

Research Article

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Investigating the role of different stabilizers of PVCs by using a torque rheometer

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Abstract: Poly(vinyl chloride) (PVC) is one of the versatile thermoplastic materials that have tremendous applications almost everywhere but it is thermally unstable at high temperatures. Processing of PVC at elevated temperatures requires the use of thermal stabilizers that are considered crucial additives for the protection of PVC during both processing and useful life usage. Several thermal stabilizers are available commercially that mostly obstruct the dehydrochlorination reaction. Choosing appropriate stabilizer systems for a specific application is cumbersome. A Brabender torque rheometer at a constant temperature of 180°C and variable shear stress was used to evaluate the stabilizing efficiency of 12 different stabilizer systems combined with PVC. Fusion time, induction period, minimum torque, and rheological stability time were determined in order to evaluate the investigated stabilizer systems. It was found that dibutyl tin mercaptide was the best stabilizer, while the mixture of lead stabilizers was the worse one.

Keywords: poly(vinyl chloride), stabilizers, thermal degradation, dehydrochlorination

1 Introduction

Poly(vinyl chloride) (PVC) is one of the most worldwide used thermoplastics with a vast spectrum of properties including low cost, simple processing, and flammability resistance. The rigid PVC form exhibited good market growth in major PVC product applications, i.e., pipes, due

to its magnificent functional properties and cost competitiveness [1,2].

Because of the structural defect in the PVC structure due to the presence of allylic chloride atoms, it is extremely sensitive to heat. There have been many attempts to improve the thermal stability of this polymer because almost all the shaping processes encompass high-temperature usage. Even at lower processing temperatures, PVC undergoes decomposition and loses hydrogen chloride (HCl), and as a result, there is deterioration in its physical and mechanical properties. The HCl elimination is a chain reaction with a special mechanism called “zipper elimination.” The chemical breakdown is usually accelerated by heat, releasing HCl, which leads to discoloration and polymer degradation. It is possible to inhibit the released HCl and stabilize PVC, or suppress the catalytic effect of HCl in this reaction by adding different heat stabilizers.

Heat stabilizers are usually used as a major additive for PVC in order to protect it against high temperatures during processing and the high heat it may encounter during its shelf time and storage. Thermal stabilizers of PVC must have the ability to neutralize HCl evolved during the degradation and to interrupt the conjugated polyene formation [2–4].

As reported in the literature, PVC stabilizers could be classified either as primary or secondary, organic or inorganic, and many other classifications. Various thermal stabilizer types have been widely used in a large range of PVC commercial formulations to enhance their thermal stability, especially through the shaping process. Lead and tin stabilizers were the first ones to be used successfully to stabilize PVC. Until recently, these materials still accounted for the major portion of the stabilization system used, with lead being used in industrial pipe compounds and alkyl tin mercaptide in portable water pipes, profiles, etc. But a wide new variety of PVC stabilizers are used currently, including salts of calcium, barium, cadmium, lead, or zinc of the carbonic, phosphoric, benzoic, and stearic acids as well as organic compounds based on tin, organic phosphates and using heavy metal carboxylates and organo- tin mercaptides [6,7].

The mechanism of degradation is complex, and many attempts were made to reveal this confusing mystery.

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Starnes [5] presented a detailed review of the proposed mechanism of PVC thermal dehydrochlorination and stated that the detailed mechanism of polyene termination seems to be difficult to track down. Folarin and Sadiku [6] reported that the mechanisms of stabilization include the replacement of labile chlorine atoms, scavenging chlorine radicals and HCl, and addition across polyene sequences and aromatic alkylation. Chabira and Sebaa [7] reported that differential scanning calorimetry and thermogravimetry are two powerful tools providing useful information for understanding the mechanism of degradation of PVC. They implemented dibasic lead stearate and a mixture of (Ba/Cd/Zn) metal salt carboxylate, as stabilizers, and investigated the changes using differential scanning calorimetry and thermogravimetry. They found that during processing, the dibasic lead stearate is only relatively consumed, while almost all of the mixture of (Ba/Cd/Zn) metal salt carboxylate reacts.

There are many approaches for determining the extent of thermal degradation depending on the physical or chemical changes that occur in the polymer. Many instruments were used depending on the properties to be studied. Wu and Wicks [8] developed an experimental procedure using liquid sampling and fluorescence measurement to determine the performance of stabilizers based on the change in fluorescence emission after thermal aging. Bodecchi et al. [9] used Fourier transform infrared spectroscopy for understanding the behavior of calcium and zinc carboxylate PVC heat stabilizers.

Amar et al. [10] used lead-based stabilizers to study the thermal aging of PVC, which was performed in an oven at 60°C. The RPVC showed a growing carbonyl band in the IR spectrum with the aging time. Borukaev et al. [11] used a complex stabilizer based on a mixture of calcium and zinc stearates and investigated their thermal stability by determining its effect on the time of the induction period and determining some mechanical and rheological properties of PVC used for cable production. Jubsilp et al. [12] compared the effects of organic-based stabilizers with traditional lead and calcium zinc heat stabilizers in rigid PVC pipe applications. They proved that the organic-based stabilizer provided a good impact on preventing the autocatalytic thermal degradation of the PVC samples due to the lower gelation speed and the longer fusion time. Tomaszewska et al. [13] studied the thermal stability of PVC by using visual color changes and thermogravimetric tests. The melt flow index was also recorded to identify the degradation-induced changes in processing properties. Fechter et al. [14] developed and proposed a method for simulating the torque–temperature curves by using Python programming language from a thermal stability test on PVC using a thermal rheometer.

The principles for selecting the most suitable stabilizer systems depend on the cost, toxicity, and processing technique besides some critical factors, namely the induction period, rheological stability time, and the value of minimum torque in the plateau. In this article, we test and evaluate the activity of 12 common PVC thermal stabilizer systems by implementing a Brabender torque roll mill as a vital method for detecting the aforementioned critical factors.

2 Experimental work

2.1 Materials

Suspension PVC resin (BASF) with a K -value of 60 (M_w : 100,000 and M_n : 51,000) was used in this study. The following types of stabilizers were investigated:

1. Ba/Cd/Zn stabilizer: *Irgastab BC103* (Ciba-Geigy).
2. Ba/Cd carboxylates: *Mark 235* (Argus Chemical Corporation, Witco Chemicals).
3. Metal-free stabilizer: Thio-di-ethylene-glycol- β amine stabilizer, *Irgastab A70* (Ciba-Geigy).
4. Lead stabilizers:
 - Dibasic lead phosphite, *Dyphos* (NL Industrial Chemicals).
 - Dibasic lead stearate, *DS-207* (NL Industrial Chemicals).
 - A mixture of dibasic lead stearate/dibasic lead phosphite (1:2) (1 part DS-207:2 parts Dyphos).
5. Organo-tin stabilizers (sulfur free):
 - Di- n -octyl tin maleate (C_8H_{17})₂Sn(OOCH=CHOO)₂, *Thermolite 813* (M&T Chemicals).
 - Dibutyl tin mono-alkyl maleate (C_4H_9)Sn(OOCH=CHOR)₂, where R = C_4 + C_8 , *Thermolite 25* (M&T Chemicals).
6. Organo tin mercaptide:
 - Dibutyl tin-bis-(lauryl mercaptide) (C_4H_9)₂Sn(SC₁₂H₂₅)₂, *Mark A* (Argus).
 - Dibutyl S,S-bis-(isooctyl thioglycolate) (C_4H_9)₂Sn(SCH₂COOC₈H₁₇)₂, *Mark 292* (Argus) equivalent to Thermolite 31 (M&T Chemicals).
 - Di- n -octyl tin S,S-bis-(isooctyl thioglycolate) (n -C₈H₁₇)₂Sn(SCH₂COOC₈H₁₇)₂, *Advastab T M 188* (Advance Div., Carbise).
 - Dibutyl tin mercaptide, *Irgastab 15 MS* (Ciba-Geigy).

2.2 Sample preparation

The dry blend mixtures (PVC/stabilizer system = 100:3 parts by weight) were prepared using a mixer-type Henschell FM4, fitted with a temperature indicator mounted inside the mixing chamber.

Table 1: Fusion time and induction period of PVC stabilizer systems

Stabilizer systems	Fusion time (s)	Induction period (min)	Increase in the induction period (%)
Without stabilizer	30	3.0	—
Irgastab BC 103	40	5.0	66.6
Irgastab A 70	35	5.2	73.3
Thermolite 25	30	6.5	116.6
Dibasic lead phosphite	40	7.0	133.3
Thermolite 813	50	9.0	200.0
Mixture of lead stabilizers	50	9.0	200.0
Mark 235	35	10.7	256.6
Dibasic lead stearate	180	11.0	266.6
Mark A	40	11.5	276.6
Advastab 188	35	13.0	333.3
Mark 292	50	14.0	366.6
Irgastab 15 MS	45	15.5	416.6

2.3 Rheological properties

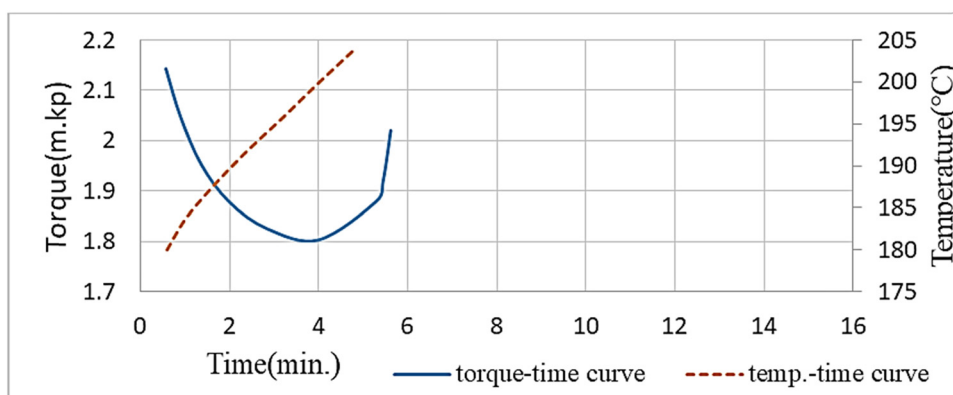
The measurements of PVC systems were carried out using a Brabender torque roll mill heated at 180°C. The temperature of the melt was continuously measured and recorded using a Fe/Co thermocouple, fitted inside the test chamber. The speed of the rotors was 60 rpm. The Brabender test chamber was sealed with a special cover and the gases that evolved during the degradation of the PVC were collected in distilled water by vacuum evacuation. Hydrogen chloride gas is the main product of PVC degradation when subjected to high temperatures. In order to evaluate the thermal stability of PVC compounds, bromothymol blue, an indicator, was added to distilled water to determine the induction period, i.e., the time till HCl elimination occurs. It is worth mentioning that the measured torque is a function of the melt viscosity, which is related to the flow property of the plastic melt.

3 Results and discussion

The fusion rate plays an important role in the processing of rigid PVC, especially in the extrusion technique. The fusion time is defined as the time required to convert a cold formulation of PVC when introduced in an extruder to a melt.

The experimental results indicated that the chemical structure of the heat stabilizer has a notable effect on the fusion rate of PVC systems. The control for comparison was pure PVC with no added stabilizer.

Table 1 sorts the induction period of the studied stabilizer systems in increasing order. It can be seen that the fusion time obtained varied between 30 and 50 s, except the fusion time of the PVC/lead stearate system, which has a value of 180 s. This may be due to the higher melting point of this stabilizer besides its strong lubrication properties. Therefore, this stabilizer is not used alone in practice but it is usually mixed with other stabilizers. It is worth

**Figure 1:** Torque–time and temperature–time for PVC without any stabilizers.

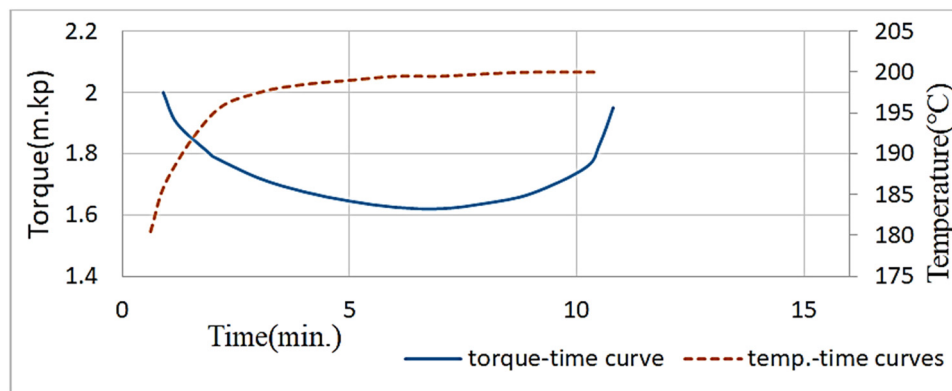


Figure 2: Torque-time and temperature-time for PVC with a Mark 235 stabilizer system.

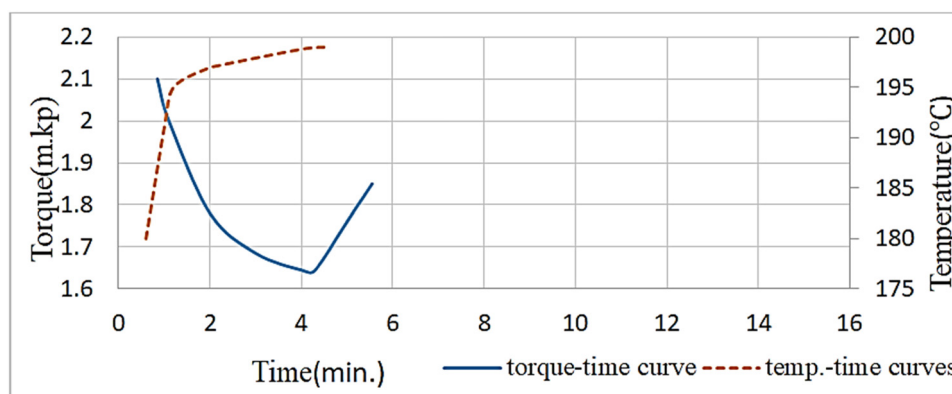


Figure 3: Torque-time and temperature-time for PVC with an Irgastab BC103 stabilizer system.

mentioning that the fusion rate of any particular stabilizer system can be easily controlled by using lubricants, resins, and other formulation components.

On the other hand, it was found that the four systems based on organo-tin mercaptide were far superior to other stabilizers, while the fusion time measurements indicate

that most of the stabilizers used were equivalent under the experimental conditions.

The induction period can be expressed in terms of chemical changes, and it is defined (in the case of PVC) as the time required for the evolution of hydrogen chloride gas. The experimental results obtained show that the used

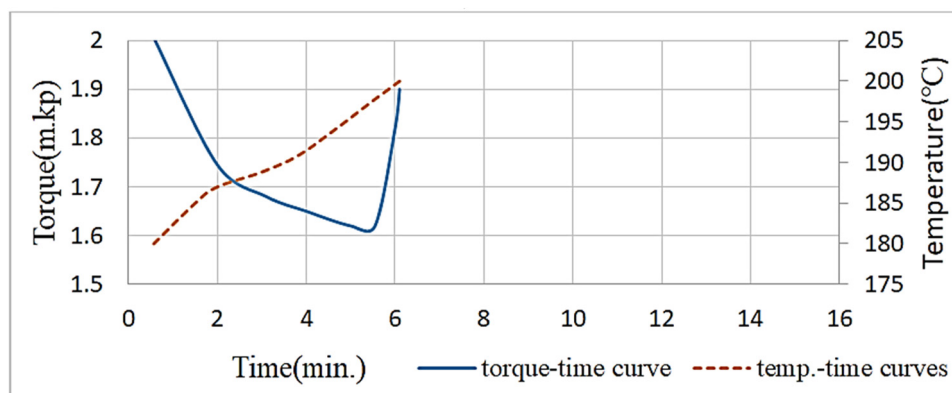


Figure 4: Torque-time and temperature-time for PVC with an Irgastab A 70 stabilizer system.

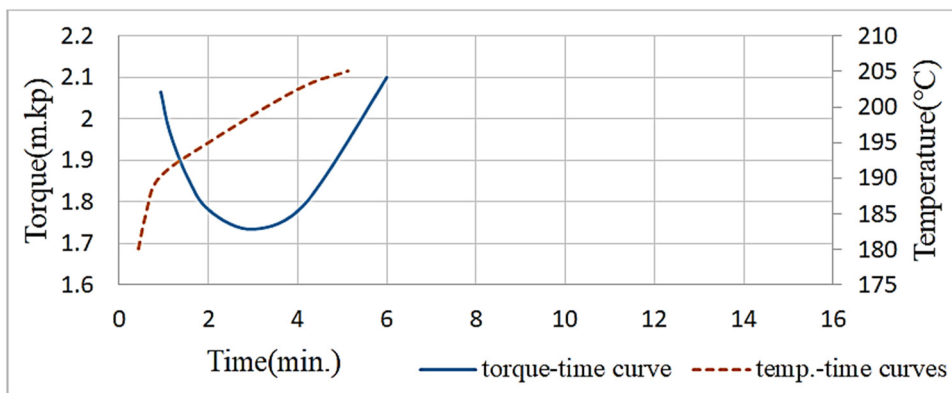


Figure 5: Torque–time and temperature–time for PVC with a dibasic lead phosphite stabilizer system.

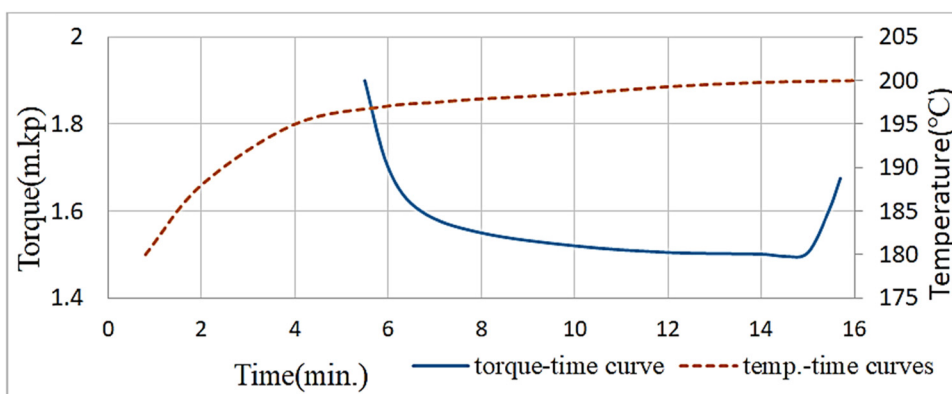


Figure 6: Torque–time and temperature–time for PVC with a dibasic lead stearate stabilizer system.

stabilizers have different effects on the induction period of hydrogen chloride evolution. Table 1 illustrates the induction periods obtained under the experimental conditions mentioned above. The results confirm the occurrence of interaction between the PVC chain and the stabilizer; several articles imply this fact [8,15–17].

These results showed that three stabilizer groups having different efficiencies are obtained. These stabilizers are classified as high-, medium-, and low-efficiency stabilizers. The high-efficiency stabilizers are the organo-tin mercaptide, and the increase in the induction period ranges between 276 and 416% compared to non-stabilized PVC. The comparison of the

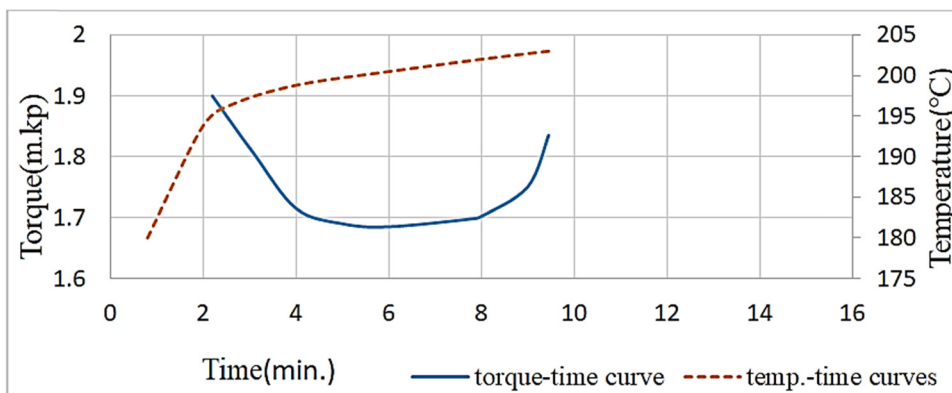


Figure 7: Torque–time and temperature–time for PVC with a mixture of dibasic lead stearate and dibasic lead phosphite systems.

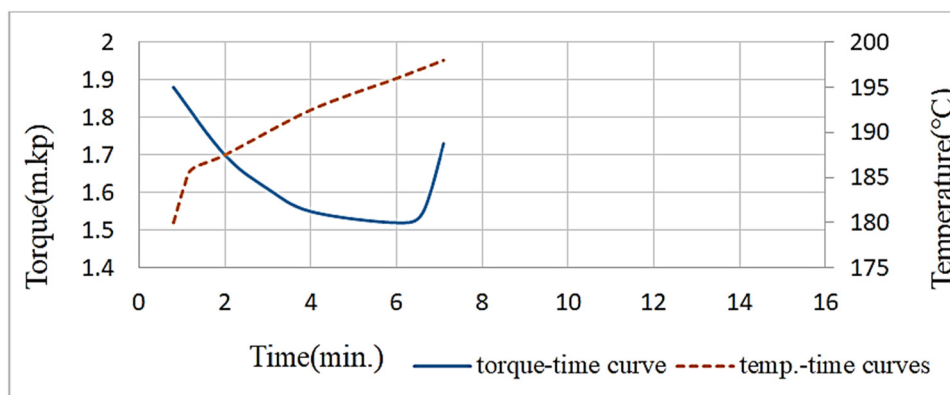


Figure 8: Torque–time and temperature–time for PVC with a Thermolite 25 stabilizer system.

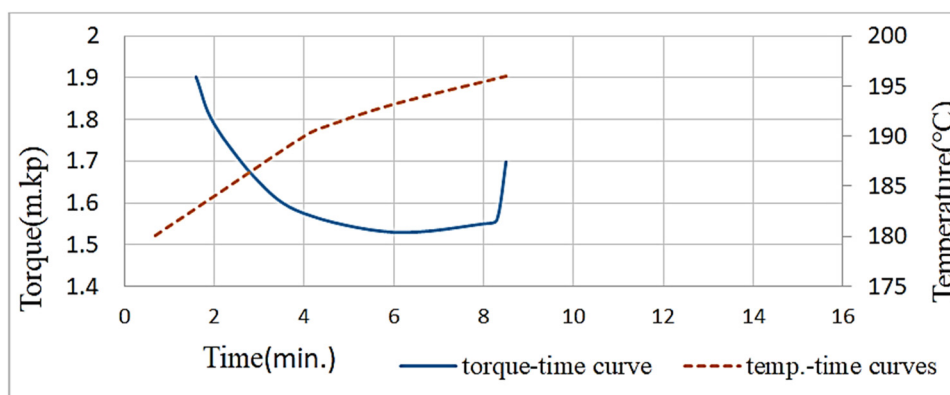


Figure 9: Torque–time and temperature–time for PVC with a Thermolite 813 stabilizer system.

efficiency of the four types of organo-tin mercaptide stabilizers used showed that dibutyl tin mercaptide (Irgastab 15MS) has the highest efficiency. The sulfur-free organo-tin stabilizers were found to be less efficient than the organo-tin mercaptides and their ability for stabilization varies from each

other. The induction period increased by 116% when dibutyl tin monoalkyl maleate was used versus 200% di-*n*-octyl tin maleate was used.

From the above data, it is clear that the stabilizers containing dibutyl groups are less efficient than di-*n*-octyl

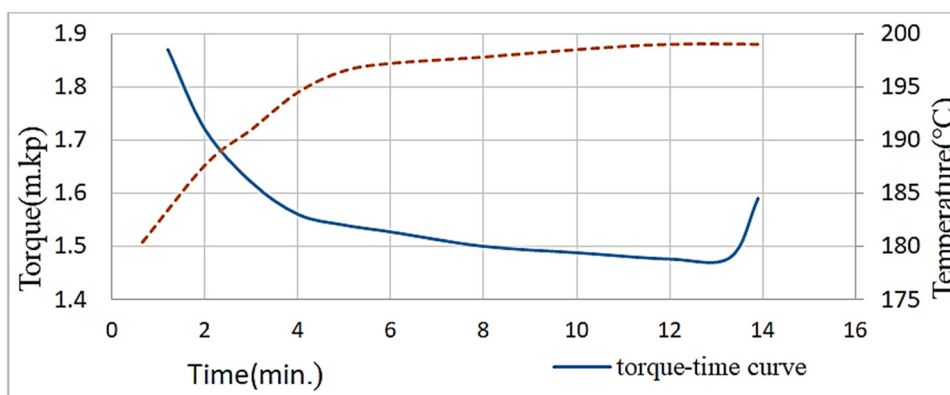


Figure 10: Torque–time and temperature–time for PVC with a Mark 292 stabilizer system.

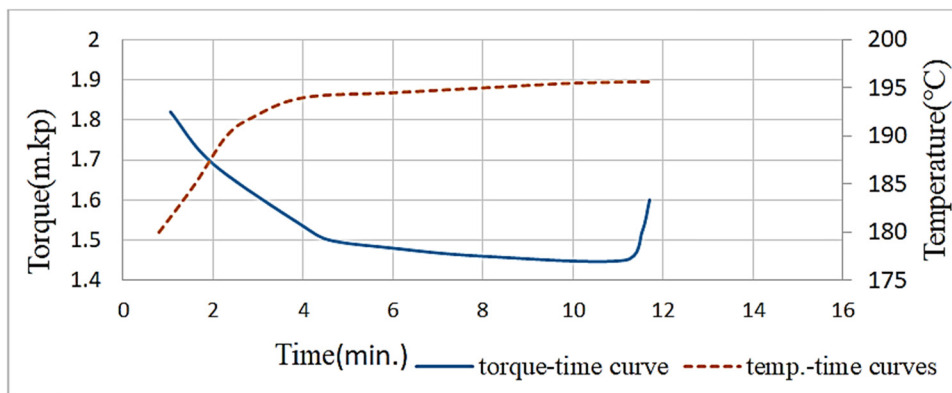


Figure 11: Torque–time and temperature–time for PVC with a Mark A stabilizer system.

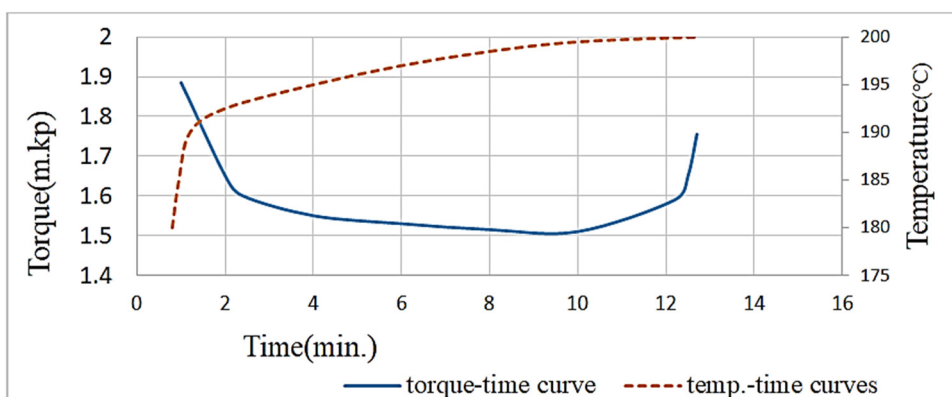


Figure 12: Torque–time and temperature–time for PVC with an Advastab 188 stabilizer system.

groups. Lead and Ba/Cd stabilizers could be classified as medium stabilizers for PVC. The mixture of lead stearate/lead phosphite (1:2) part stabilizers is considered a medium-low stabilizer. In spite of its lead content, this type of stabilizer is still in use for the production of potable water pipes in local plants.

The torque–time and temperature–time data obtained from Brabender measurements for various PVC dry blends are represented in Figures 1–13. The rheological curves (torque–time curves) showed that non-stabilized PVC has the highest minimum torque in the plateau and reaches 1.8 m kp (17.652 N m), as shown in Figure 3. The time of

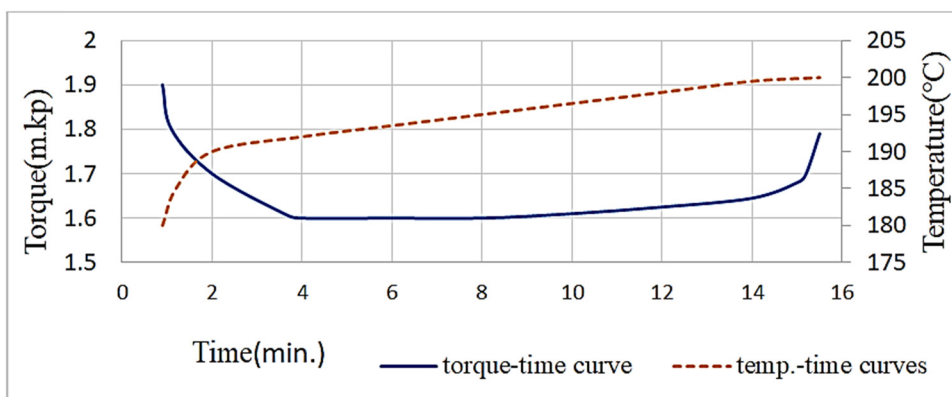


Figure 13: Torque–time and temperature–time for PVC with an Irgastab 15 MS stabilizer system.

Table 2: Torque value and the rheological stability periods of PVC stabilizer systems

Stabilizer systems	Minimum torque (m kp)	% Decrease	Rheological stability period (min)
Without stabilizer	1.80	—	2.0
Irgastab BC 103	1.68	6.6	1.5
Irgastab A 70	1.63	9.4	2.5
Thermolite 25	1.52	15.5	3.0
Dibasic lead phosphite	1.74	3.3	2.0
Thermolite 813	1.52	15.5	4.5
Mixture of lead stabilizers	1.67	7.2	4.0
Mark 235	1.63	9.4	7.0
Dibasic lead stearate	1.50	16.6	8.0
Mark A	1.45	19.4	7.5
Advastab 188	1.62	10.0	9.0
Mark 292	1.47	18.3	9.0
Irgastab 15 MS	1.60	11.1	12.0

constant torque is defined in this study as the rheological stability period, where the torque can vary within 5%.

The minimum torque value and the rheological stability time are shown in Table 2. The results showed that the different stabilizer systems used decreased the torque and tend to increase the time of rheological stability, except Ba/Cd/Zn stabilizer (Irgastab BC 103) as shown in Figure 3. It can be concluded that the decrease in torque has a positive effect on the flow properties and consequently on the production rate. Thus, a general rule for selecting the suitable stabilizer system is to prefer those that reveal the lowest torque in the plateau.

The results indicate that both dibutyl tin-bis-(lauryl mercaptide) stabilizer (Mark A) and dibutyl *S,S*-bis-(isooctyl thio glycolate) (Mark 292) showed the greatest decrease in torque while, in contrast, dibasic lead phosphite (Dyphos) showed the lowest decrease. This indicates that the following stabilizers cannot be applied with PVC formulations: Ba/Cd/Zn stabilizer (Irgastab BC103), thio-di-ethylene-glycol- β amine stabilizer (Irgastab A70), dibutyl tin monoalkyl malate (Thermolite 25), and dibasic lead phosphite (Dyphos).

The rheological stability period of the final plastic product is affected by the processing time, i.e., the time of the exposure of the polymer system to heat at different stages of the processing. This study suggests that the time of heat exposure during processing should not exceed 50% of the rheological stability time.

The remaining 50% or more of the stability time is expected to be enough to prevent the degradation of the polymer during its use. If we excluded the four previous stabilizer systems mentioned above, it can be seen from Table 2 that the rheological stability time of the mixture of lead stabilizers is about 4 min, which represents the lowest rheological stability period among the rest efficiently used stabilizers according to their application in PVC.

The measured temperature of the polymer melt in the rheological stability period was between 190 and 200°C, which is about 10–20°C higher than the test chamber temperature. This difference is very likely due to pressure and friction effects resulting from shear stresses in the test chamber.

4 Conclusions

The importance of a Brabender torque rheometer for selecting heat stabilizers has been demonstrated. Several parameters, e.g., the fusion time, induction period, minimum torque, and rheological stability time, have been suggested and measured with sufficient accuracy. All these factors were important for determining the performance of the heat stabilizers of RPVC.

By heating the samples to 180°C and applying shear inside the Brabender test chamber, the obtained results indicated that the stabilizers' efficiency decreased in the following sequence: dibutyl tin mercaptide (Irgastab 15 MS), dibutyl *S,S*-bis-(isooctyl thio glycolate; Mark 292), di-*n*-octyl tin *S,S*-bis(isooctyl thioglycolate; Advastab TM188), dibutyl tin-bis-(lauryl mercaptide; Mark A), Ba/Cd carboxylates (Mark 235) and finally the mixture of lead stabilizers. However, the other stabilizers studied cannot be recommended for use with PVC.

Conflict of interest: Authors state no conflict of interest.

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