A novel conceptional approach for calculating the stability time related to converting the anticipated degradation from the curve of conductivity for flexible poly (vinyl chloride)

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Abstract

The current study introduces a novel method for calculating the stability time by a new approach based on the conversion of degradation from the conductivity curve results obtained by the conventional method. The stability time calculated by the novel method is shorter than the time measured by the conventional method. The stability time in the novel method can be calculated by the endpoint of the tangency of the conversion curve with the tangent line. This point of tangency represents the stability time, as will be explained in detail. Still, it gives a clear and accurate envisage of the dehydrochlorination behavior and can be generalized to all types of polyvinyl chloride compared to the stability time measured by conventional ones based on measuring the conductivity which cannot be used to compare different compounds because PVC-based compounds may include varying amounts of PVC. As a result, the conventional method is inapplicable in all cases. For example, specific conductivity of 60 µS/cm indicates the same quantity of HCl but a different degradation grade. If this conventional approach is used alone, the results obtained will be inaccurate. Therefore, the novel method possesses greater sensitivity and accuracy for these differences in PVC-based compounds.

Keywords: stability time, thermal dehydrochlorination, novel evaluation, flexible poly (vinyl chloride)
Kulcsszavak: stabilitási idő, termikus dehidroklórozás, új értékelés, lágyított poli (vinil-klorid)

1. Introduction

The unique characteristics of polymers in general, including poly (vinyl chloride) (PVC), have made them a real competitor to the rest of the materials in various applications that require high performance and quality such as aerospace, automotive, medical and electronics applications [1-4]. However, like everything in this universe, there is nothing entirely perfect, and polymers, despite their distinctive characteristics, suffer from a significant deterioration in their thermal resistance at high temperatures. This is the primary determinant of their choice in such applications that require high thermal resistance. In addition, the type of polymer will determine the decomposition behavior at high temperatures and the resulting compounds [5-8]. In the case of poly (vinyl chloride), when the temperature rises from 170 °C and above, the chlorine and hydrogen will be removed from the poly (vinyl chloride) molecules. This released chlorine and hydrogen will react to create hydrogen chloride (HCl), which also will be released as a product of degradation as shown in *Fig. 1* [5]. This removal process of HCl is called dehydrochlorination, which will be activated and stimulated by high temperatures. The degradation of the PVC structure is randomly generated through the lattice defects created during the polymerization process, and these defects are allylic chlorine atoms and tertiary chlorine atoms [5, 9-12]. During the polymerization process, tertiary chlorine and allylic chlorine atoms are produced due to branch formation and polymerization termination. Poly (vinyl chloride) degradation is initiated at the defects created by these atoms [13,14]. During the process, new defects caused by hydrogen chloride are generated, which add to the existing defects resulting from polymerization. When there is no interference from the stabilizer, whether due to incompetence or lack thereof, stops the release of HCl, the zipper-like continuation will continue.

A light yellow color will develop when six to seven conjugated double bonds are formed after the formation of HCl and conjugated double bonds, i.e., polyene sequences. With increasing conjugation length, this light yellow appearance can darken to red, brown, and black [15-20]. When the temperature is not reduced, this cycle of dehydrochlorination will be repeated and restored rapidly and significantly. At this stage, the decomposition becomes permanent and will cause structural and apparent deformation of the material [21, 22]. Due to the fact that poly (vinyl chloride) is heated to soften phase during processing, such as extrusion or rolling, minimizing HCl release is a priority. This can only be accomplished by halting or minimizing decomposition. Numerous studies have established HCl's autocatalytic activity on poly (vinyl chloride) degradation

[10, 23]. As we know, the conventional method used to evaluate the thermal degradation of poly(vinyl chloride) depends on exposing a sample of poly (vinyl chloride) placed in the device cylinder to high temperatures in order to measure the stability time, which represents the time at which the polymer begins to release HCl, i.e., starting of degradation [24-31].

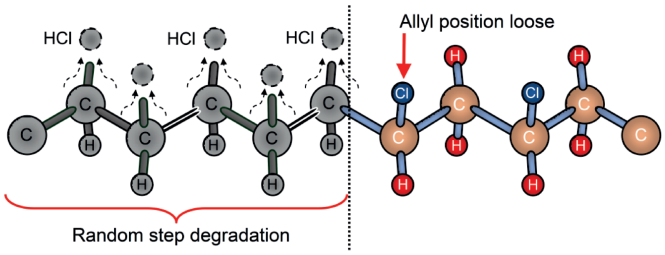

Fig. 1 Mechanism of poly(vinyl chloride) thermal degradation
1. ábra A poli(vinil-klorid) termikus lebomlásának mechanizmusa

As a result, the dehydrochlorination conversion rate is approximately 0.9% at 60 µs/cm conductivity. At these measuring conditions, there will be errors in the measurement and consequently a glitch in the obtained results and their accuracy in giving the correct concept and a clear and non-misleading vision of the degradation [32]. The reason for this state lies in the fact that not all poly (vinyl chloride) based compounds contain the same amount of poly (vinyl chloride). Therefore, it becomes difficult to compare the degradation behavior of these different compounds. So, another method of measurement must be relied upon to be more adapted to these compounds and provide a high level of accuracy and not be affected by the different amounts of poly (vinyl chloride), but rather on the principle of measuring them on other parameters that can give the same degradation behavior but more precisely as we have mentioned even if it was in a shorter time. The novel developed method is based on determining the level i.e. the conversion of degradation from the conductivity curve, which is obtained through the dehydrochlorination test performed by the conventional method [5]. In practice, this developed method is considered more accurate in measuring the level of decomposition of poly (vinyl chloride) because it depends on the measurement of a stable parameter, which is the conductivity, which gives sufficiently precise results in the measurement as mentioned for all types of poly (vinyl chloride). The advantage of the novel method is that the measured stability time is shorter than in the case of the conventional method. Despite this, it clearly describes the degradation behavior of poly (vinyl chloride).

2. Methodology

2.1 Materials

The poly (vinyl chloride) mixture or blend generally consists of primary powder of PVC and additives that give it its distinctive characteristics, as shown in *Fig. 2*.

1. Primary powder: 100 phr of PVC suspension type S-507070 (Ongrovil®).
2. Additives: two groups of additives were used, which included:

a. Essential additives are necessary to give the basic characteristics of PVC synthesis. These additives are 70 phr DOP Bis (2-ethylhexyl-phthalate) as a plasticizer; 1.5 phr of Ca-Zn based (Newstab-50®) stabilizer; and finally 0.3 phr of Wax E (Licowax®E) as an external lubricant. The suppliers of these materials are BorsodChemZrt., DEZA, a. s. CO., Betaquímica CO., and Clariant International Ltd, respectively.

b. Additional additives and the aim of adding them are to improve the initial properties and give new properties to the possibility of using poly (vinyl chloride) in more comprehensive applications with outstanding performance. This study added 1-5 wt.% of Oxydtron as a flame retarding-stabilizing agent was added. Oxydtron is a unique mineral nanocement additive applied to improve the workability and durability of concrete. Oxydtron is composed of several chemical compounds and copolymers. The supplier of Oxydtron is Bioekotech.

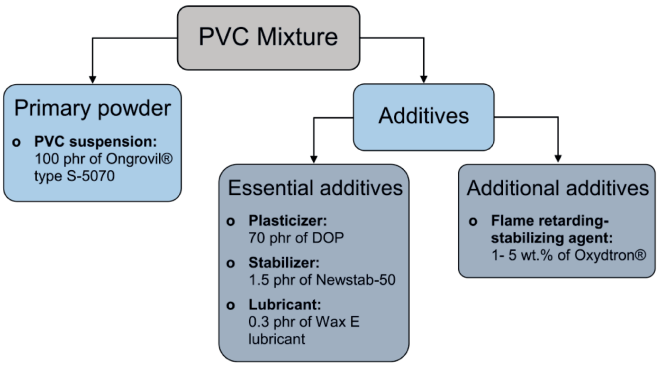

Fig. 2 Components of flexible poly(vinyl chloride) mixture
2. ábra lágyított poli(vinil-klorid) keverék összetevői

2.2 Mixing process

The mixing process includes two main stages, preparatory and definitive mixing, as shown in *Fig. 3*, with specific processing conditions listed in *Table 1*.

1. **Preparatory mixing:** It can also be called primary mixing. This mixing aims to configure poly (vinyl chloride) basic formulation mixture. In this stage, all the basic components of the poly (vinyl chloride) mixture (primary powder and essential additives) are mixed using a mechanical mixer type MTI-Mischtechnik to produce poly (vinyl chloride) basic formulation mixture. This stage takes place with a specific time of 40 minutes divided into three steps, each step having a particular speed, temperature, and time. The three steps of preparatory mixing are:

   i. **Initiatory mixing:** In this step, all the solid ingredients are mixed first, where the PVC suspension, stabilizer, and wax lubricant are put together in the mixer and started to rotate at 600 rpm speed and 30 °C temperature for two minutes. Then, during the rotation, the liquid plasticizer is gradually poured over the solid mixture, and the ingredients are left to mix well for three minutes at the same speed of rotation.

ii. **High speed-temperature mixing:** The mixing speed will be increased to 2700 rpm at this step. As a result of the high rotational speed, the shearing of particles between the mixture's components will increase, leading to rises steadily from room temperature to 150 °C. This step takes 15 minutes. The plasticizer will reach deeper into the PVC particles with speed stability, resulting in a homogeneous structure with better manufacturing properties.

iii. **Cooling:** The PVC mixture will be cooled by reducing the mixing speed to 600 rpm and pumping cooling water between the walls of the mixer. At this step, the mixture remains for 20 minutes, during which its temperature drops 150 °C to below 45 °C. At this step's end, the PVC mixture's temperature will reach 30 °C.

2. **Definitive mixing:** It can be called metaphorically secondary mixing. In this stage, the Oxydtron will be added in various weight ratios (1, 3, and 5 wt.%) to the poly (vinyl chloride) basic formulation mixture produced by the preparatory mixing stage. Then, the final mix will be mixed by a laboratory blender type Snijders scientific-LB20E at room temperature with 500 rpm speed for 1 minute.

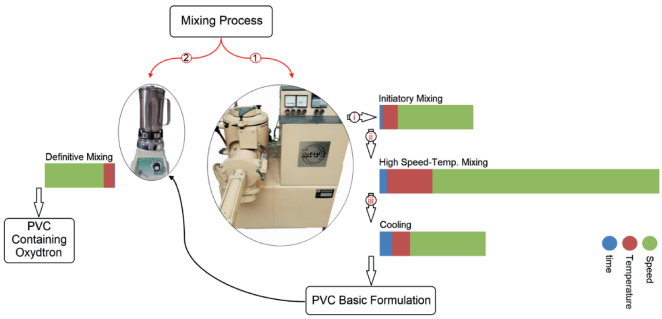

Fig. 3 The procedure of mixing process
3. ábra A keverési folyamat eljárása

Parameter	Preparatory mixing			Definitive mixing
	Initiatory mixing	High speed-temp. mixing	Cooling	
Time, min	5	15	20	1
Temperature, °C	30 °C	From 30 °C increased to 150 °C	From 150 °C dropped to 45 °C and reached to 30 °C at the end	Room temp.
Speed, rpm	600	2700	600	500

Table 1 Processing conditions of preparatory mixing
1. táblázat Az előkészítő keverés feldolgozási feltételei

2.3 Samples preparation and testing

The samples of dehydrochlorination test were prepared using twin-screw extrusion machine type Schloemann BT-50 as pellets with 3 mm diameter and 2 mm thickness. The dehydrochlorination behavior of flexible poly (vinyl chloride) containing Oxydtron has been measured by conventional method using Metrohm 763 Thermomat found at BorsodChem Zrt., Hungary. This test was completed according to ISO 182-3:1993 standard [33] with temperature 200 °C.

3. The procedure of calculating stability time

The procedure for calculating the stability time includes the following steps:

1. **Data collection:** the data of dehydrochlorination results obtained by the conventional method have been stored as a Notepad file, as shown in *Fig. 4. a*. These stored data represent time in seconds (s) and measured values of conductivity (µS/cm).

2. **Data analysis:** A data conversion program developed specifically to extract the concentrations of HCl from the stored data of dehydrochlorination has been used to analyze those data. The conversion program requires entering the quantity of poly(vinyl chloride) alone without other components. This program converted conductivity to HCl concentration using the conversion function depending on the Foxboro data table, which represents the conductivity vs. concentration for common solutions [34]. The HCl concentration is illustrated by the following equation [32]:

$$\lg(c) = -1.05788 + 0.9882 \times \lg(k) + 0.003988 \times (\lg(k))^2 \quad (1)$$

Where:
(c) the HCl concentration measured in mg/l,
(k) the specific conductivity measured in µS/cm.

Since the Metrohm 763 Thermomat device in the conventional method usually utilizes a quantity of water of 50 ml, the absorbed HCl can be measured, which will be c/20. In addition, if the exact mass of PVC in the testing sample can be determined, then the conversion of degradation can be estimated by converting the dehydrochlorination curve using the following equation [32]:

$$k = m_{HCl}/0.584 \times m_{PVC} \quad (2)$$

This is because 58.4% of HCl is produced during the whole degradation of poly (vinyl chloride)'s basic formulation.

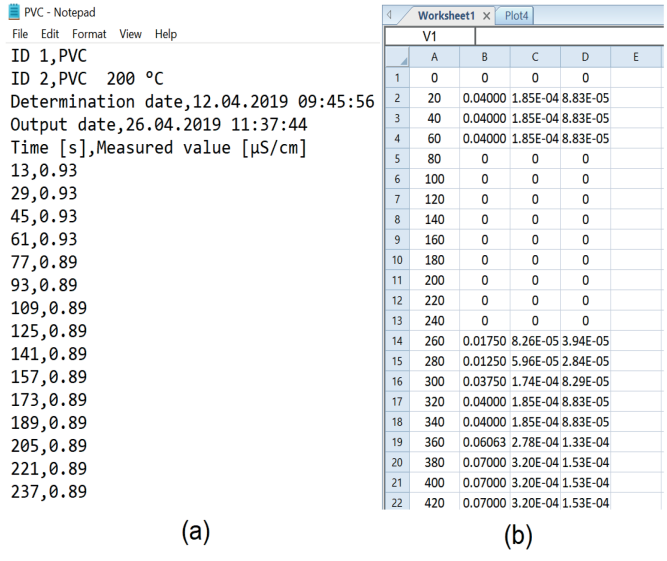

Fig. 4 (a) The stored results as notepad file in Metrohm 763 Thermomat database, and (b) Columns of the result files obtained by data conversion program
4. ábra (a) A metrohm 763 Thermomat adatbázisban jegyzettömbfájlként tárolt eredmények, és (b) Az adatkonverziós program által kapott eredményfájlok oszlopai

3. **Organizing output data:** When the data from the analysis step is imported, four reorganized data types will appear, distributed over four columns, as shown in *Fig. 4b*. These four reorganized data represent:
   i. Time in seconds in steps given by the program (20 or 30 s) (Column A).
   ii. Interpolated conductivity in µS/cm (Column B).
   iii. HCl evolved in mg, not the concentration but in the 50ml water (Column C).
   iv. Conversion in percent (after inputting the PVC in mg for the program) (Column D).

4. **Calculation of stability time:** Here, we get the stability time by locating the endpoint of the tangency between the conversion curve and the tangent line, where this point of tangency represents the stability time, as shown in *Fig. 5*.

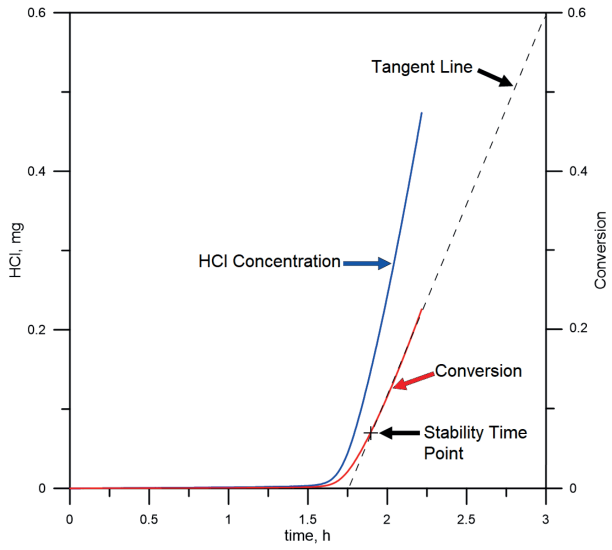

Fig. 5 Calculating the stability time by the novel method
5. ábra A stabilitási idő kiszámítása az új módszerrel

4. Results and discussion

4.1 Dehydrochlorination

As the temperature rises, the structure of poly (vinyl chloride) becomes unstable, which results in a significant release of hydrogen chloride (HCl) by the dehydrochlorination process and accompanied by a decrease in the resistance of poly (vinyl chloride). As a result, the conjugated polyene sequences are formed during the dehydrochlorination process of poly (vinyl chloride), leading to degradation. The poly (vinyl chloride) goes through three significant stages of degradation, namely initiation, propagation, and termination. The entry of the polymer into any of these stages depends on its thermal resistance, the temperature to which it is exposed, the period of exposure, and the percentage of plasticizer. These exceptional circumstances will determine the extent of deformation and damage to the poly (vinyl chloride) [35, 36]. The degradation behavior of flexible poly (vinyl chloride) has been shown in *Fig. 6*, which represents the dehydrochlorination test for flexible poly (vinyl chloride) not containing additional additives at 200 °C analyzed by the conventional standard and novel methods. As we can note from this figure, the dehydrochlorination results are represented by the relationship between conductivity and time for poly (vinyl chloride) measured by the conventional method (a). In contrast, the results obtained by the novel method are related to HCl concentration time and conversion parameters (b). From the two methods we can see that the poly (vinyl chloride) undergoes severe degradation when exposed to such a high temperature, and the thermal stability is greatly decreased, as explained above [37-40].

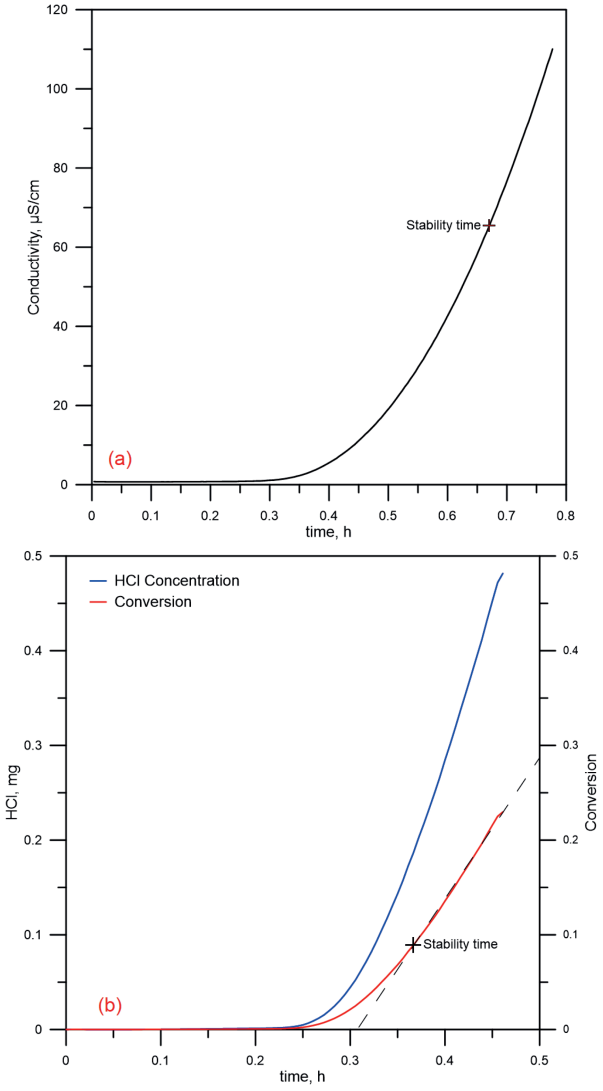

Fig. 6 Analysis of the degradation behavior of pure flexible poly(vinyl chloride) by (a) conventional and (b) novel methods during the dehydrochlorination process at 200 °C
6. ábra Tiszta, hajlékony poli (vinil-klorid) lebomlási viselkedésének elemzése a) hagyományos és b) új módszerekkel a 200 °C-on történő dehidroklórozási folyamat során

From *Fig 6.b.* we can see how quickly and sharply HCl loss occurs, where the slope of the curve is extremely steep (414×10^{-6} %s^{-1}). Poly (vinyl chloride) has this characteristic due to its limited thermal resistance at elevated temperatures. When HCl is released into the poly (vinyl chloride) structure, this heat resistance lowers more and more as the structure of poly (vinyl chloride) is significantly distorted [35]. Activation energy plays an essential role in the degradation process. The

low activation energy of poly (vinyl chloride) compared to other polymers such as polyethylene, polystyrene, or polypropylene causes it to enter the initiation stage of degradation at relatively low temperatures of about 100 °C. Under temperatures above 100 °C, unstable and reactive allylic and tertiary chlorines will produce chloride ions or chlorine radicals. The removal of chlorine from the poly (vinyl chloride) structure will also stimulate the release of hydrogen, leading to the formation of a double bond. Finally, the HCl will be created and released as a degradation product. The allylic group will be introduced when HCl is released from the poly (vinyl chloride)'s structure. This process will act as a self-stimulant or catalyzed to remove more HCl. Thus, poly (vinyl chloride) quickly enters the second degradation stage (propagation), followed by complete burning, representing the termination's third stage [41-47].

The important thing that can be deduced from *Fig. 5* is the difference between the stability time measured by the novel method and the conventional method one, where the stability time measured by the novel method is considerably shorter than that measured by the conventional method by 8.25%, at relatively low conductivity rates (less than 60 µS/cm), as listed in the *Table 2* which represents the stability time of flexible poly (vinyl chloride) containing Oxydtron as measured by the novel method and compares the results with the measurements obtained by the conventional method. Noting that the actual value of the conductivity in the case of the conventional method, based on which the stability time was calculated, is not exactly 60 µS/cm, but somewhat higher than it, which is what found when analyzing the conductivity values in the original notepad files.

Material	Stability time measured by novel method, h	Stability time measured by conventional method standard, h	time difference between the two methods, %
PVC	0.367	0.400	8.25
PVC+1wt.% of Oxydtron	0.622	0.670	07.16
PVC+3wt.% of Oxydtron	0.772	0.850	10.10
PVC+5wt.% of Oxydtron	0.783	0.860	09.83

Table 2 Stability time of flexible poly(vinyl chloride) containing Oxydtron measured by novel method and conventional method at 200 °C

2. táblázat Az Oxidtront tartalmazó hajlékony poli (vinil-klorid) stabilitási ideje új módszerrel és hagyományos módszerrel mérve 200 °C-on

The best way to increase the thermal resistance of polymers in general and poly (vinyl chloride) in particular is to use additional additives with the essential additives that make up the polymer. This new, improved behavior can be clearly seen from *Fig. 7*, representing the dehydrochlorination test for flexible poly (vinyl chloride) containing 1 wt.% of Oxydtron measured at 200 °C and analyzed by the novel and conventional methods. Looking at this figure, it will be apparent that reducing the value of the slope to 335×10^{-6} %s^{-1} and extending the time to complete degradation from (0.46 h) to (0.78 h) are indications of an increase in the thermal resistance of the flexible poly (vinyl chloride) after adding Oxydtron. Therefore, from the point of view of the analytical meaning, it can be said that the poly (vinyl chloride) has a more stable structure at elevated temperatures. The Oxydtron will act as an inhibitor for polyenes synthesis by reducing the tendency for allylic chloride groups production. This will prevent the poly (vinyl chloride) from entering the propagation stage, thereby extinguishing the fire. As observed previously in the novel method plot, the conventional method also shows the improvement in the degradation behavior of flexible poly (vinyl chloride) after adding 1 wt.% of Oxydtron.

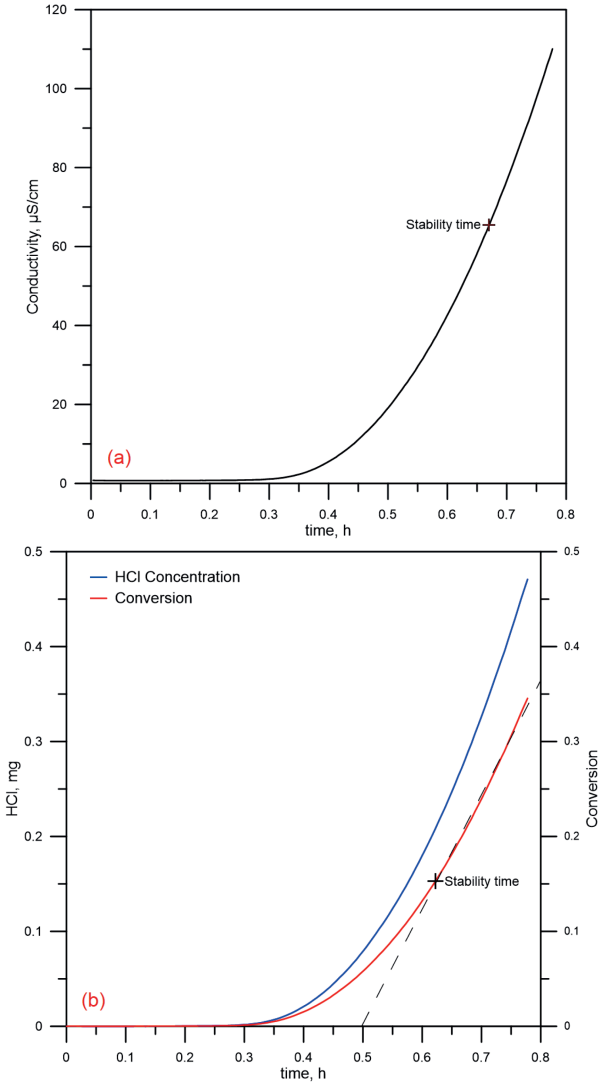

Fig. 7 Degradation behavior of flexible poly(vinyl chloride) containing 1wt.% of Oxydtron during dehydrochlorination process at 200 °C analyzed by (a) conventional and (b) novel methods

7. ábra Az 1wt.% Oxydtront tartalmazó rugalmas poli (vinil-klorid) lebomlási viselkedése a 200 °C-on végzett dehidroklórozási folyamat során, a) hagyományos és b) új módszerekkel elemezve

After the Oxydtron has been added, we notice that the stability time measured by the novel method remained shorter than that of the conventional method by 7.16%, as shown in *Table 2*. Adopting the HCl concentration criterion instead of conductivity in determining the stability time will be better and more accurate in determining the actual degradation time. As we know, the stability time in the conventional method is recorded after releasing a sufficient amount of HCl capable of generating an increase in conductivity at the range of 60 µS/cm

[37, 48, 49]. At the novel method, the short stability time is also accompanied by a low value of the conductivity, at which time value will be recorded. The sharp increase in conductivity with a long time interval because the addition of Oxydtron increased the thermal stability of poly (vinyl chloride) by creating a synergistic stabilizing effect with the original stabilizer. This synergistic stabilizing behavior is due to the composition of Oxydtron, which consists of numerous compounds such as oxides and carbonates, which function as synergistic agents with the original stabilizer, improving the thermal stability of poly (vinyl chloride).

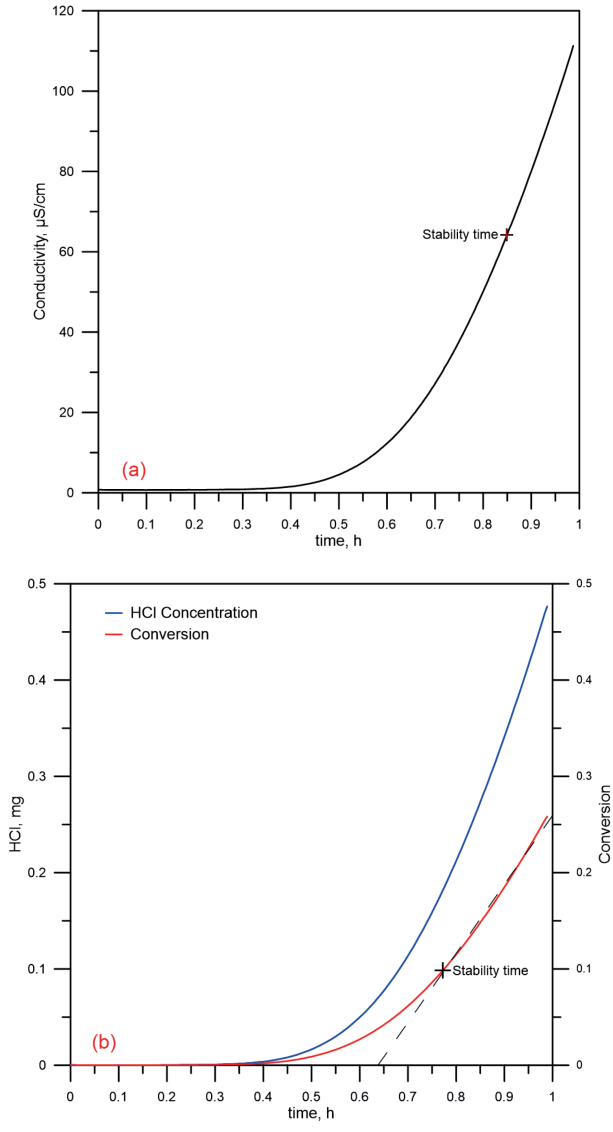

Fig. 8 Degradation behavior during dehydrochlorination process at 200 °C analyzed by (a) conventional and (b) novel methods for flexible poly(vinyl chloride) containing 3 wt.% of Oxydtron

8. ábra Lebomlási viselkedés a 200 °C-on történő dehidroklórozási folyamat során a) a 3 wt.% Oxydtront tartalmazó rugalmas poli (vinil-klorid) hagyományos és b) új módszereivel elemezve

Increasing the proportions of Oxydtron to 3 wt.% and 5 wt.% will further improve the thermal stability of flexible poly (vinyl chloride), which positively reflects its resistance to thermal degradation. The improvement in the degradation behavior of the flexible poly (vinyl chloride) after adding 3 %wt. and 5 %wt. of Oxydtron nanocement is shown in *Fig. 8* and *Fig. 9* respectively. At 3 wt.% addition, the slope of the conversion rate dropped to 199×10^{-6} $\%s^{-1}$, and at 5 wt.% addition kept going down to 165×10^{-6} $\%s^{-1}$, indicating that the degradation resistance has been enhanced, with an increase in the overall degradation time to 0.99 h and 1.02 h, respectively. On the other hand, for the conventional method, the conductivity also increases with the increased of the proportion of artificial silica added. As a result of the improvement in degradation resistance of poly (vinyl chloride) after adding Oxydtron with weight fractions of 3 wt.% and 5 wt.%, the stability time will also increase after these additions. The stability time rises from 0.772 h in the case of 3 wt.% of Oxydtron to 0.783 h in the case of adding 5 wt.% of Oxydtron. However, this rise in the stability time is still shorter than the measured by the conventional method by 10.10% and 09.83% at Oxydtron ratios of 3 wt.% and 5 wt.%, respectively, as is evident from *Table 2*.

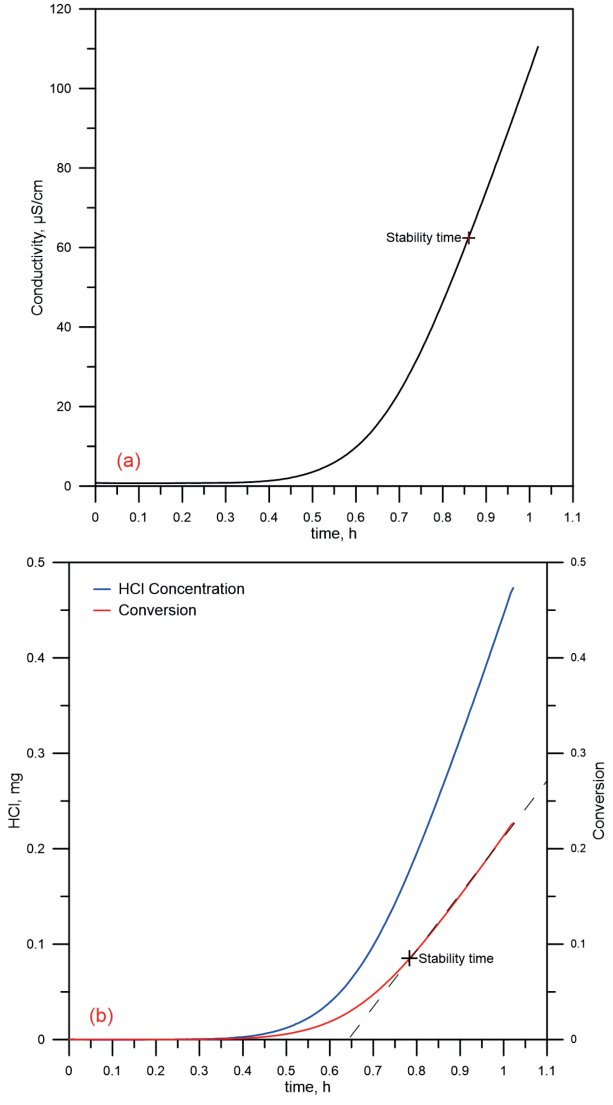

Fig. 9 Degradation behavior of flexible poly (vinyl chloride) containing 5 wt.% of Oxydtron during dehydrochlorination process at 200 °C and analyzed by (a) conventional and (b) novel methods

9. ábra Az 5 wt.% Oxydtront tartalmazó rugalmas poli (vinil-klorid) lebomlási viselkedése 200 °C-on történő dehidroklórozási eljárás során, amelyet a) hagyományos és b) új módszerekkel elemeznek

5. Conclusions

Through the results of the stability time obtained from the novel method and compared with the conventional method, it will become apparent that the entry of poly (vinyl chloride) to the initiation stage of degradation is faster than we expected. So the degradation entry to the next stage, which is propagation down to the stage termination stage, will be shorter. Therefore, more care must be taken when poly (vinyl chloride) is exposed to high temperatures while providing maximum protection through appropriate additives. In contrast to the conventional method, the novel developed method describes better the process in particular in case of PVC compounds. It shows a good agreement with the discoloration and initial color changes.

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