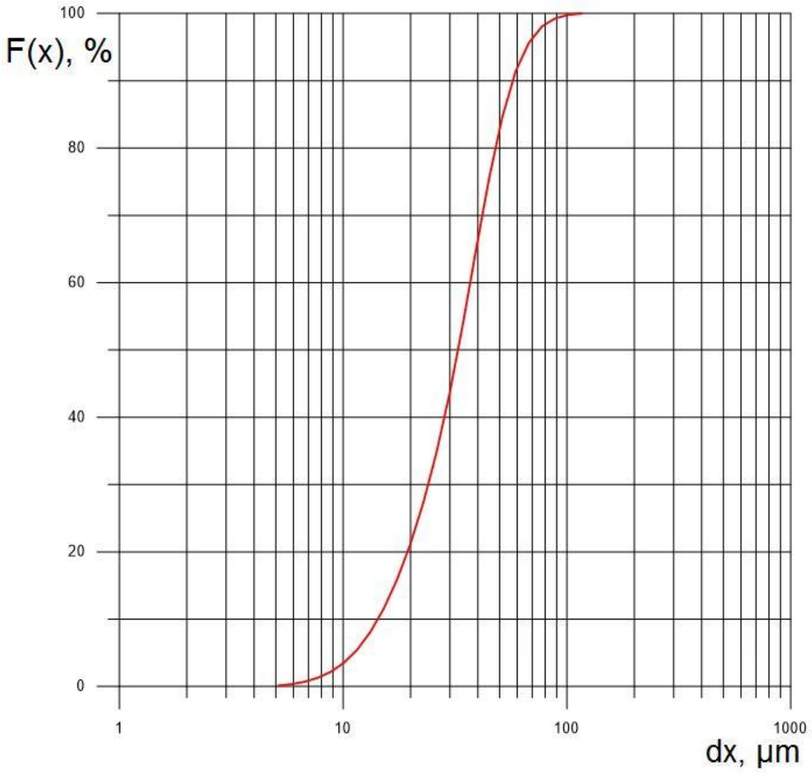


Figure 7.16. Particle size distribution analysis for Oxydtron

7.5.13 FLIR Thermal Gradient Image Analysis

Thermal analysis for L.O.I extruded and rolled samples using a thermal imaging camera (FLIR Systems) to determine the thermal gradient before and after the addition of Oxydtron and the effect of these additions on the heat affected zone (HAZ). Image and object parameters of this analysis shown in Table 7.10.

Table 7.10. Image and object parameters of FLIR analysis

Parameter	Description/ Value
Camera Model	FLIR SC660
Emissivity	0.5
Reflected apparent temperature	20 °C
Object distance	1.0 m

Chapter Eight: Results and Discussion

This section will review what we got from the results after completing the tests on plasticized poly(vinyl chloride) containing Oxydtron. And also my interpretation and analysis of these results.

8.1 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 8.1. The best optimum L.O.I increment is obtained with extrusion samples because the operating conditions (temperature, pressure, and time) are controlled uniformly. These results prove that the L.O.I is a process-dependent property, and this is being confirmed for the first time [121]. From the first pair of bars in this figure, we can see that the poly(vinyl chloride) basic formulation has a low L.O.I value (22.2% and 21.6%) for extrusion and rolling processing, respectively. Even though the flame resistance of poly(vinyl chloride) is considered high compared to other polymers, but this behavior is normal due to the low flame resistance of polymers in general, which is caused by the structure of these materials (especially organic) therefore it will ignite easily and rapidly when exposed to direct fire [6,126]. Therefore, the simple and optimum solution to improve the flame retarding of polymers at high temperatures by adding additives. These additives can be used as fillers or coating layers depending on the application for which the material is used [121,168].

This improvement in flame retardation can be clearly seen in the second pair of bars where the value of L.O.I of poly(vinyl chloride) was increased to (23.4% and 22.3%) for extrusion and rolling processing, respectively after adding 1% wt. Oxydtron. The flame retardation of poly(vinyl chloride) is increasingly rising with increasing of Oxydtron percentage additives, where we can note from the third pair of bars that L.O.I for poly(vinyl chloride) reached to (25.5% and 24.8%) after adding 3% Oxydtron; and the optimum L.O.I value was obtained by 5% Oxydtron addition (27.8% and 26.4%) as shown in fourth two bars; where the flame retardation improvement rate reached to 25.22% (for extrusion) and 22.22% (for rolling) more than poly(vinyl chloride) basic formulation.

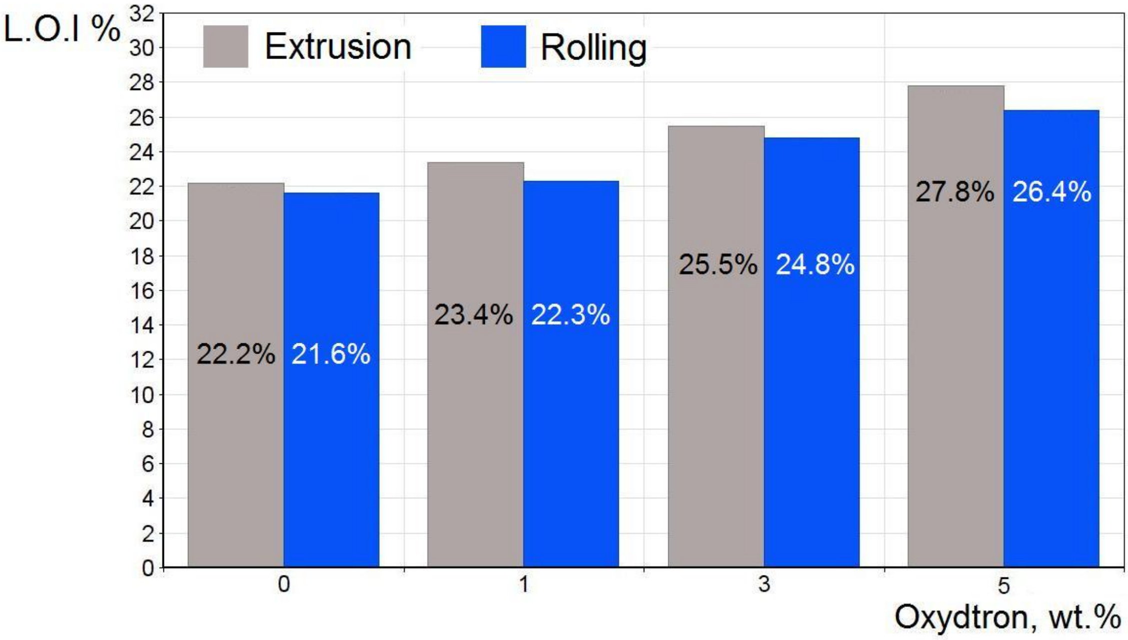


Figure 8.1. Limiting oxygen index (L.O.I) test results for plasticized poly(vinyl chloride) containing Oxydtron

This behavior of flame retarding can be explained by understanding the working mechanism of Oxydtron as flame retardant which does not depend on the changes that occur in its structure when exposed to high temperatures (as with conventional flame retardants) but depends on creating additional stabilizing synergistic action with the original stabilizer as were discovered that the Oxydtron is an excellent polymer stabilizer and proved by the thermal tests. This additional and unexpected stabilizing synergistic behavior is due to Oxydtron's composition which consists of many compounds such as calcium carbonate ($CaCO_3$) which is considered as a universal stabilizer for poly(vinyl chloride) and also silicon dioxide (SiO_2) in addition to many other compounds. These oxides and carbonates will act as a synergist agent with the original stabilizer leading to increase the thermal stability of poly(vinyl chloride); where the trio system materials "Original stabilizer-Silicon dioxide-Calcium carbonate" will effectively form a physical barrier against degradation of poly(vinyl chloride) structure. On the other hand, calcium carbonate is a flame retardant agent, so its presence within the unique structure of Oxydtron helps to increase the flame resistance of poly(vinyl chloride). This stabilizing mechanism is not achievable with traditional flame retardants, so without flame, it cannot act as a flame retardant, instead that these flame retardants will work only as fillers that can change the flame resistance of poly(vinyl chloride) slightly. Also, many of the oxides included in the composition of Oxydtron can interact and form other compounds that reduce the flame reactions and act as a stabilizer. The ability of the compound to dissociate and react depends on the combustion temperature.

Table 8.1 represents improvement percentage of L.O.I results for plasticized poly(vinyl chloride) containing Oxydtron.

Table 8.1. Improvement percentage of L.O.I results for plasticized poly(vinyl chloride) containing Oxydtron

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

8.2 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 8.2 which represent the behavior of plasticized poly(vinyl chloride) containing Oxydtron under static heat stability test at 190°C. It can be seen from this figure below that the color of poly(vinyl chloride) will change very rapidly with different gradients from transparent to dark depending on the time period of exposure to heat. This change is very rapid because of the low thermal resistance of poly(vinyl chloride) compared with the other materials like metals and ceramics; where the color change started from the transparent appearance to pale yellow, and then turns yellowish orange, and then turn to yellowish red, then change the appearance to pale red, then to dark red, and then brown, until it becomes completely dark (black) at the end of the test [109,126,148,156]. In general, it is not possible to distinguish between all these chromatic gradients with human eyes only, so a spectrophotometer device was used for this purpose [148,9].

Figure 8.2. Static heat stability test at 190°C for plasticized poly(vinyl chloride) containing Oxydtron (OX symbol)

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) as we mentioned above; where the Oxydtron will decrease the tendency of poly(vinyl chloride) discoloration. Also using of Oxydtron as a filler will improve the thermal resistance of poly(vinyl chloride) and increase the efficiency of original stabilizer, it is like forming a kind of synergistic action between them, which is reflected in the reduction of the degradation process. The discoloration resistance of poly(vinyl chloride) will increase by increasing the percentage of Oxydtron additives.

8.3 Color Change Measurement

Figure 8.3 shows the yellowing behavior (Δb*) 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 and it is a normal behavior due to low thermal stability at elevated temperatures for poly(vinyl chloride) and other polymers in general [170,171]. The yellowish change is increased by increasing the period of exposure to heat until the yellowing degree starts to decrease and color gradients are shifted towards the darker appearance and then the color becomes completely black. At this point, it can be said that the total breakdown of poly(vinyl chloride) has occurred [172-174]. After adding Oxydtron to poly(vinyl chloride), the yellowing is greatly reduced and depends on the percentage of Oxydtron additive to reach a peak of 5% Oxydtron; in addition the transformation period to dark color has been extended. This means that poly(vinyl chloride)'s tendency to degrade is greatly reduced.

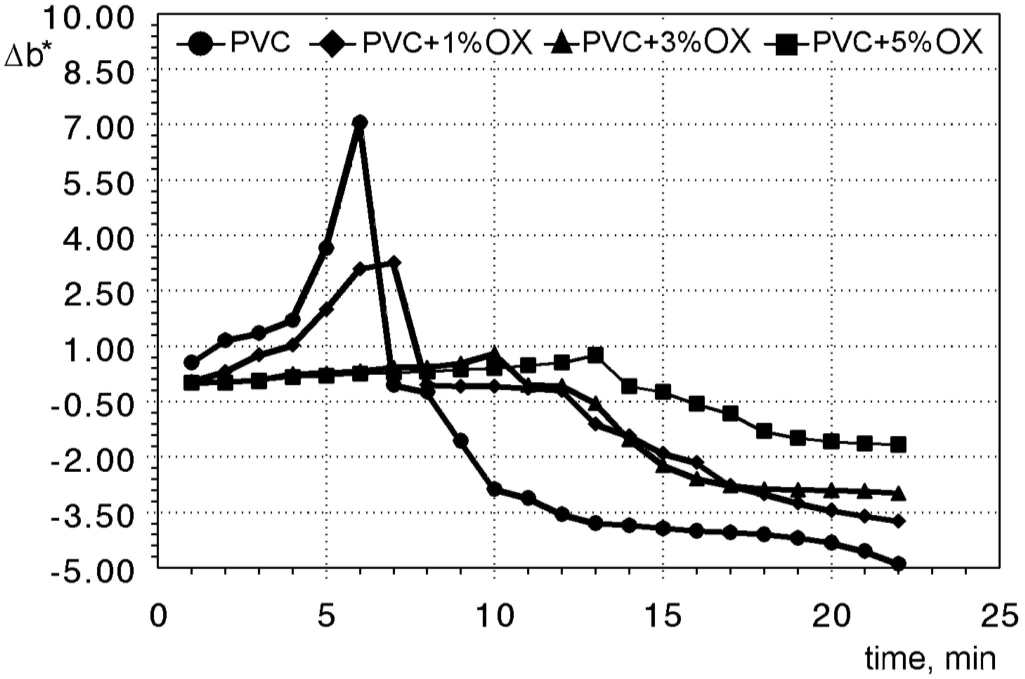


Figure 8.3. Detecting the yellowish changes of plasticized poly(vinyl chloride) containing Oxydtron (OX) for static heat stability samples tested at 190°C

Figure 8.4 represents the lightness changes (ΔL*) of plasticized poly(vinyl chloride) as a function of Oxydtron additives. We can observe from this figure, 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 more darker appearance until becomes fully black by constantly exposed to high temperatures. This is considered as a normal behavior for poly(vinyl chloride) due to low thermal resistance [171]. 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 longer time at the same temperature range and period, where the lightness appearance decreases gradually and not sharply until an optimal lightness curve is obtained at 5% Oxydtron.

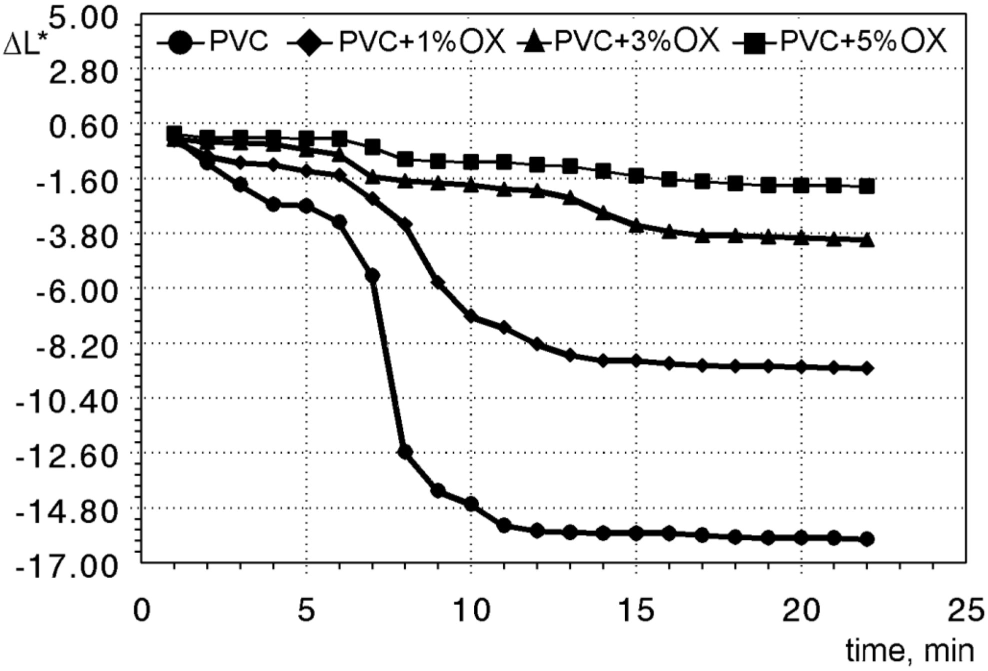


Figure 8.4. Lightness changes of plasticized poly(vinyl chloride) as a function of Oxydtron (OX) additives for static heat stability samples tested at 190°C

8.4 Congo-Red Test

I have noticed from Figure 8.5 which represents the congo-red test for plasticized poly(vinyl chloride) containing Oxydtron 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 [116,175]. But after adding Oxydtron the stability of poly(vinyl chloride) has been improved, where this behavior is the outcome of the synergistic action of Oxydtron with Newstab stabilizer which is calcium-zinc based stabilizer as mentioned and this synergistic action will increase the stability of poly(vinyl chloride) against discoloration and reduced the chlorine release. 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. This means the release of hydrochloric acid (HCl) has been reduced as a result of the thermal stability improvement of poly(vinyl chloride) structure, which will reduce the degradation rate as a final result. The optimum result obtained by congo-red test was with 5% Oxydtron addition where the time was 86.8% longer than poly(vinyl chloride) of basic formulation. Table 8.2 represents a summary of the improvements in discoloration period for plasticized poly(vinyl chloride) containing Oxydtron.

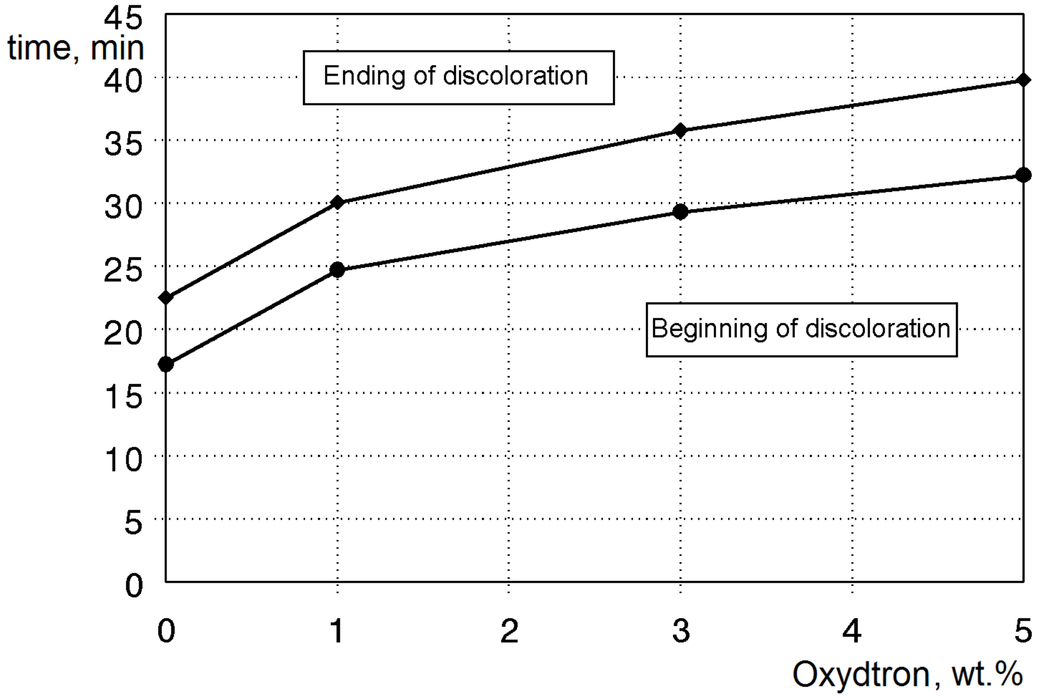


Figure 8.5. Beginning and ending of discoloration in congo-red test for plasticized poly(vinyl chloride) containing Oxydtron at 200°C

Table 8.2. Extended discoloration period for plasticized poly(vinyl chloride) containing Oxydtron

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

8.5 Differential Scanning Calorimetry Measurements (DSC)

Figure 30 represents the DSC measurements for extruded and rolled plasticized poly(vinyl chloride) containing Oxydtron in the same temperature range of 30°C-240°C. This test was used for investigating the gelation behavior before and after adding Oxydtron additives. From this figure, we note that there are differences between gelation grades (fusion degrees) and gelation temperatures for both processing methods, where the gelation grade and gelation temperature are more significant in the case of extrusion than rolling. From Figure 8.6, a, can be observe that Oxydtron shifted gelation temperature (fusion temperature) towards higher level than poly(vinyl chloride) of basic formulation, where the temperature has been rising to 201°C after 1wt.% Oxydtron addition instead 177°C in case of poly(vinyl chloride) alone; in the same time the gelation grade dropped from 78% for poly(vinyl chloride) to 74.7% for the same percentage and operation conditions of Oxydtron. Although of the increase in the percentage of Oxydtron additives, the temperature remains stable at 201°C with continued decrease of the gelation grade, where it dropped to 73.3% with 3wt.% Oxydtron and then reached a maximum reduction at 5wt.% Oxydtron with a value of 72.4% where the gelation grade was 8% less than poly(vinyl chloride) basic formulation.

If we assumed that the chemical composition of Oxydtron, which including calcium compounds, has a role in this unusual behavior, and these compounds would reduce the gelation grade (as in the case of Ca-based stabilizers [176]), but why in the same time the gelation temperature has been increased?. So this will be an incomplete explanation. The closest explanation to reality is related to the segmental mobility of PVC. Since the ratio of PVC and plasticizer is constant, the Oxydtron is a completely inorganic material, so it does not take out plasticizer from the system. And due to glass transition temperature (T_g) changed (depending on DMA analysis results), the smallest particles of Oxydtron influenced the segmental mobility of PVC. And this might be because its high polarity slightly hindered the free rotation of ester groups.

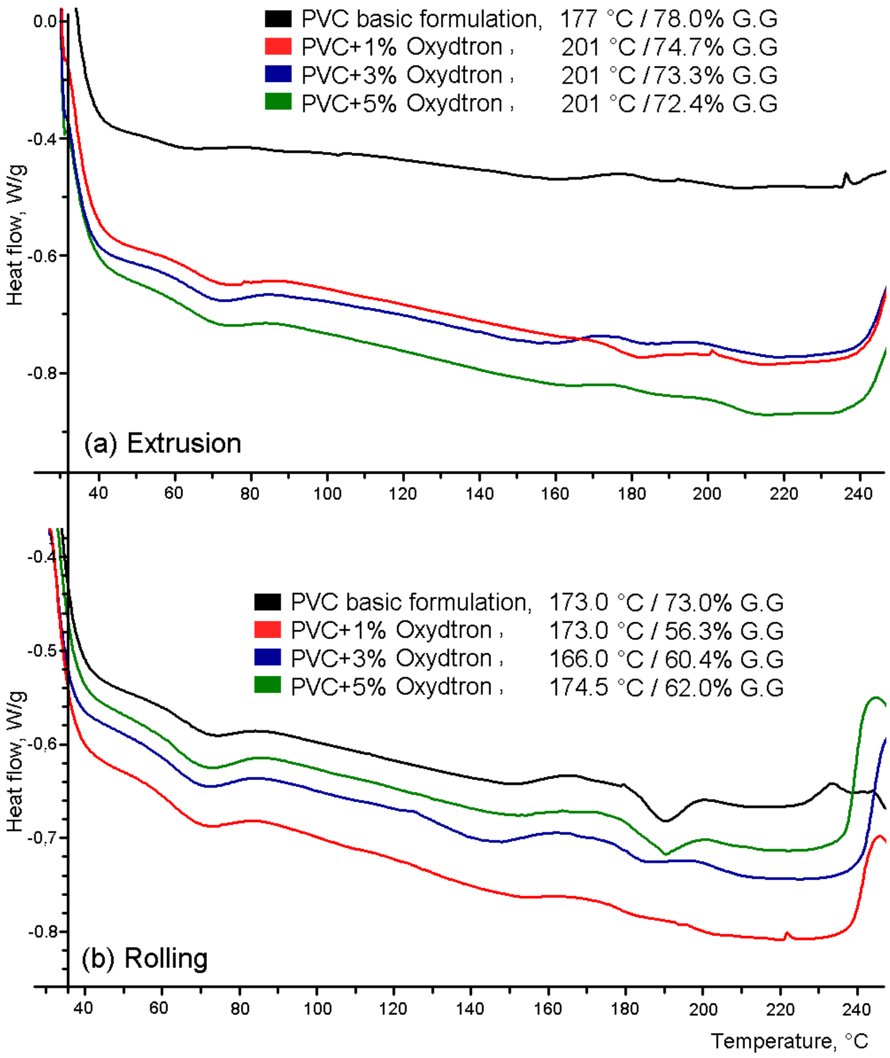


Figure 8.6. Gelation behavior for (a) extruded, (b) rolled plasticized poly(vinyl chloride) containing Oxydtron measured by DSC at 30°C-240°C temperature range

The same behavior applies for rolled samples but being slightly unstable and not ideal as extruded samples, where the history of poly(vinyl chloride) affects the final product properties. It is clear from the Figure 30,b that the gelation temperature remains constant while the gelation grade falls, when adding 1wt.% Oxydtron. The drop of gelation grade will continue with increasing of Oxydtron percentage. However, when 5wt.% Oxydtron is added, the gelation temperature will rise higher than poly(vinyl chloride) basic formulation. At this ratio, the rolled poly(vinyl chloride) behavior containing Oxydtron is similar to that of extruded ones. This difference in behaviors is due to the fact that the structure of poly(vinyl chloride) is subject to significant changes during the rolling process. It is initially rolled at

170°C into plates; these plates are then pressed to the desired thickness at 175°C. Therefore, the poly(vinyl chloride) structure is overstressed, resulting in early yields at a lower temperature than in the extruded product [103].

Summary of the correlation between gelation grades, gelation temperatures, and Oxydtron content processed with extrusion and rolling shown in Table 8.3.

Table 8.3. Summary of the correlation between gelation grades, gelation temperatures, and Oxydtron content at different processing methods

	PVC	PVC+1wt.% Oxydtron	PVC+3wt.% Oxydtron	PVC+wt.5% Oxydtron
	Extrusion			
Gelation temperature, °C	177	201	201	201
Gelation grade, %	78	74.7	73.3	72.4
	Rolling			
Gelation temperature, °C	173	173	166	174.5
Gelation grade, %	73	56	60.4	62

8.6 Dehydrochlorination Tests

8.6.1 Results of Novel Evaluation Method

The thermal degradation of poly(vinyl chloride) does not happen in one step, but actually, it is a sequential dehydrochlorination that leads to creating conjugated polyene sequences. This sequential process goes through three stages which are initiation, propagation, and termination [177]. At high temperatures, the structure of poly(vinyl chloride) becomes less stable leading to the release of hydrogen chloride (HCl) strongly, and as a result, the resistance of poly(vinyl chloride) starts to decrease as shown in Figure 8.7, which represents a dehydrochlorination test for plasticized poly(vinyl chloride) basic formulation at 170°C, 180°C, and 190°C respectively.

From the Figure 8.7,a we see that the HCl loss is very rapid and the slope of the curve is very sharp (high inclination). This is a normal behavior for poly(vinyl chloride) due to the low thermal resistance in high temperatures (for polymers), so, at initiation stage of dehydrochlorination, the structural segments of poly(vinyl chloride) will release hydrogen chloride (HCl), and this cause these structural segments to turn into allylic chloride groups. This thermal resistance of poly(vinyl chloride) decreases more and more as the release of HCl increases where the structure of poly(vinyl chloride) is strongly deformed. When the first stage is not obstructed, the degradation will enter the second stage, propagation. In this stage, the allylic chloride groups will begin to elongate very rapidly and be converted into polyenes as the degradation process progresses [177].

The dehydrochlorination will reach to third stage which is termination, where the bonds between atoms begin to break down and huge amounts of chlorine-containing compounds are released and finally the material will be completely burnt [177,178]. This is observed from the high slope of the curve (134×10^{-6} $\%s^{-1}$) and at this point, the poly(vinyl chloride) reached the degree of total degradation. The time for break down at 170°C is (2.211 hr). The thermal resistance of the poly(vinyl chloride) decreases more, and chlorine-containing compounds loss becomes rough as the temperature increases furthermore to 180°C and 190°C.

This action can be seen in Figure 8.7, b, and c, where the curves (b) and (c) have very high slope (246×10^{-6} $\%s^{-1}$ and 272×10^{-6} $\%s^{-1}$) respectively, and the time for to break down at temperatures 180°C, and 190°C are (1.144 hr. and 0.694 hr.) respectively. Table 8.4 represents a summary of the slopes values and time of dehydrochlorination test for poly(vinyl chloride) basic formulation.

Table 8.4. Slopes and DHC time for poly(vinyl chloride) basic formulation

Temperature, °C	170	180	190
Slope, 10^{-6} $\%s^{-1}$	134	246	272
DHC time, hr.	2.211	1.144	0.694

The dehydrochlorination behavior of poly(vinyl chloride) will be changed after adding Oxydtron additives, where the structure of poly(vinyl chloride) show more stability at high temperatures as shown in Figure 8.8, which represents the dehydrochlorination test for plasticized poly(vinyl chloride) at 170°C, 180°C, and

190°C respectively after adding 1wt.% of Oxydtron. The slope of the curve at 170°C (a) had been decreased from (134×10^{-6} %s^{-1}) for poly(vinyl chloride) basic formulation (Figure 8.8, a) to (73×10^{-6} %s^{-1}) after Oxydtron addition. This means the poly(vinyl chloride) structure became more stable and the tendency to release HCl containing compounds has been decreased and the period of degradation extended from (2.211 hrs) before adding Oxydtron to (4.75 hrs) after Oxydtron additions. Even when the temperature rises, the plasticized poly(vinyl chloride) maintains its resistance, and this is evident by the Figure 8.8, b, c.

Where the value of the curves b and c reached (176×10^{-6} %s^{-1} and 223×10^{-6} %s^{-1}) respectively, at a time of (1.34 hr.) and (1.983 hr.) respectively, which is a significant improvement in the structure of the plasticized poly(vinyl chloride) after adding Oxydtron to it. From my point of view, and depending on the results I obtained, the Oxydtron will hinder the formation of allylic chloride groups, which will lead to the prevention of polyenes formation. This will delay the poly(vinyl chloride) entering the propagation stage, and thus the fire will be extinguished.

A summary of the slopes values and time of dehydrochlorination test for poly(vinyl chloride) containing 1wt.% Oxydtron are shown in Table 8.5.

Table 8.5. Slopes and time of dehydrochlorination test for poly(vinyl chloride) containing 1wt.% Oxydtron test

Material	Slope, 10^{-6} %s^{-1}			DHC time, hour		
	170°C	180°C	190°C	170°C	180°C	190°C
PVC basic formulation	134	246	272	2.211	1.144	0.694
PVC+1wt.% Oxydtron	73	176	223	4.750	1.983	1.340

When the weight fraction of Oxydtron additives increases to 3wt.%, the stability of thermal resistance of plasticized poly(vinyl chloride) will rise, and this behavior can be illustrated by Figure 8.9, which represent the dehydrochlorination results of plasticized poly(vinyl chloride) containing 3wt.% Oxydtron at 170°C, 180°C, and 190°C respectively. From the curve (a) at 170°C, we notice that the slope of the conversion rate curve will decrease, i.e., the degradation resistance has been increased, wherein this case, the slope of conversion rate became (62×10^{-6} %s^{-1}) with an increase in the total degradation time to (4.84 hrs.). And when the temperature increases to 180°C (curve (b)), the slope of conversion rate will reduce to (163×10^{-6} %s^{-1}) and increasing the total degradation time to (2.133 hrs.). Even at the higher temperature (190°C), as the curve (c) indicates, the degradation rate can decrease, conversion rate became (155×10^{-6} %s^{-1}), and the degradation time has considerably increased to (1.533 hr.) compared to the previous addition.

A summary of the slopes values and time of dehydrochlorination test for poly(vinyl chloride) containing 3wt.% Oxydtron are shown in Table 8.6.

Table 8.6. Summary of the slopes and DHC time for poly(vinyl chloride) containing 3wt.% Oxydtron compared to the basic formulation and containing 1wt.% Oxydtron

Material	Slope, 10^{-6} %s^{-1}			DHC time, hour		
	170°C	180°C	190°C	170°C	180°C	190°C
PVC basic formulation	134	246	272	2.211	1.144	0.694
PVC+1wt.% Oxydtron	73	176	223	4.750	1.983	1.340
PVC+3wt.% Oxydtron	62	163	155	4.840	2.133	1.533

With the increasing proportion of Oxydtron to 5wt.%, the degradation resistance of plasticized poly(vinyl chloride) will increase, as shown in Figure 8.10, which represent the dehydrochlorination results of plasticized poly(vinyl chloride) containing 5wt.% Oxydtron at 170°C, 180°C, and 190°C respectively. It is clear from this figure that the curve tends to rise gradually with a low slope, which means that the rate of degradation has decreased, where at 170°C we can see that the slope of the conversion rate curve (a) became (53×10^{-6} %s^{-1}) and the degradation time extended to (5.2 hrs.). And at 180°C, the slope of the curve (b) is (142×10^{-6} %s^{-1}) and the degradation time was extended to (2.144 hrs.). When the test temperature rises to 190°C, the value of the conversion rate curve (c) will be (120×10^{-6} %s^{-1}) and the value of degradation time will be its (1.710 hr.). The slopes values for all Oxydtron weight fractions are illustrated in Table 8.7. So, the optimum improvements of degradation rate obtained by 5wt.% 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.

Table 8.7. Comparison of the correlation between slopes, DHC time, and Oxytron content

Material	Slope, 10^{-6} %s^{-1}			DHC time, hour		
	170°C	180°C	190°C	170°C	180°C	190°C
PVC basic formulation	134	246	272	2.211	1.144	0.694
PVC+1wt.% Oxydtron	73	176	223	4.750	1.983	1.340
PVC+3wt.% Oxydtron	62	163	155	4.840	2.133	1.533
PVC+5wt.% Oxydtron	53	142	120	5.200	2.144	1.710

Table 8.8 represents a summary of improvement percentage of DHC time for plasticized poly(vinyl chloride) containing Oxydtron.

Table 8.8. Improvement percentage of DHC time for plasticized poly(vinyl chloride) containing Oxydtron

	PVC	PVC+1wt.% Oxydtron	PVC+3wt.% Oxydtron	PVC+5wt.% 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%

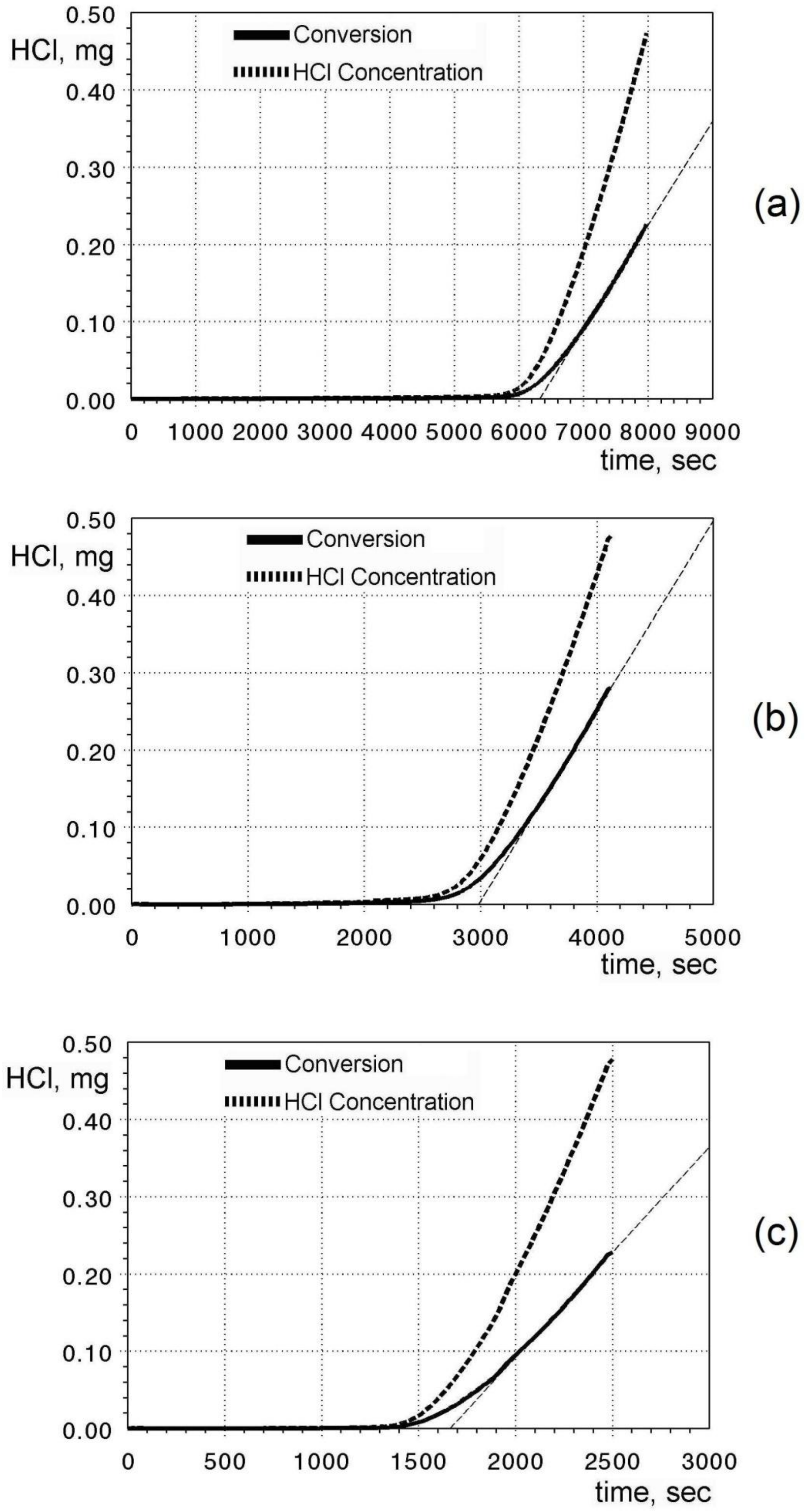


Figure 8.7. Dehydrochlorination test for plasticized poly(vinyl chloride) basic formulation at (a) 170°C, (b) 180°C, and (c) 190°C respectively

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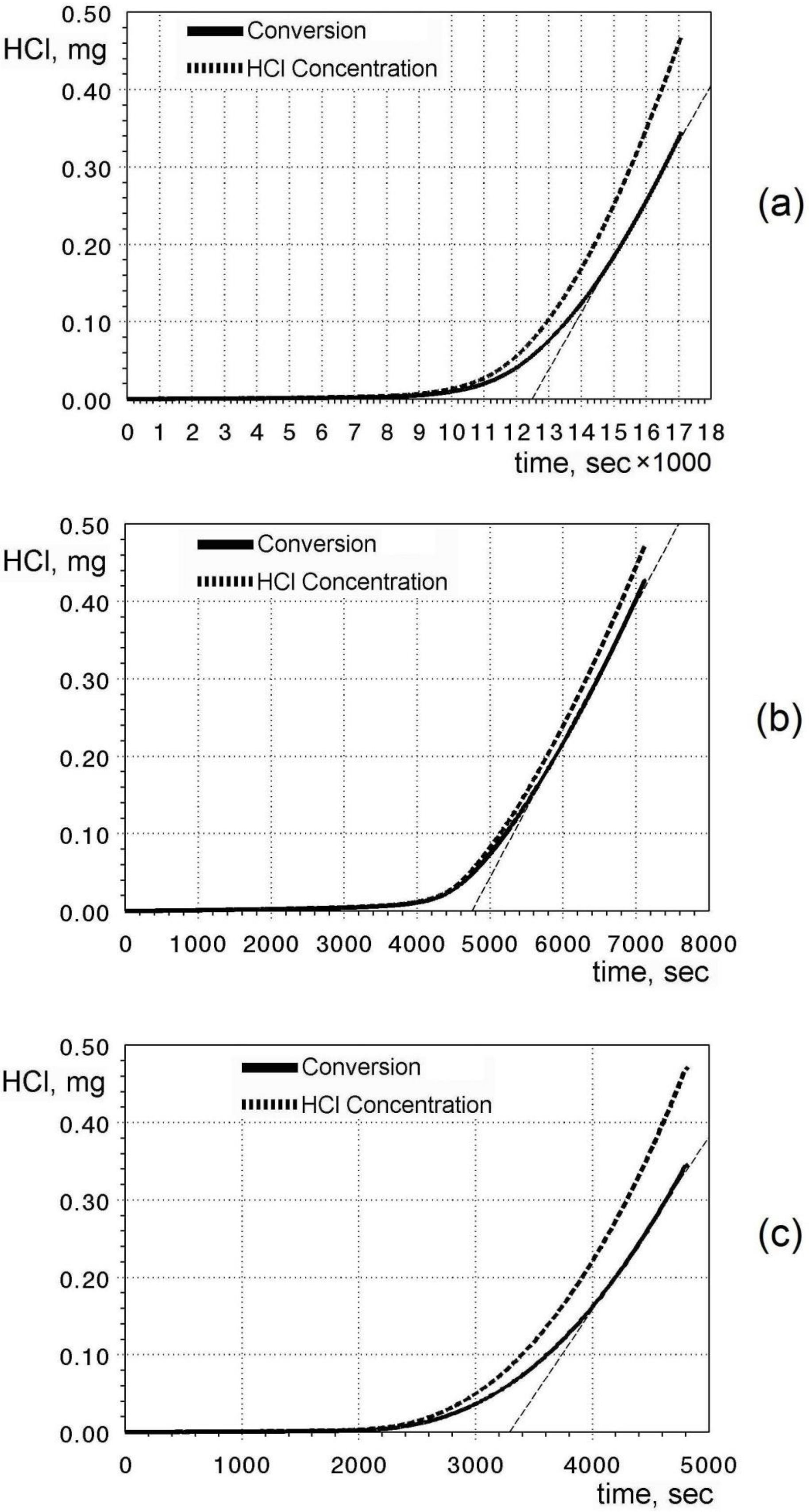

Figure 8.8. Dehydrochlorination test of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron at (a) 170°C, (b) 180°C, and (c) 190°C respectively

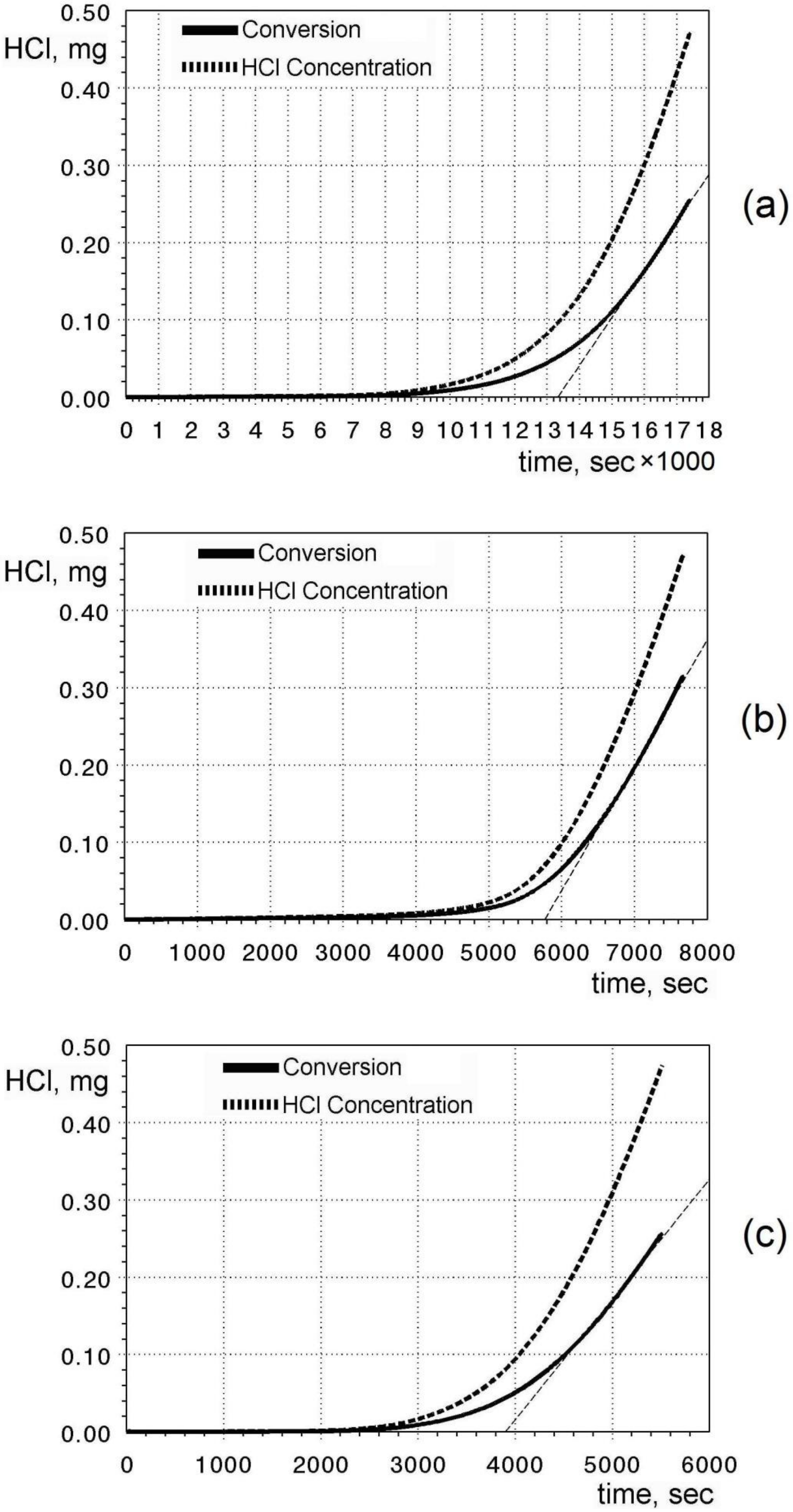

Figure 8.9. Dehydrochlorination test of plasticized poly(vinyl chloride) containing 3wt.% Oxydtron at (a) 170°C, (b) 180°C, and (c) 190°C respectively

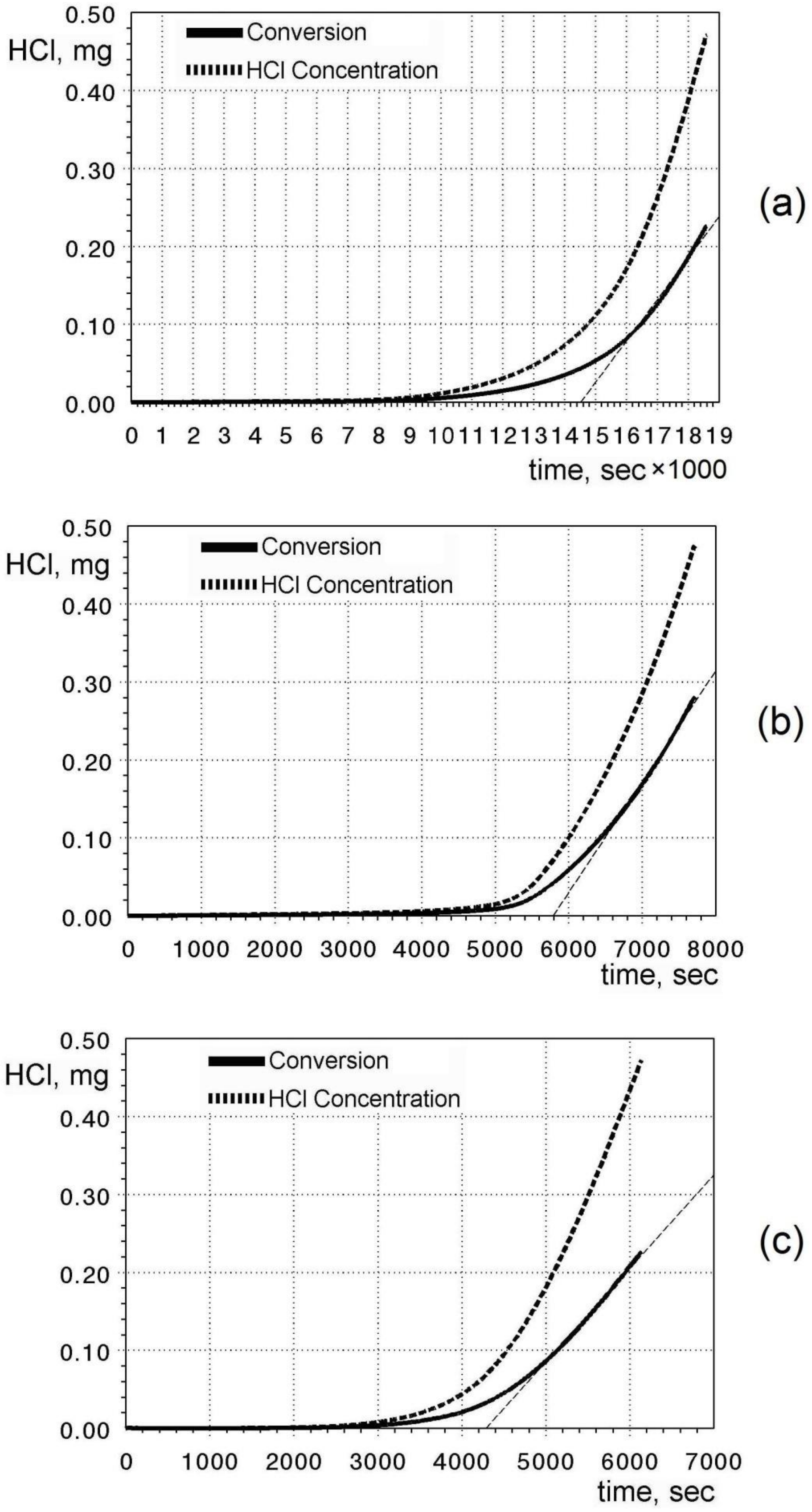

Figure 8.10. Dehydrochlorination test of plasticized poly(vinyl chloride) containing 5wt.% Oxydtron at (a) 170°C, (b) 180°C, and (c) 190°C respectively

8.6.2 Results of Standard Method

In this section, the standard method's dehydrochlorination graphs, which depend on measuring the conductivity, have been illustrated. The main aim of including these figures is to make a practical comparison between it and the novel evaluation method adopted in this dissertation. Otherwise, the exact reasons of degradation that I mentioned previously apply to this method as well, and therefore I will not repeat them.

Figure 8.11 represents the conductivity of plasticized PVC basic formulation measured by standard method at 170°C, 180°C, and 190°C, respectively. We noted from this figure that the induction time and stability time were short, which means that the thermal stability of poly(vinyl chloride) is significantly reduced at high temperatures [179,180]. As mentioned earlier, adding Oxydtron will improve the thermal resistance of poly(vinyl chloride). This is also evident in Figure 8.12, which represents the conductivity of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron measured by standard method at 170°C, 180°C, and 190°C respectively, where the synergistic action of Oxydtron increased the induction time and stability time.

When increasing the weight fraction of the Oxydtron additions to 3wt.% and 5wt.%, there will be a significant increase in the poly(vinyl chloride) conductivity, represented by the rise in the value of induction time and the stability time, as shown in Figure 8.13 and Figure 8.14, which represent conductivity of plasticized PVC containing 3wt.% and 5wt.% Oxydtron measured by standard method at (a) 170°C, (b) 180°C, and (c) 190°C respectively. This incremental is due to the growing synergistic action between the poly(vinyl chloride) and the Oxydtron.

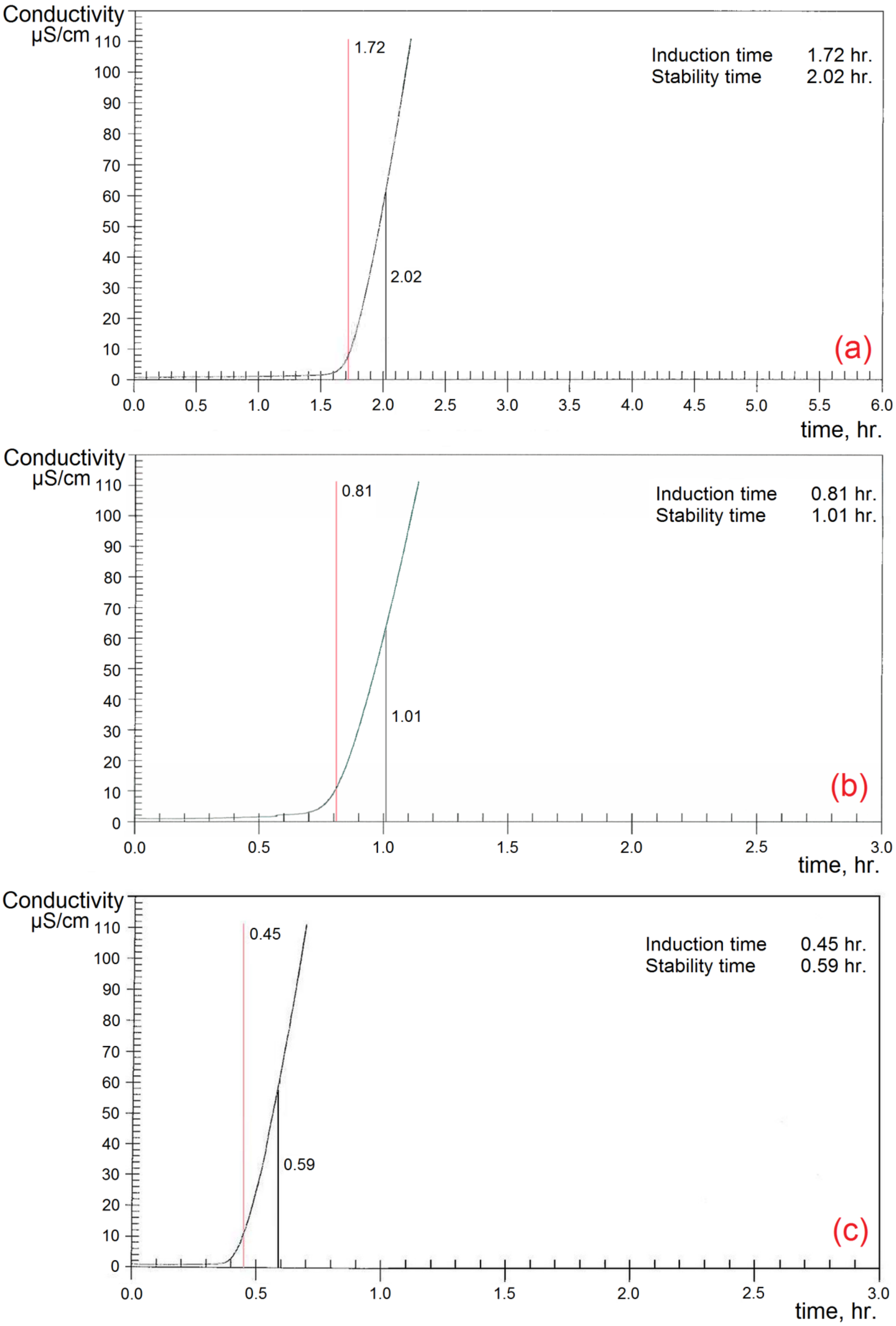

Figure 8.11. Conductivity of plasticized poly(vinyl chloride) basic formulation measured by standard method at (a) 170°C, (b) 180°C, and (c) 190°C

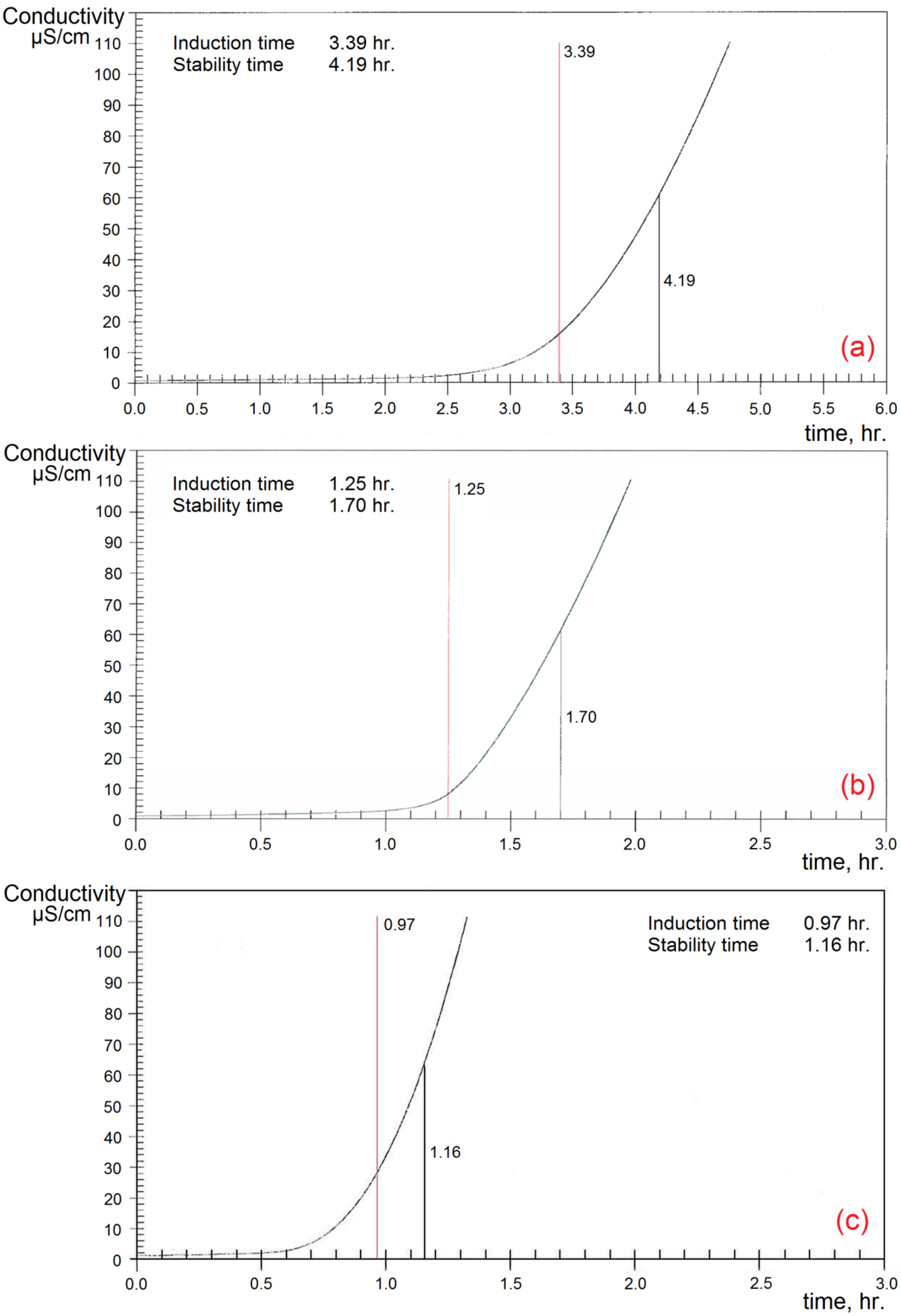

Figure 8.12. Conductivity of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron measured by standard method at (a) 170°C, (b) 180°C, and (c) 190°C

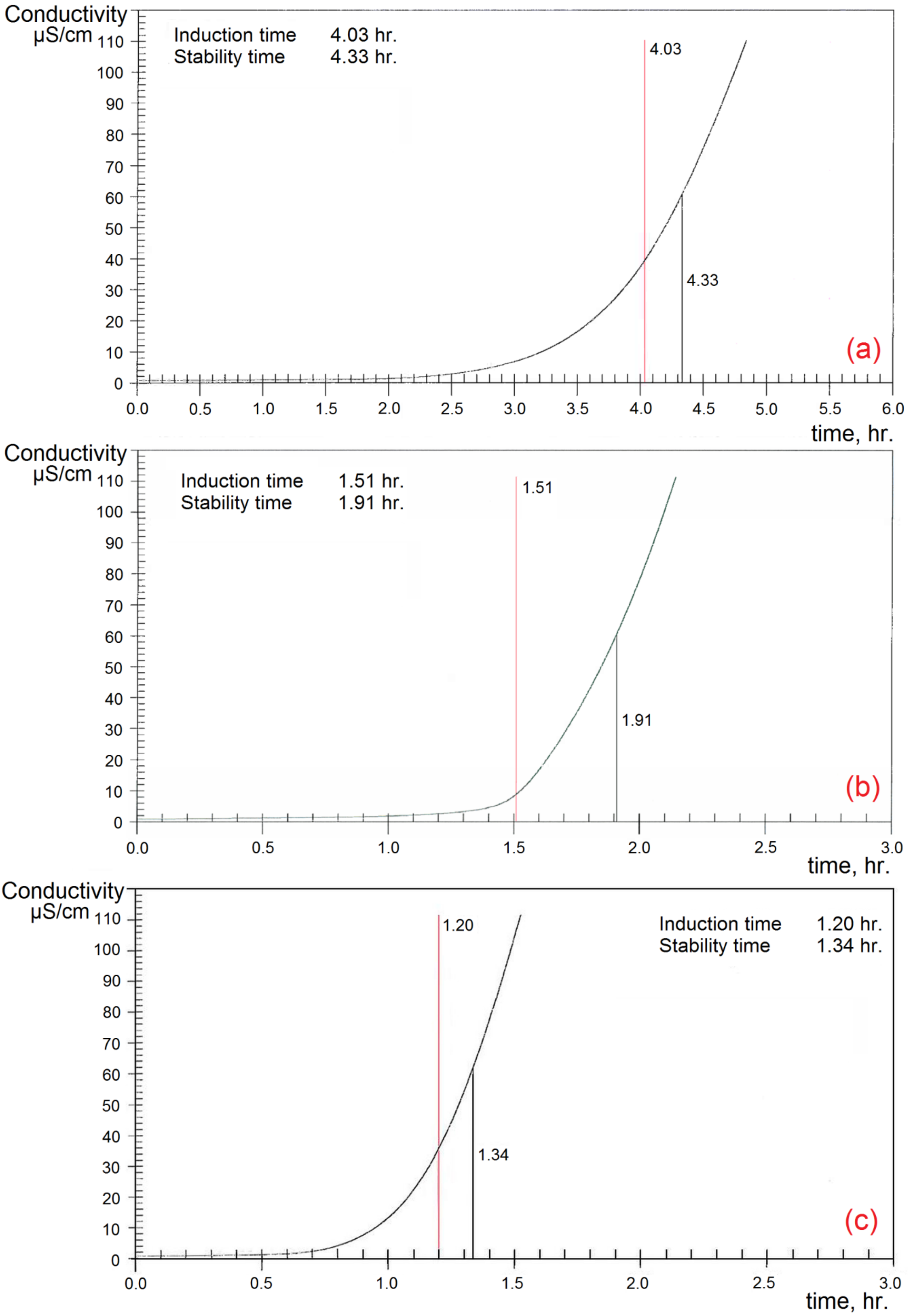

Figure 8.13. Conductivity of plasticized poly(vinyl chloride) containing 3wt.% Oxydtron measured by standard method at (a) 170°C, (b) 180°C, and (c) 190°C

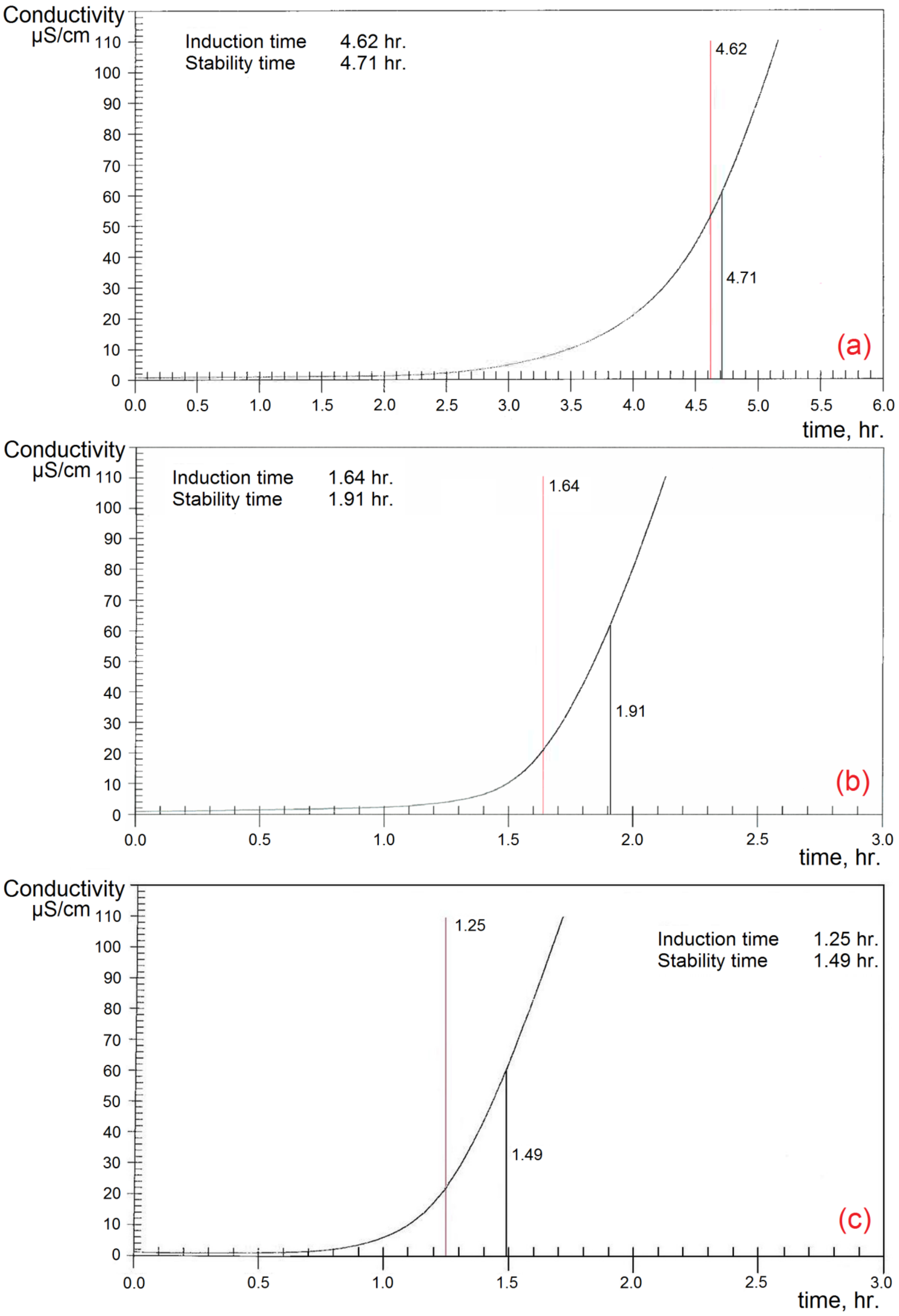

Figure 8.14. Conductivity of plasticized poly(vinyl chloride) containing 5wt.% Oxydtron measured by standard method at (a) 170°C, (b) 180°C, and (c) 190°C

Table 8.9 represents a summary of the induction time and stability time of plasticized poly(vinyl chloride) containing Oxydtron, measured by standard method at 170°C, 180°C, and 190°C, respectively.

Table 8.9. Induction time and stability time of PVC containing Oxydtron measured by standard method at 170°C, 180°C, and 190°C

	PVC basic formulation	PVC + 1wt.% Oxydtron	PVC + 3wt.% Oxydtron	PVC + 5wt.% Oxydtron
	At 170°C			
Induction time, hr.	1.72	3.39	4.03	4.62
Stability time, hr.	2.02	4.19	4.33	4.71
	At 180°C			
Induction time, hr.	0.81	1.25	1.51	1.64
Stability time, hr.	1.01	1.70	1.91	1.91
	At 190°C			
Induction time, hr.	0.45	0.97	1.20	1.25
Stability time, hr.	0.59	1.16	1.34	1.49

8.7 Capillary Rheometry Analysis (Extrusiometery)

It is known that the inlet pressure drop (Δp) can be measured practically by using capillaries that are of different lengths while maintaining a constant diameter [181,182]. Figure 8.15 represents the length correction of plasticized poly(vinyl chloride) basic formulation at speed 60 rpm, accomplished with three different capillaries length (15, 30, and 45 mm) have the same diameter (3 mm) and (L/D) were (5, 10, 15). And Table 8.10 represents Bagley correction and slope values of plasticized poly(vinyl chloride) basic formulation at the same three temperatures.

Table 8.10. Bagley correction and slope values of plasticized poly(vinyl chloride) basic formulation at 160°C, 170°C, and 180°C

Temperature, °C	160	170	180
Bagley Correction	8.35	8.00	7.28
Slope	3.52	3.00	2.49

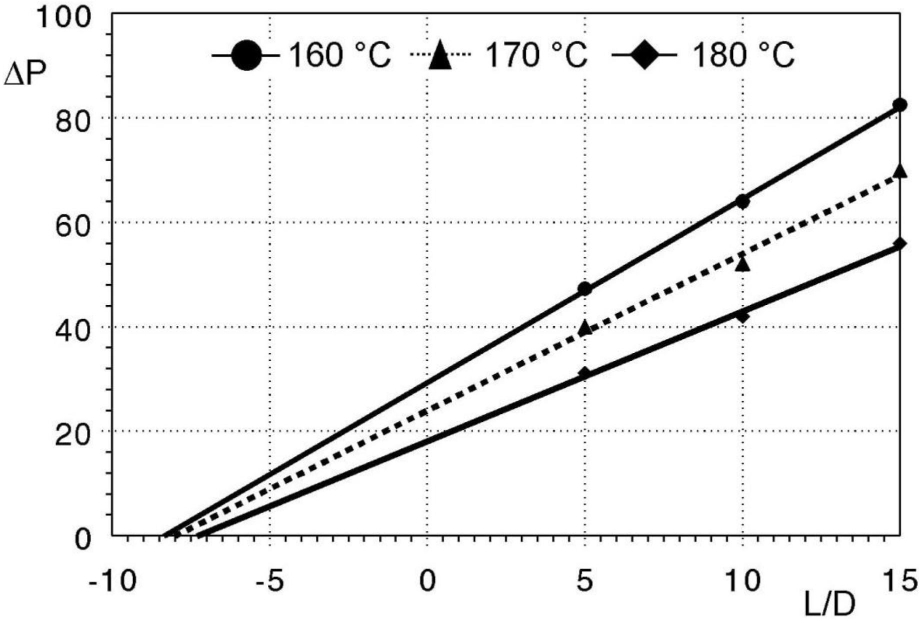

Figure 8.15. Length or Bagley correction for plasticized poly(vinyl chloride) basic formulation at 160°C, 170°C, and 180°C respectively

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 [183,184]. The pressure drop is proportional to the capillary length, where the pressure drop is more significant with the longer capillary. However, it is inversely proportional to the temperature as the higher the temperature, the lower the pressure drop. This condition is also similar to the Bagley correction, as shown in Table 8.10. 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.

Figure 8.16 represents the length correction of plasticized poly(vinyl chloride) containing (1wt.%) Oxydtron at 160°C, 170°C, and 180°C respectively at speed 60 rpm. Table 8.11 represents the Bagley correction and slope values for poly(vinyl chloride) containing (1wt.%) Oxydtron at the same temperature and speed. From this figure and the table, 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 [185-187], therefore, the shear stress values in the case of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron will be higher than poly(vinyl chloride) basic formulation.

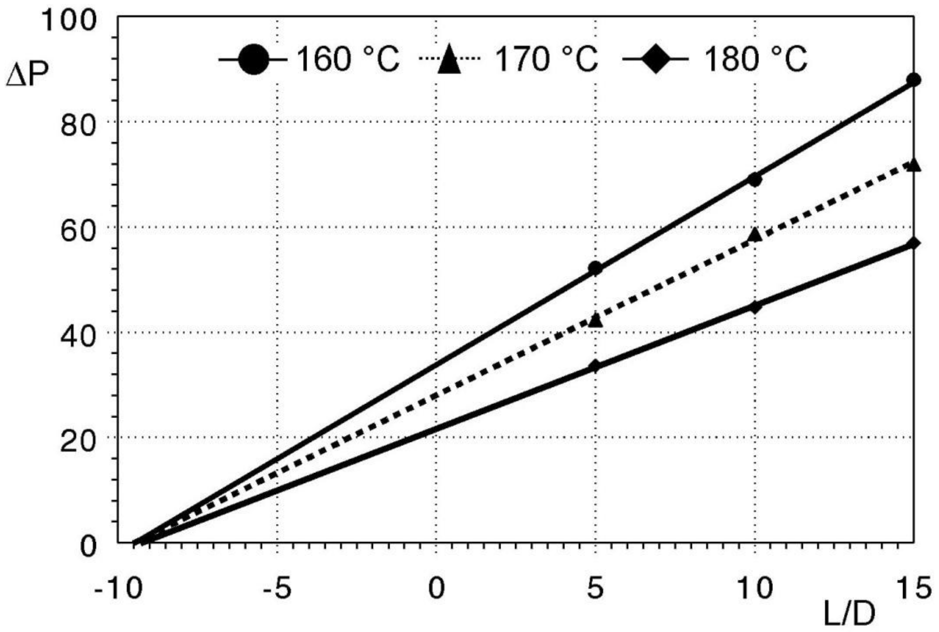

Figure 8.16. Length or Bagley correction for of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron at 160°C, 170°C, and 180°C respectively

Table 8.11. Bagley correction and slope values of plasticized poly(vinyl chloride) containing 1wt.% Oxydtron at 160°C, 170°C, and 180°C

Temperature, °C	160	170	180
Bagley Correction	9.10	9.07	8.90
Slope	3.64	3.04	2.38

Still, the higher correction values show higher melt elasticity, and it can be evident that the length correction could be the measure of melt elasticity. For that, I didn't find any reference. Also, through Figure 8.16 we observe that the fitting will be much better, and the slope values are higher than in poly(vinyl chloride) basic formulation where the particles will increase the shear stress because it an effect filler in terms of mechanical properties. We also found that the plasticized poly(vinyl chloride) containing Oxydtron are less sticky to the exit mold hole, and this will happen to the extrusion barrel, which will reduce the viscosity of the melt.

With an increase in the weight fraction of Oxydtron to 3wt.%, the improvement of length correction increases, which is what we can see in Figure 8.17, which represent the Bagley correction for of plasticized poly(vinyl chloride) containing 3wt.% Oxydtron at 160°C, 160°C, 170°C, and 180°C respectively. The Bagley correction and slope values for poly(vinyl chloride) containing 3wt.% Oxydtron at the same temperature and speed are represented in Table 8.12.

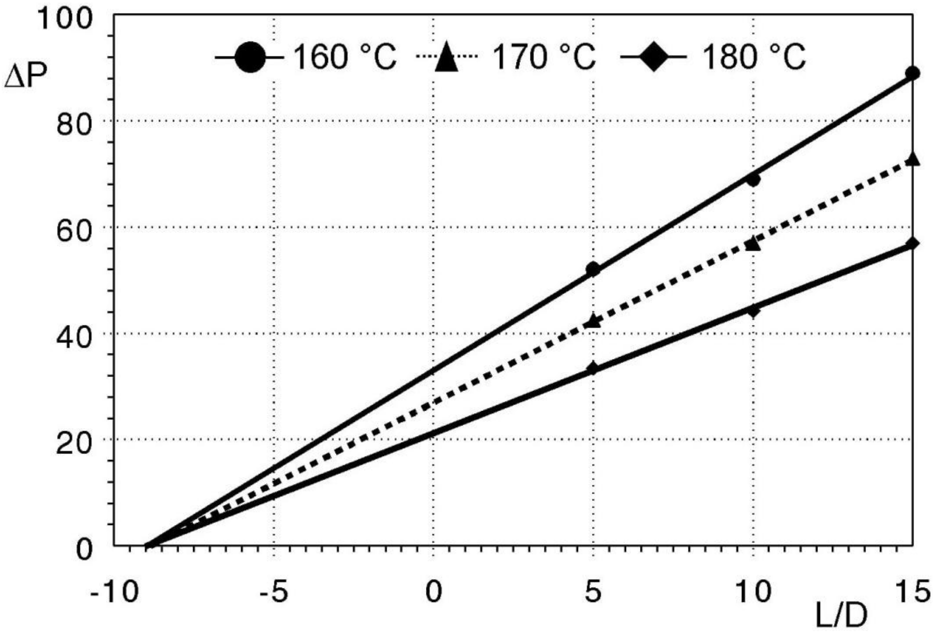

Figure 8.17. Length or Bagley correction for plasticized poly(vinyl chloride) containing 3wt.% Oxydtron at 160°C, 170°C, and 180°C respectively

Table 8.12. Bagley correction and slope values of plasticized poly(vinyl chloride) containing 3wt.% Oxydtron at 160°C, 170°C, and 180°C

Temperature, °C	160	170	180
Bagley Correction	9.44	9.31	9.17
Slope	3.60	2.93	2.34

There has also been an improvement in the drop in pressure, which means that the melt's elasticity has improved further, as explained earlier. Although the length correction continues to decrease with increasing temperatures (which is normal), it maintains higher accuracy levels than the poly(vinyl chloride) basic formulation or containing 1wt.% Oxydtron. This is possibly the key reason why Oxydtron is so successful because of this additive's role in counteracting the segmental movement, and the polymer structure will consist of liquid-like molecules that increased the elasticity. The perfect results were achieved in the length correction enhancement by applying 5% Oxydtron, which can be seen in Figure 8.18, which displays the Bagley correction for plasticized poly(vinyl chloride) containing 5% Oxydtron at 160°C, 160°C, 170°C, and 180°C respectively, and in Table 8.13. The Oxydtron continues to sustain a high degree of length correction as the additional percentage increases to 5wt.%.

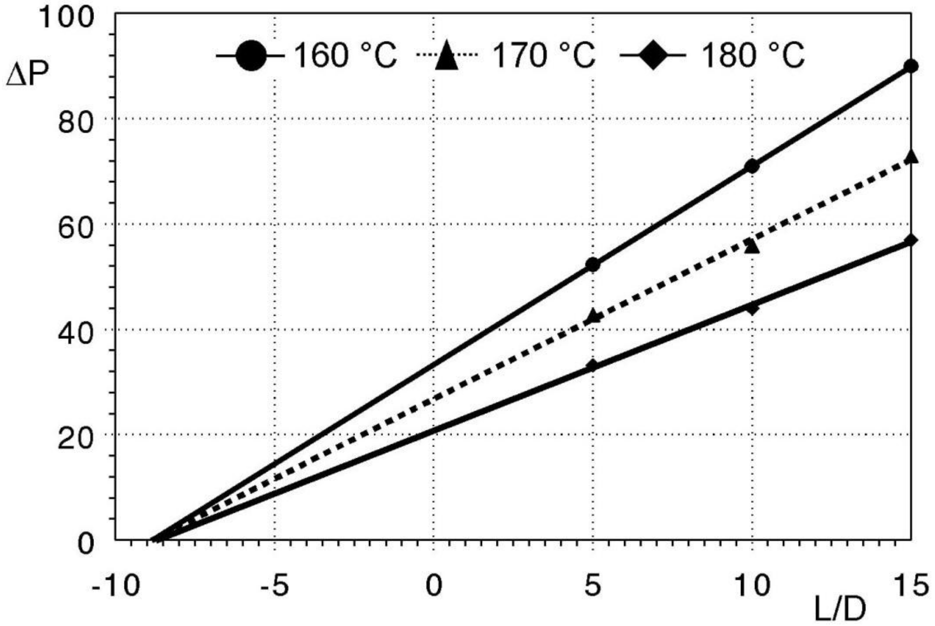

Figure 8.18. Length or Bagley correction for plasticized poly(vinyl chloride) containing 5wt.% Oxydtron at 160°C, 170°C, and 180°C respectively

Table 8.13. Bagley correction and slope values of plasticized poly(vinyl chloride) containing 5wt.% Oxydtron at 160°C, 170°C, and 180°C

Temperature, °C	160	170	180
Bagley Correction	9.57	9.45	9.26
Slope	3.62	2.92	2.31

Also, we can see from Figure 8.19, which represents Bagley correction as a function of Oxydtron weight fraction that the Bagley correction increases with increasing of Oxydtron addition. Even 1wt.% of Oxydtron significantly increases the Bagley correction, and adding further Oxydtron, the correction continues to rise. That means the additive increased the melt elasticity. The elasticity of poly(vinyl chloride) melt decreases by increasing temperature, and the viscous flow becomes dominant. Because the Bagley correction represents the energy being necessary to alter the flow geometry, the Bagley correction of the plasticized poly(vinyl chloride) decreases by increasing temperature. But this drop in Bagley correction will be less in the presence of Oxydtron, as shown in Figure 8.20 which represents Bagley correction as a function of processing temperature.

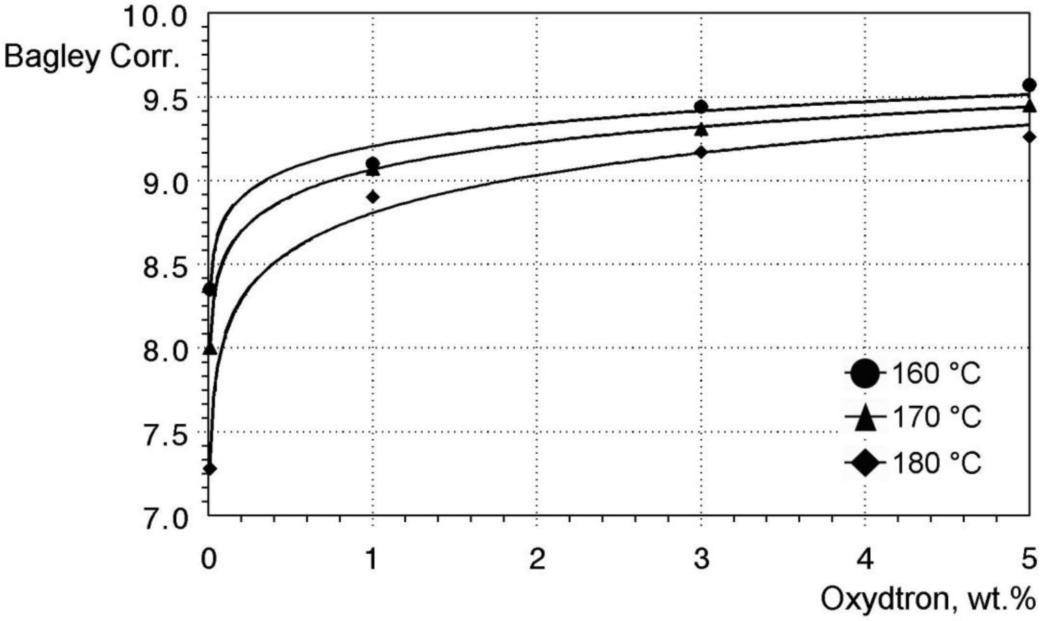

Figure 8.19. Bagley correction as a function of Oxydtron wt.% at 160°C, 170°C, and 180°C respectively

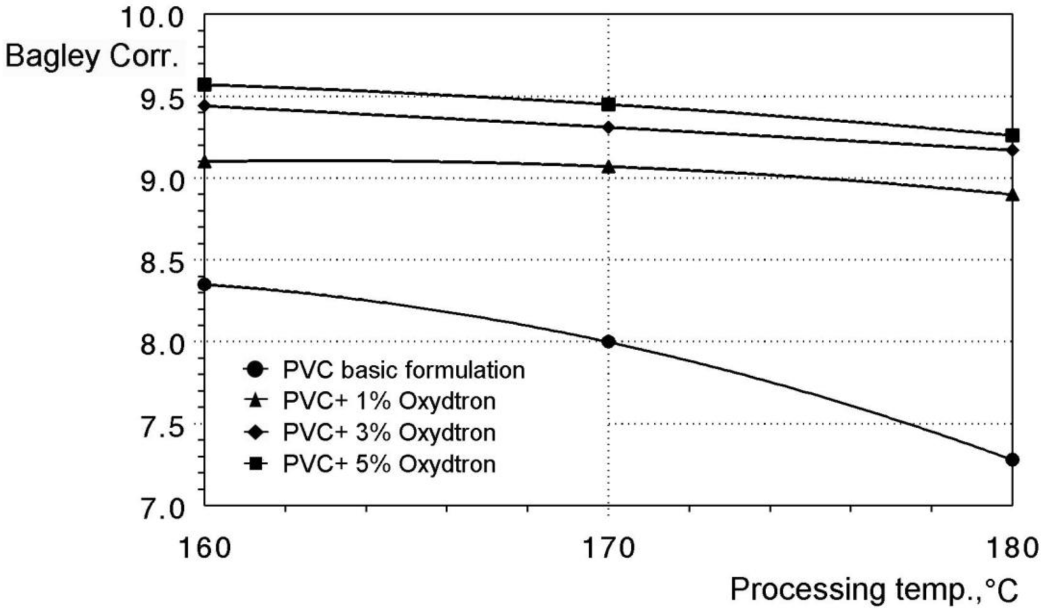

Figure 8.20. Bagley correction as a function of processing temperature

8.8 Dynamic Mechanical Analysis (DMA)

From Figure 8.21, 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 [188].

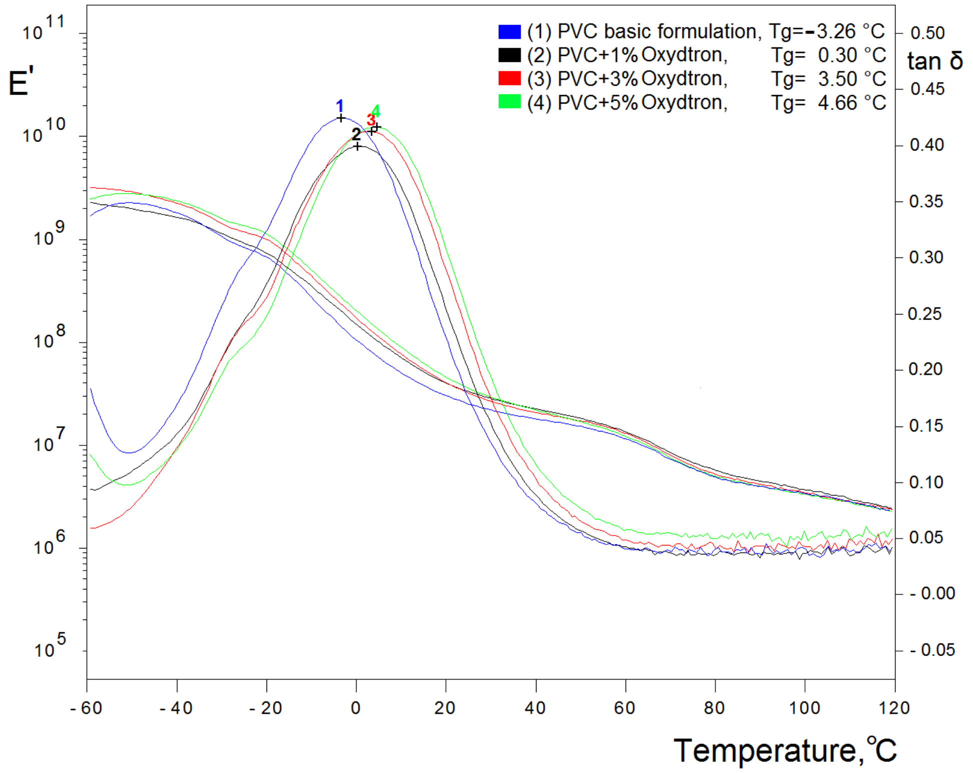

Figure 8.21. Dynamic mechanical analysis for plasticized poly(vinyl chloride) containing Oxydtron

From Figure 8.21 we can note that the frequency dependence of the glass transition is very well visible. So, the relaxation time for this process can be calculated from the following equation:

$$\tau = 1/\omega \qquad (18)$$

Where:

τ: the relaxation time.

ω: the angular frequency.

Figure 8.22 represents the relaxation time for plasticized poly(vinyl chloride) containing Oxydtron, calculated based on the temperature test data with temperatures range -20°C, -10°C, and 0°C. Evidently, τ (T) (relaxation time at T temperature) is independent of frequency; the temperature of maxima is shifted to higher temperatures by increasing frequency because shorter relaxation time appears at higher temperature.

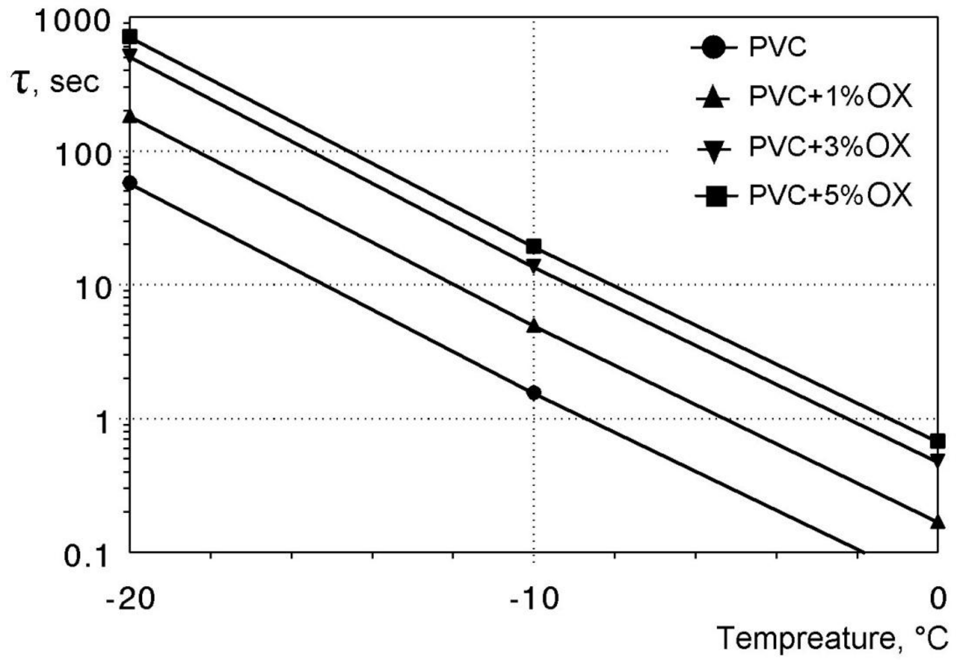

Figure 8.22. The relaxation time for plasticized poly(vinyl chloride) containing Oxydtron as a function of temperature

Also, we can see that the relative increase of relaxation time is almost linear by Oxydtron content as shown in Figure 8.23, and at 5wt.% Oxydtron reached to 12 times (12.458) more than poly(vinyl chloride) basic formulation. The relative increase is the same at different temperatures.

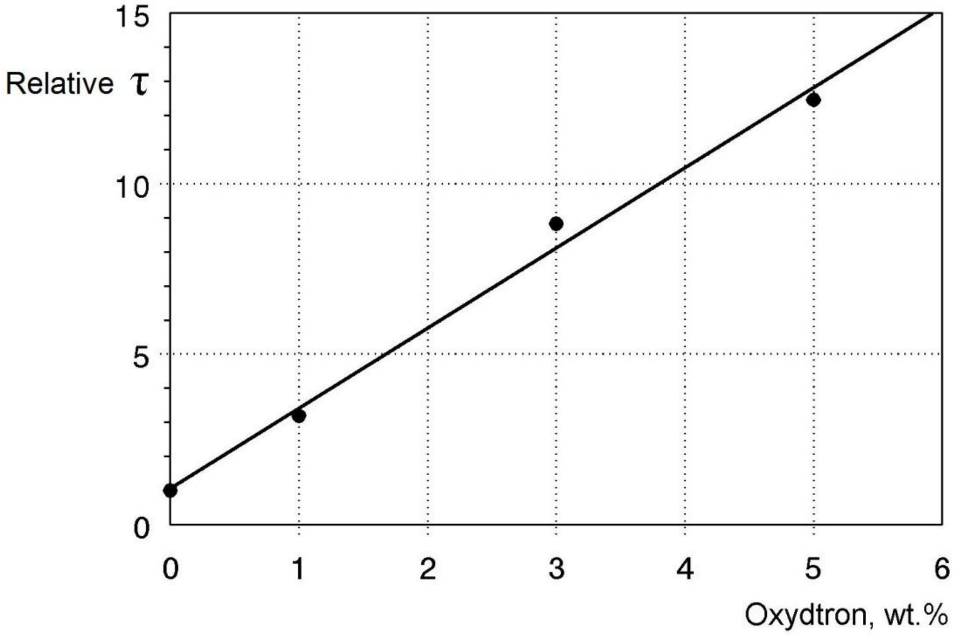

Figure 8.23. The relative relaxation time as a function of Oxydtron content

8.9 Heat Affected Zone (HAZ) Analysis

8.9.1 FLIR Thermal Gradient Analysis

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 HCl 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 8.24. This behavior is due to the dehydrochlorination of poly(vinyl chloride). Through Figure 8.25,a we notice that the heat affected zone is wide in poly(vinyl chloride) basic formulation, which is evidence of its low thermal and flame resistance and its rapid degradation at high temperatures of heating or combustion. The actual change in this critical zone begins after the addition of 1wt.% Oxydtron, as shown in Figure

8.25,b. The FLIR imaging test showed the beginning of the receding of the thermal effect in this zone than before adding the Oxydtron, leading to an increase in the thermal stability of the poly(vinyl chloride). The HAZ recedes further with the rise in the weight fraction of Oxydtron to 3wt.% and 5wt.% as shown in Figure 8.25,c, and d, resulting in increased resistance and stability of the poly(vinyl chloride) at such high temperatures, which reduces the degradation risk.

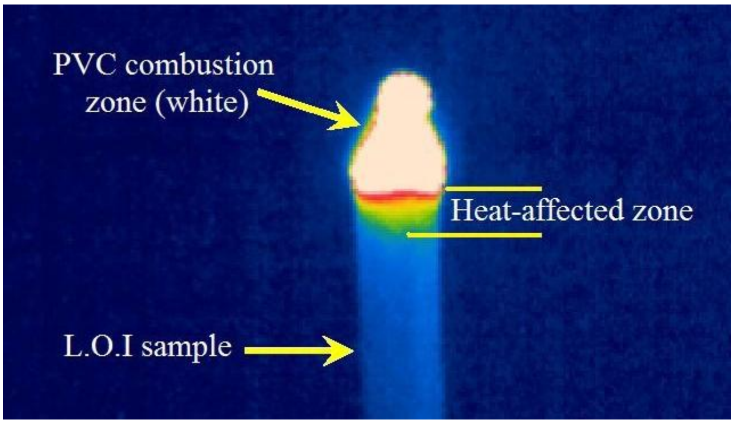

Figure 8.24. FLIR thermal gradient image for heat affected zone (HAZ) [3]

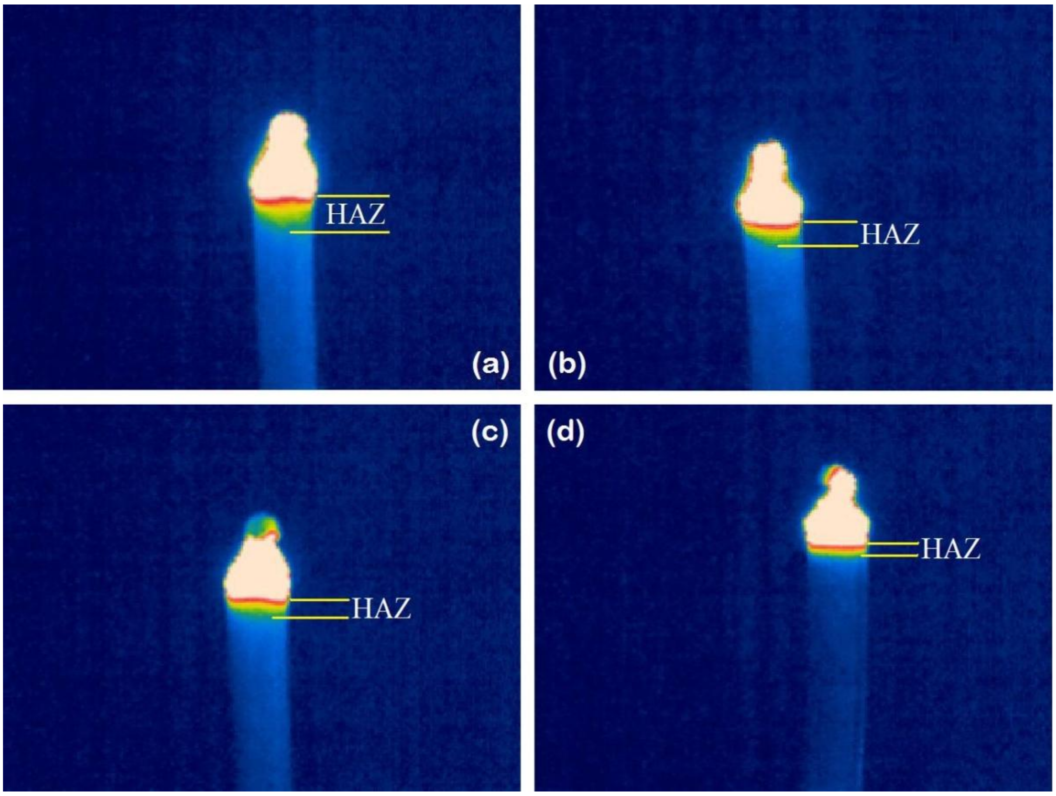

Figure 8.25. FLIR analysis for HAZ after L.O.I test in (a) PVC basic formulation, (b) PVC+1wt.% Oxydtron, (c) PVC+3wt.% Oxydtron, and (d) PVC+5wt.% Oxydtron

Also, I found that when re-testing the same sample again after cutting the burned area, the under layers have been ignited faster, and the HAZ area is wider, as shown in Figure 8.26. This behavior was dissimilar to the original sample tested for the first time, which means the heat affected layer has low flame resistance due to less chlorine [3].

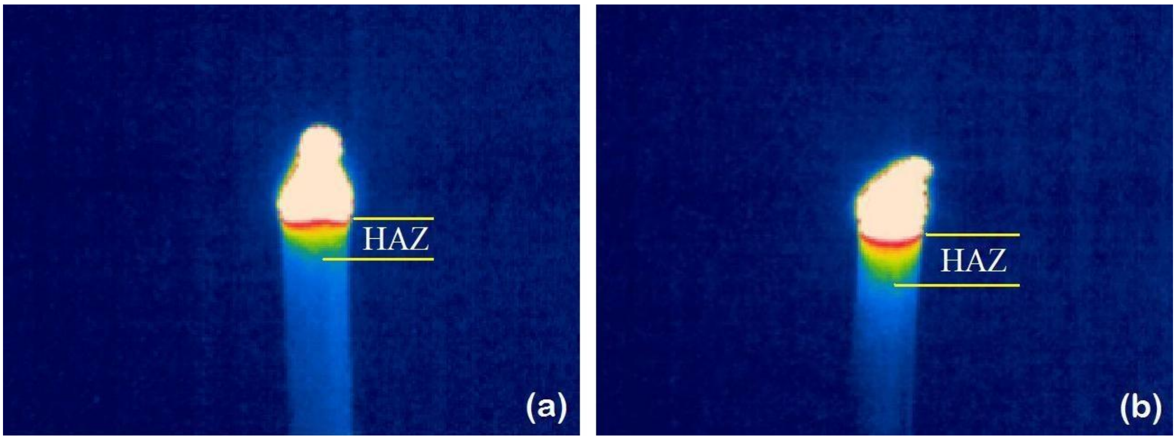

Figure 26. FLIR for extruded plasticized poly(vinyl chloride) basic formulation HAZ when (a) testing for the first time, (b) re-testing after cutting the burnt layer

8.9.2 Scanning Electron Microscopy Analysis

The images obtained from SEM for plasticized poly(vinyl chloride) basic formulation indicate that the chlorine percentage decreased accompanied by an increase in carbon percentage after the L.O.I test, as compared to the poly(vinyl chloride) SEM images before and after this test, as seen in Figure 8.27 and Figure 8.28 which represents the SEM - energy dispersive X-ray microanalysis for unburned and burned plasticized poly(vinyl chloride) basic formulation respectively. This critical condition will be modified, and the resistance of poly(vinyl chloride) to ignition will improve following the Oxydtron additions as shown in Figure 8.29, 30, and 31 respectively, where the percentage of chlorine in the poly(vinyl chloride) composition has been maintained within adequate levels (if not constant).

In contrast, the carbon content remains in the poly(vinyl chloride) structure within the acceptable level because the reactions that generated CO and converted to CO_2 have been reduced, the flame reactions were inhibited due to the hampered hydrocarbon oxidation by the synergistic action of Oxydtron-original stabilizer, which interferes with these flame reactions [91,189-191]. And this means that the chlorine emitted from the heat affected zone has been reduced. This is due to additional stabilizing synergistic action created by Oxydtron, which, together with the original stabilizer (Calcium-Zinc-based stabilizer), will enhance the thermal stability of poly(vinyl chloride).

The synthesis of Oxydtron plays a vital role in this synergistic behavior. Its composition contains several oxides that possess high thermal resistance and stability to elevated temperatures, such as calcium carbonate, silicon dioxide, titanium dioxide, etc. These oxides and carbonates can serve as a synergist agent with the original stabilizer to improve poly(vinyl chloride) thermal stability. The L.O.I test is carried out in several steps until obtained the required result, so as mentioned above, every time the test is carried out and fails, the burned layer is cut, and repeated the test for the same sample. Therefore, the layer located directly under the combustion zone will be affected by heat and is thermally stressed. Hence, its ignition is faster than it does not give correct and reliable results on the material's resistance.

However, after adding the Oxydtron, this heat affected layer will be perfect even if it is not the same as the condition before the test. Therefore, it ignites relatively slowly when re-testing as if it was burning for the first time, indicating an improvement in this layer's thermal resistance [3,75,100].

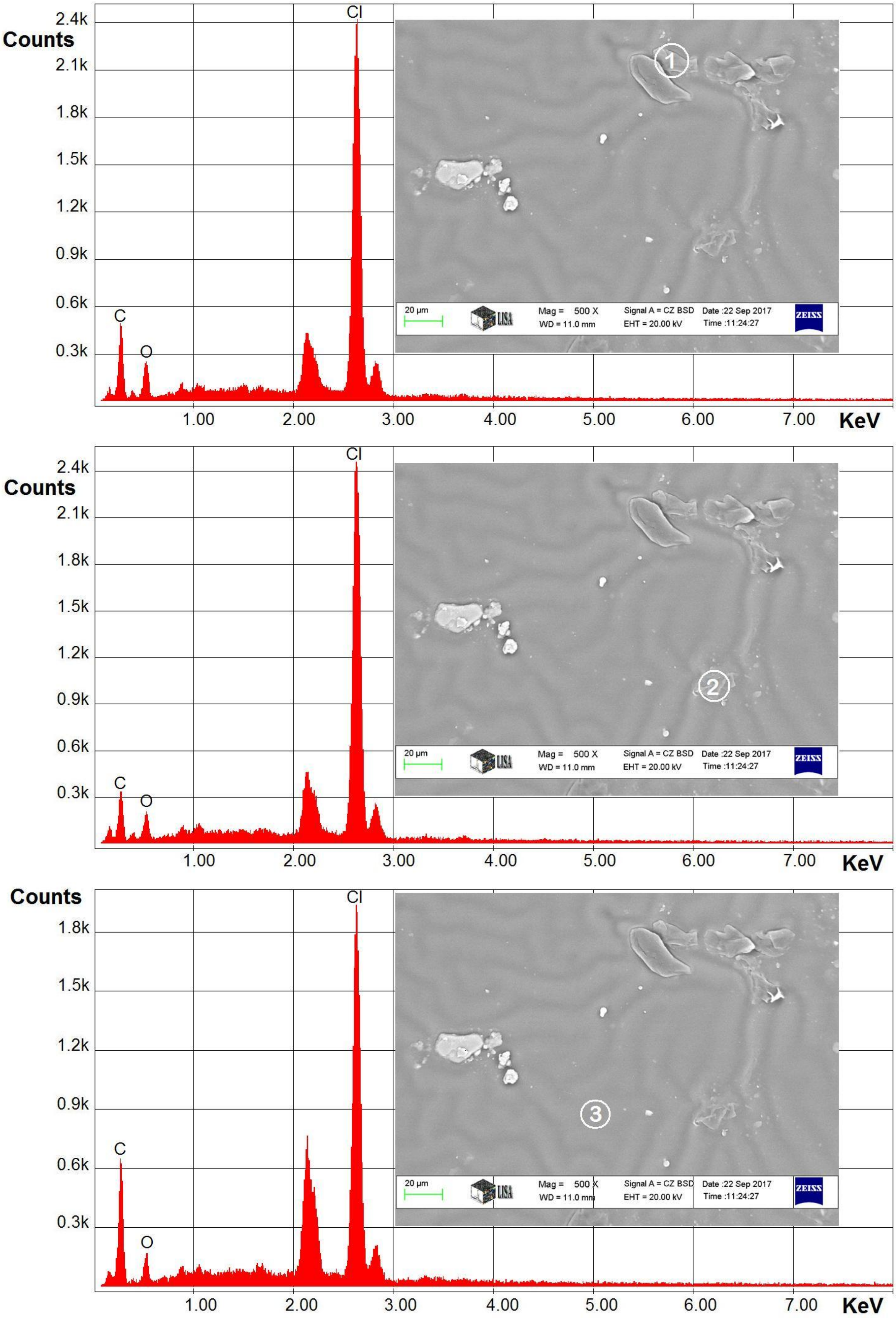

Figure 8.27. SEM - energy dispersive X-ray microanalysis for unburned plasticized poly(vinyl chloride) basic formulation processed by extrusion

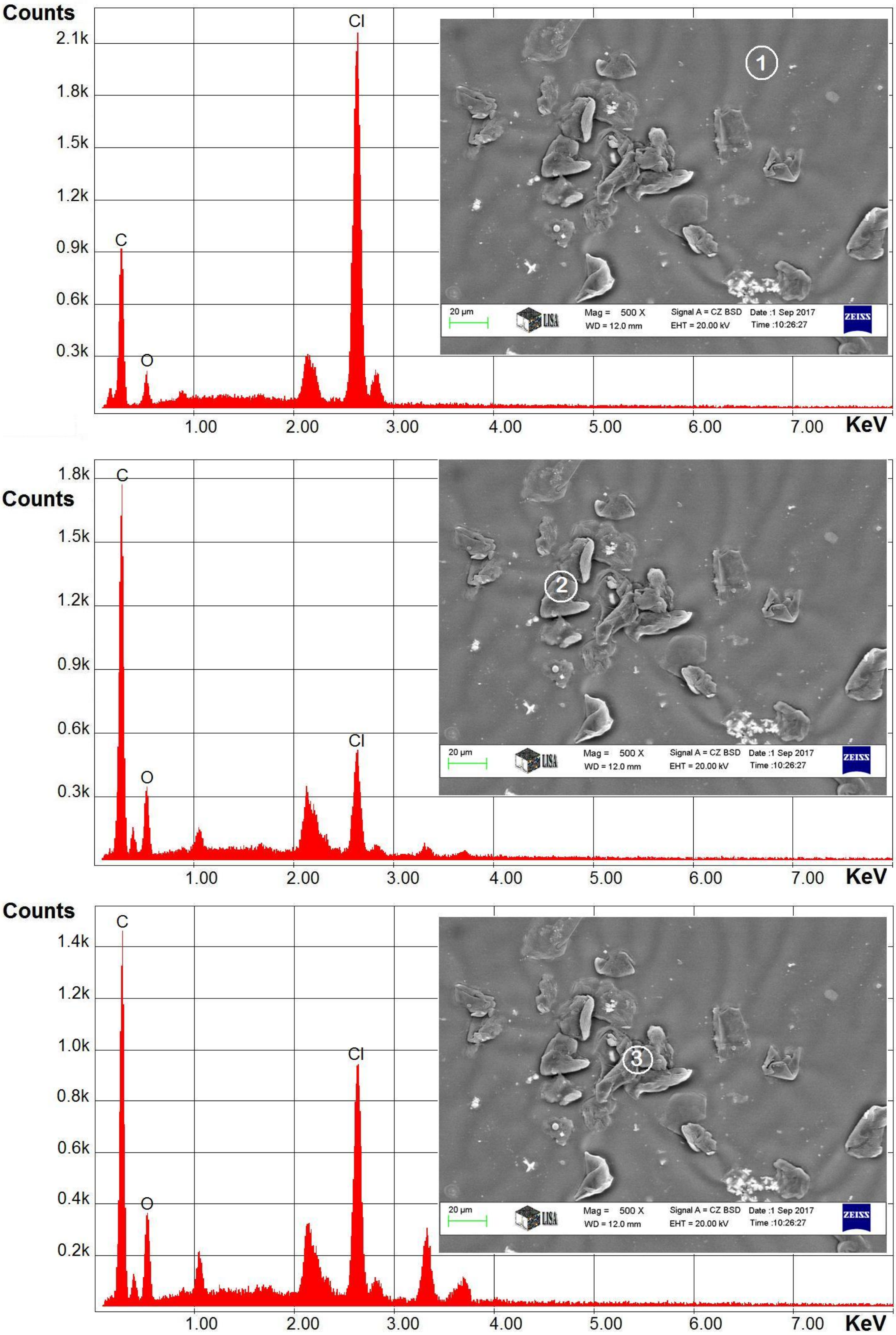

Figure 8.28. SEM - energy dispersive X-ray microanalysis for HAZ in burned plasticized poly(vinyl chloride) basic formulation processed by extrusion

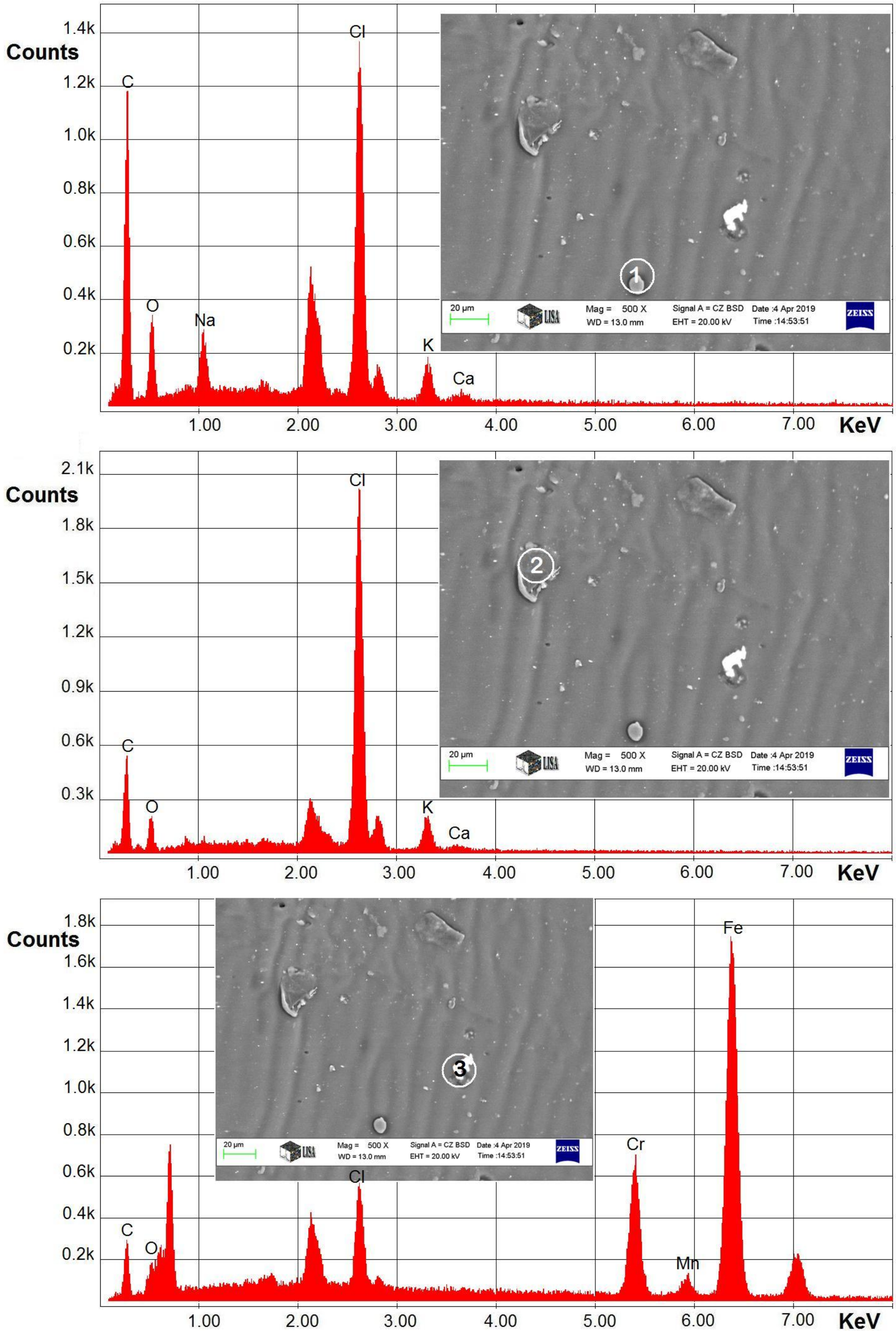

Figure 8.29. SEM - energy dispersive X-ray microanalysis for HAZ in burned plasticized poly(vinyl chloride) containing 1wt.% Oxydtron processed by extrusion

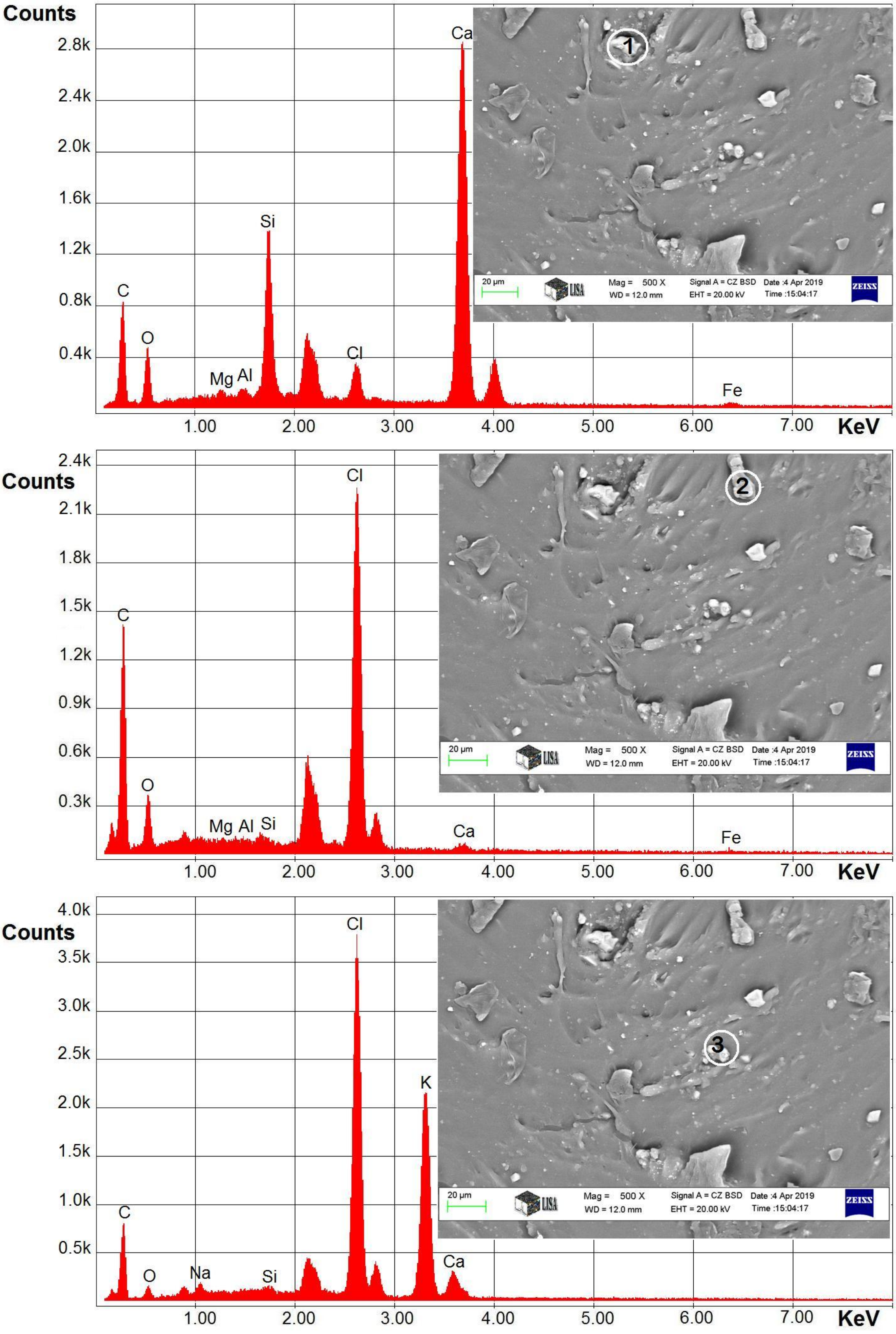

Figure 8.30. SEM - energy dispersive X-ray microanalysis for HAZ in burned plasticized poly(vinyl chloride) containing 3wt.% Oxydtron processed by extrusion

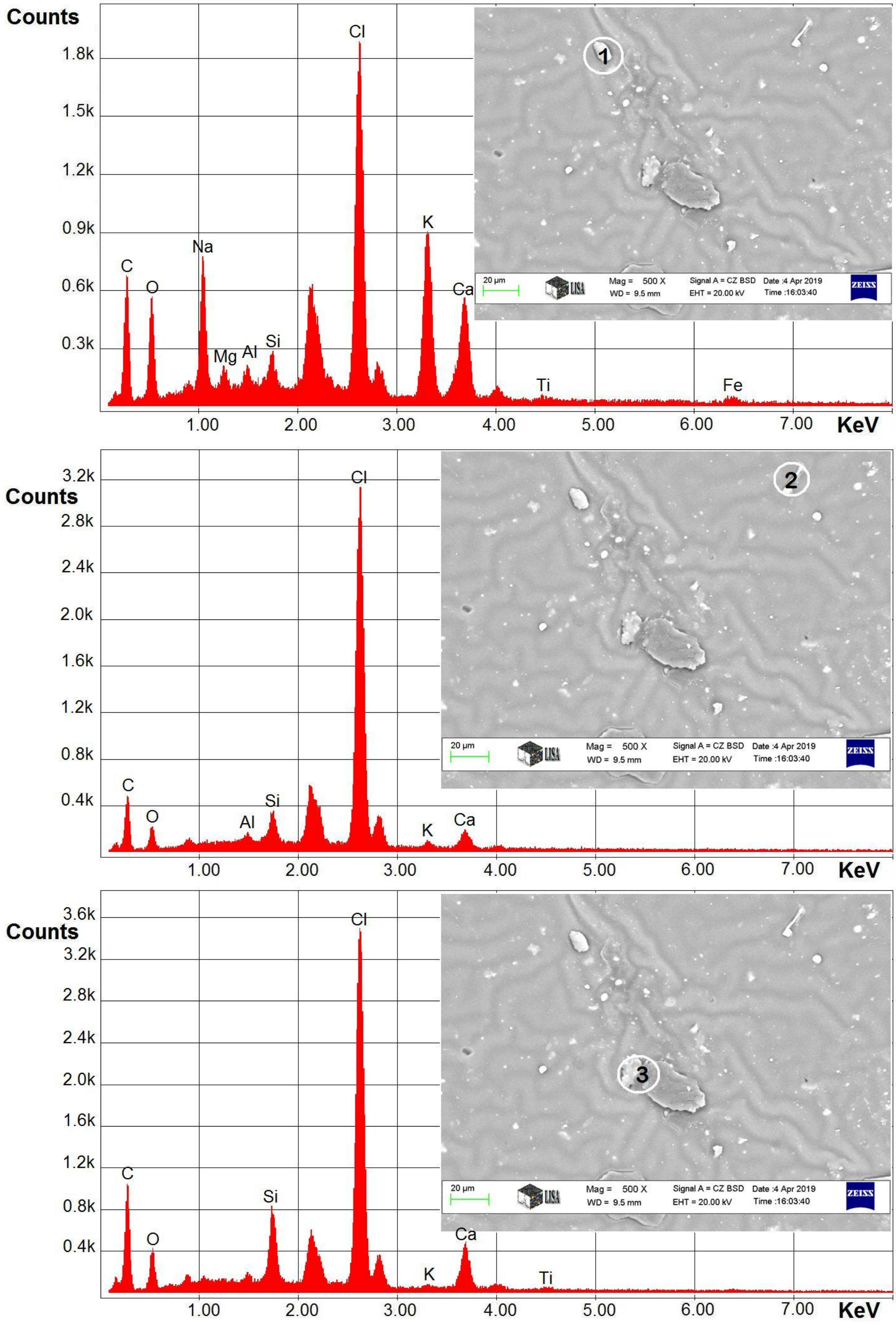

Figure 8.31. SEM - energy dispersive X-ray microanalysis for HAZ in burned plasticized poly(vinyl chloride) containing 5wt.% Oxydtron processed by extrusion

8.9.3 Processing Method

The size of the heat affected zone depends on the type of processing method, as it is wider in rolling samples than in extrusion samples, as shown in Figure 8.32. Since the rolling sample is exposed to processing temperatures more prolonged than the one-stage extrusion, the rolling sample is more heat stressed. Also, the rolling temperature is irregular along the length of the roll, which causes the concentration of the elements to varying from one point to another depending on the amount of heat that was exposed during the rolling. This thing will accelerate it's 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.

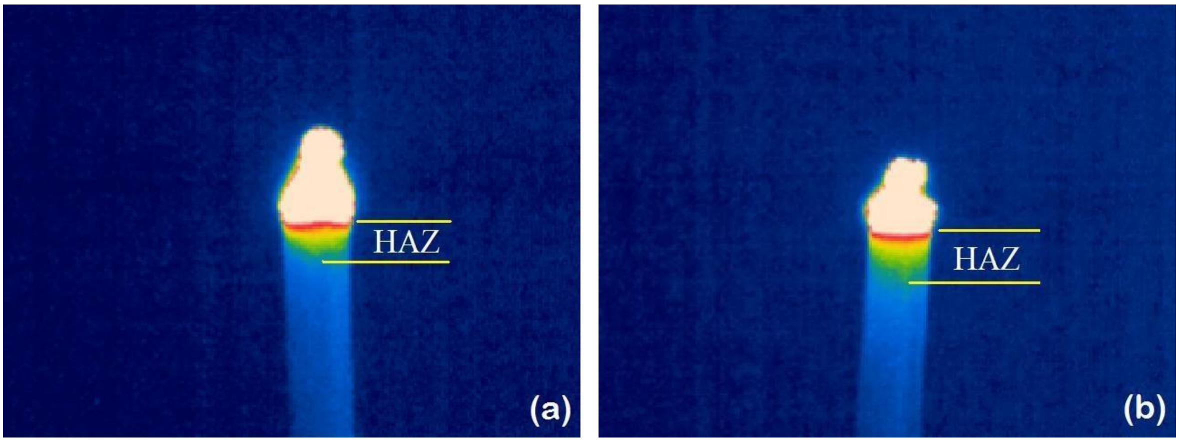

Figure 8.32. FLIR for HAZ of (a) extruded plasticized poly(vinyl chloride) basic formulation, (b) rolled plasticized poly(vinyl chloride) basic formulation

Since the properties and composition of poly(vinyl chloride) depends on its history as mentioned before, any irregularity in the conditions of the processing (especially temperature and time) will lead to deterioration of properties and forming heterogeneous structure as shown in Figure 33 represent SEM - energy dispersive X-ray microanalysis of plasticized poly(vinyl chloride) produced by rolling. When comparing this figure with Figure 8.27, which represents plasticized poly(vinyl chloride) produced by extrusion, we will find that there are fundamental differences between the two samples structures processed by rolling and extrusion, where the ratios of the essential elements of carbon, hydrogen, and oxygen were low and irregular distribution in the rolling samples than in the samples of extrusion [124].

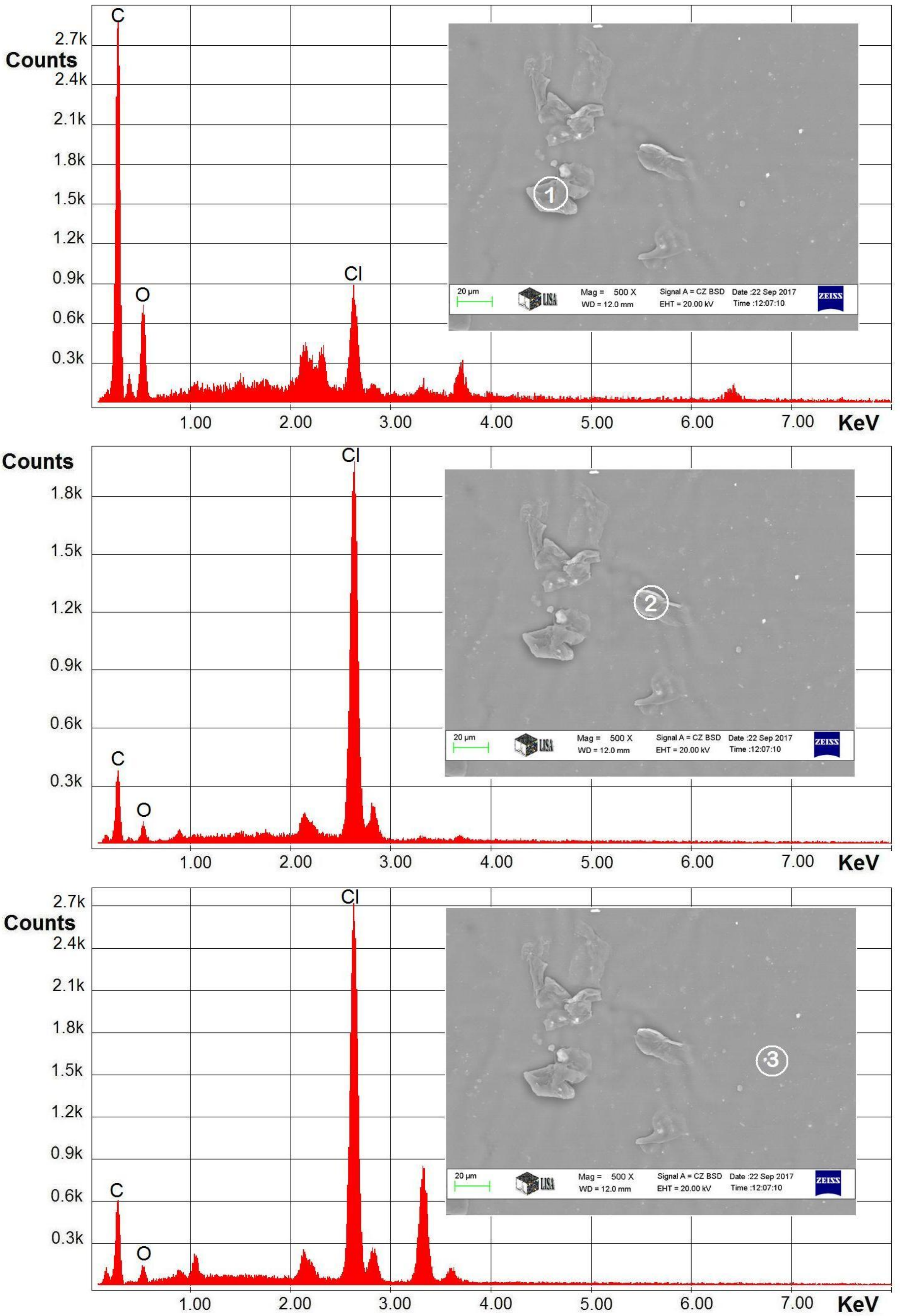

Figure 8.33. SEM - energy dispersive X-ray microanalysis for unburned plasticized poly(vinyl chloride) basic formulation processed by rolling

DOI: 10.14750/ME.2021.039

Chapter Nine: Conclusions

The critical points obtained from the tests performed on plasticized poly(vinyl chloride) (basic formulation and containing Oxydtron) will be summarized in the conclusions section. There are two groups of conclusions: about tests of poly(vinyl chloride) containing Oxydtron and those relating to processing methods.

9.1 Conclusions of tests for plasticized PVC containing Oxydtron

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 µS/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.

9.2 Conclusions of processing methods

1. 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.

2. The optimum properties results were obtained with extruded poly(vinyl chloride) and the thermal tests limiting oxygen index and differential scanning calorimetry have proven that

3. 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.

DOI: 10.14750/ME.2021.039

Chapter Ten: New Scientific Results

The tests that have been done on plasticized poly(vinyl chloride) revealed many new results that could lead to open a new horizon in the poly(vinyl chloride) industry. These results can be included as follows:

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 5wt.% 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.

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.

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.

Claim 5

Due to improved thermal stability of the poly(vinyl chloride), both the rate of degradation and the discoloration -expressed either in yellowing (Δb^*) or in darkening (ΔL^*)- decreased.

Claim 6

Where discoloration period has been extended after using Oxydtron, and the most significant improvement was 86.8% more than poly(vinyl chloride) basic formulation when using 5wt% Oxydtron.

Claim 7

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

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.

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Appendix

Novel evaluation program for estimated dehydrochlorination.

```
CLS
PRINT "  Converts Thermomat txt files to 30s equidistant list."
PRINT "             Absorbtion fluid 50ml water"
PRINT "           Decimal: point; Separator; comma"
PRINT "  The .TXT extension must not be written."
CONST ln10 = 2.302585
DIM a(2500, 2): 'original data from instrument, col1=time; col2=kappa
DIM fe(1500, 4): 'col1=time; col2=kappa; col3=HCl mg; col4=conversion
INPUT "Working disk   "; w$: IF w$ = "" THEN w$ = "": PRINT "Default folder."
eleje:
INPUT "File"; n$
OPEN w$ + n$ + ".TXT" FOR INPUT AS #1
'omitting first 5 rows
FOR i = 1 TO 5: LINE INPUT #1, non$
NEXT i
1 :
   n = 1
DO WHILE NOT EOF(1)
  INPUT #1, a(n, 1), a(n, 2)
  n = n + 1
LOOP
  n = n - 1
CLOSE 1
'reduce to zero
 cr = 1000000: 'selecting the smallest conductivity
FOR i = 1 TO n
  IF cr > a(i, 2) THEN cr = a(i, 2)
NEXT i
```

```
'compensation, the smallest conductivity is subtracted from all kappa data
FOR i = 1 TO n:
  a(i, 2) = a(i, 2) - cr
NEXT i
'makeng an equidistant table with 30 s time step
'interpolacio
fe(1, 1) = 0: fe(1, 2) = 0: 'first data point
tim = 0: 'start from zero
ve = INT(a(n, 1)): 'last time
    m = 1
DO UNTIL tim >= ve
  tim = (m - 1) * 30: '30 seconds is the increment
    FOR i = 1 TO n
      IF a(i, 1) >= tim THEN EXIT FOR
    NEXT i
fe(m, 1) = tim
   mut = (tim - a(i - 1, 1)) / (a(i, 1) - a(i - 1, 1))
   fe(m, 2) = a(i - 1, 2) + mut * (a(i, 2) - a(i - 1, 2))
   m = m + 1
LOOP
   m = m – 1
' converting the conductivity into HCl mg/litre
' HCl mg/litre then HCl mg in 50 ml
FOR i = 1 TO m
  IF fe(i, 2) <= 0 THEN
  fe(i, 3) = 0
  ELSE
    s1 = LOG(fe(i, 2)) / ln10: 'log kappa
'next line is the equation calculating HCl mg/litre from conductivity
    lgc = .9882 * s1 + .003988 * s1 ^ 2 - 1.05788
    x = lgc * ln10: c = EXP(x): 'HCl mg/litre
```

```
'the mg/litre will be divided by 20 > 50 ml water
     fe(i, 3) = c / 20: ' HCl mg liberated
   END IF
NEXT i
'HCl calculation ready
INPUT "PVC in miligrams: "; p:' HCl mg at 100% conversion
p = p * .584: 'real HCl in mg at time fe(i, 1)
FOR i = 1 TO m
   fe(i, 4) = 100 * fe(i, 3) / p: ' conversion in %
NEXT i
OPEN w$ + n$ + ".ASC" FOR OUTPUT AS #1
FOR i = 1 TO m
    PRINT #1, fe(i, 1); ","; fe(i, 2); ","; fe(i, 3); ","; fe(i, 4)
    'PRINT #1, fe(i, 1); ","; fe(i, 2): 'this line is not executed
NEXT i
CLOSE 1
'ready, only administrative tasks from here
'asking for next job
PRINT "Ready! New file?  Y/N"
  DO
    B$ = INKEY$
  LOOP UNTIL B$ = "y" OR B$ = "Y" OR B$ = "n" OR B$ = "N" OR B$ =
CHR$(13)
    IF B$ = "n" OR B$ = "N" OR B$ = CHR$(13) THEN GOTO vege
GOTO eleje: start with new file
vege: 'vege means END
END
```

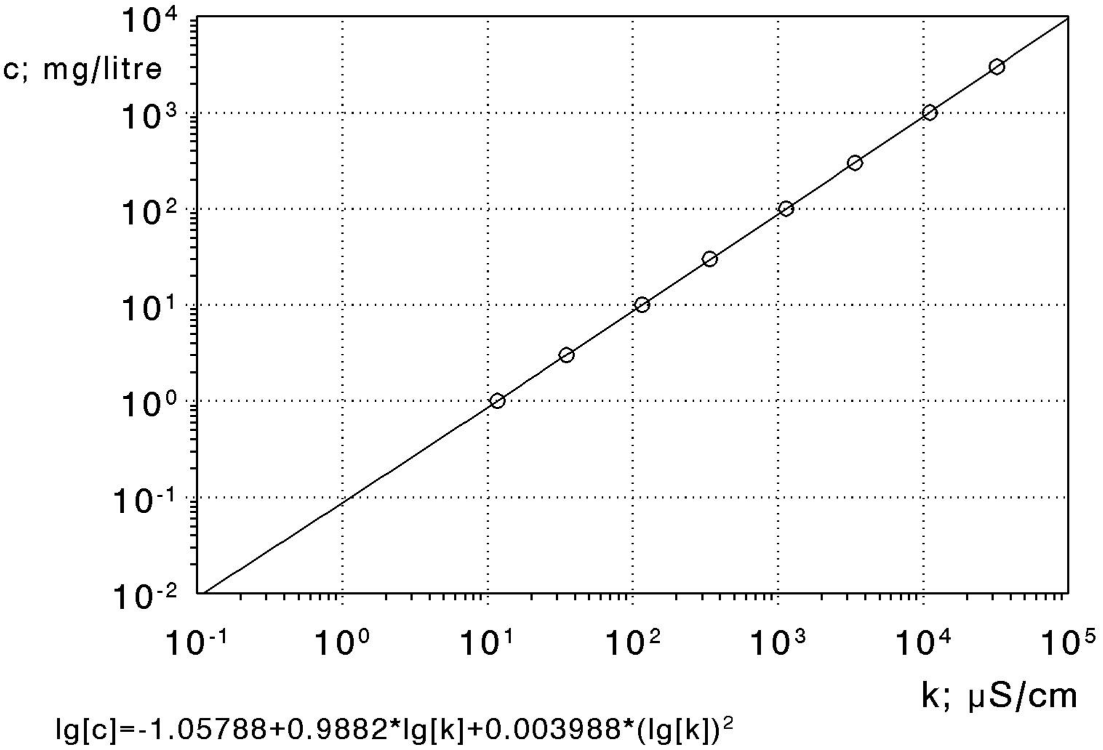

Figure 1. Conductivity of HCl solution

Table 1. Foxboro data of conductivity vs. Concentration [192]

Weight %	ppm mg/litre	Sodium Chloride, NaCl	Sodium Hydroxide, NaOH	Hydrochloric Acid, HCl	Sulfuric Acid, H_2SO_4	Nitric Acid, HNO_3	Hydrofluoric Acid, HF	Acetic Acid (a), CH_3COOH
0.0001	1	2.2	6.2	11.7	8.8	6.8	10	4.2
0.0003	3	6.5	18.4	35.0	26.1	20	30	7.4
0.001	10	21.4	61.1	116	85.6	67	99	15.5
0.003	30	64	182	340	251	199	290	30.6
0.01	100	210	603	1 140	805	657	630	63
0.03	300	617	1 780	3 390	2 180	1 950	1 490	114
0.1	1 000	1 990	5 820	11 100	6 350	6 380	2 420	209
0.3	3 000	5 690	16 200	32 200	15 800	18 900	5 100	368
1.0	10 000	17 600	53 200	103 000	48 500	60 000	11 700	640
3.0	Rarely Used	48 600	144 000	283 000	141 000	172 000	34 700	1 120
5.0	Rarely Used	78 300	223 000	432 000	237 000	275 000	62 000	1 230
10.0	Rarely Used	140 000	358 000	709 000	427 000	498 000	118 000	1 530
20.0	Rarely Used	226 000	414 000	850 000	709 000	763 000	232 300	1 600
30.0	Rarely Used	Saturated	292 000	732 000	828 000	861 000	390 000	1 405
40.0	Rarely Used	Saturated	191 000	Saturated	770 000	820 000	N/A	1 080
50.0	Rarely Used	Saturated	150 000	Saturated	620 000	717 000	N/A	740
75.0	Rarely Used	Saturated	Saturated	Saturated	182 000	340 000	7.8 (0°C)	168
100.0	Rarely Used	Saturated	Saturated	Saturated	10 000	50 000	4 (0°C)	< 1
Point of Maximum Solubility	---	26%	About 50%	37%	---	---	---	---
Point(s) of Maximum Conductivity	---	26%	16%	18.5%	31% 92.5%	31%	About 35%	19%
Maximum Conductivity	---	244 000	412 000	852 000	830 000 139 000	862 000	N/A	1 600

(a) HAc data at 18 °C