

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Study of Stabilized Poly(vinyl Chloride) Mixtures under Different Conditions of Thermal Treatment

J. Štěpek^a; Z. Vymazal^a; E. Czakó^a

^a Department of Polymers, Institute of Chemical Technology, Prague 6, Czechoslovakia

To cite this Article Štěpek, J. , Vymazal, Z. and Czakó, E.(1978) 'Study of Stabilized Poly(vinyl Chloride) Mixtures under Different Conditions of Thermal Treatment', Journal of Macromolecular Science, Part A, 12: 3, 401 — 409

To link to this Article: DOI: 10.1080/00222337808061389

URL: <http://dx.doi.org/10.1080/00222337808061389>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Study of Stabilized Poly(vinyl Chloride) Mixtures under Different Conditions of Thermal Treatment

J. ŠTĚPEK, Z. VYMAZAL, and E. CZAKÓ

Department of Polymers
Institute of Chemical Technology
166 28 Prague 6, Czechoslovakia

ABSTRACT

The consumption of stabilizers based on organic soaps with Cd/Ba molar ratios of 3, 2, and 0.4, respectively, and with a molar ratio of Ca/Zn of 1 during thermal treatment of poly(vinyl chloride) mixtures in a degradation apparatus, in a press, and in the mixing cavity of a Brabender Plastograph has been investigated on the basis of determination of chlorides by coulometric titration. The thermal stability of the mixtures has been calculated from the hydrogen chloride evolved, as found by a potentiometric method. It was found that the stabilizer was not fully consumed when the residual thermal stability reached zero. The formation of chlorides in the stabilized mixtures was slower than the hydrogen chloride evolution from the original unstabilized polymer.

INTRODUCTION

A necessary requirement for processing of poly(vinyl chloride) is its stabilization. Although the latter has been studied over many past years, it is still not clear how to answer all the questions concerning the practical applications of stabilizers.

In recent publications [1-4], the relations between the consumption of a stabilizer under thermal treatment and its efficiency, characterized by the ratio of the amount of a stabilizer consumed during the time when no free hydrogen chloride is present to the total amount of a stabilizer added to polymer, have been investigated. In the majority of these investigations, the experimental conditions differ significantly from those necessary for the processing of poly(vinyl chloride) mixtures. We have shown recently [5] that the effect of a thermal stabilizer is influenced not only by its chemical composition, but also by such other factors as the method of preparation of the mixtures and the manufacture of the samples for the measurements. This contribution is a continuation of our recent investigations [6, 7]. In these, we studied also the efficiency of stabilizers based on the organic soaps under static as well as dynamic conditions of the thermal treatment [6] and the relations among the value of the thermal stability TS, the intense change in the color of the degraded mixture, and the amount of stabilizer consumed [7]. The thermal stability TS of a poly(vinyl chloride) mixture has been defined as the maximum time of thermal treatment during which the evolution of hydrogen chloride from a sample does not change suddenly [6]. In the present investigation, we compare the consumption of stabilizers based on the organic soaps during the thermal treatment in a Brabender Plastograph, in a press, and in a degradation apparatus on the basis of the determination of free and combined hydrogen chloride.

EXPERIMENTAL

Suspension poly(vinyl chloride) was used for all measurements. Its K value was 68, weight-average molecular weight \bar{M}_w was 90,000, and number-average molecular weight \bar{M}_n was 55,000. The mix formulation was poly(vinyl chloride), 100 parts, stabilizer, 1.5 parts, lubricant, 0.5 parts. The stabilizers used are characterized as follows: stabilizer 1, molar ratio Cd/Ba = 3; stabilizer 2, Cd/Ba = 2; stabilizer 3, Cd/Ba = 0.4; stabilizer 4, Ca/Zn = 1.

The effect of static conditions during thermal treatment was investigated at 180°C in a degradation apparatus [7, 8] and in a press. The samples of the poly(vinyl chloride) mixtures were in the form of sheets (0.6 mm thickness) prepared on a laboratory two-roll mill at $180 \pm 2^\circ\text{C}$ for 5 min.

The effect of dynamic conditions for the thermal treatment was investigated in a Brabender Plastograph at a rotor speed of 50 rpm. The mechanically homogenized components of the poly(vinyl chloride) mixture were placed into the mixing cavity (volume, 30 ml), and the temperature of the mix was held constant at 180°C. After a certain

mixing time, the cavity was opened and the mixture pressed at 180°C for 2 min to form a sheet 0.6 mm in thickness.

The amount of free hydrogen chloride evolved was determined at $180 \pm 0.1^\circ\text{C}$ in a stream of air (330 ml/min) by a continuous potentiometric method [8] and plotted against time. From the dependence obtained, the values of the residual thermal stability TS_R (i.e., the thermal stability after a certain time of thermal treatment) were calculated; the TS_R values are expressed in minutes.

The consumption of stabilizer was calculated on the basis of the measurement of the amount of chlorides formed during the thermal treatment (under static as well as dynamic conditions) by the reaction of hydrogen chloride with a stabilizer. Determination of chlorides was performed as follows. A 0.2-g portion of a degraded poly(vinyl chloride) mixture was dissolved in 10 ml of cyclohexanone and then 25 ml of 0.1 N solution of HNO_3 in methyl alcohol or water was added. In this system, chlorides were titrated by a coulometric method with silver ions generated on a silver electrode. The equivalence point was determined by a biamperometric indication by two silver chloride electrodes polarized by 100 mV. The titration curves were recorded, and the amount of chloride calculated from Faraday's Law.

RESULTS

Figures 1 and 2 show the time dependence of the hydrogen chloride evolution from the stabilized and unstabilized poly(vinyl chloride) (curves 1 and 5, respectively) and of the formation of chlorides (curves 2) during the thermal degradation in the degradation apparatus as well as the time dependence of the residual thermal stability TS_R (curves 3) and of the formation of chlorides (curves 4) during pressing obtained on investigation of the static thermal treatment of poly(vinyl chloride) mixtures containing stabilizers 2 and 4, respectively. The solid lines indicate the amount of hydrogen chloride equivalent to the stabilizer present in the sample.

In the case of stabilizer 2, zero residual thermal stability ($\text{TS}_R = 0$) was found after 71 min of degradation of the poly(vinyl chloride) mixture in the degradation apparatus as well as in a press. From the time dependence of the formation of chlorides, it is evident that at $\text{TS}_R = 0$ the consumption of the stabilizer at the degradation in the degradation apparatus and in the press is 80 and 85% based on the amount of the original stabilizer, respectively.

In the case of stabilizer 4, however, the zero residual thermal stability ($\text{TS}_R = 0$) was found after 45 min degradation of poly(vinyl

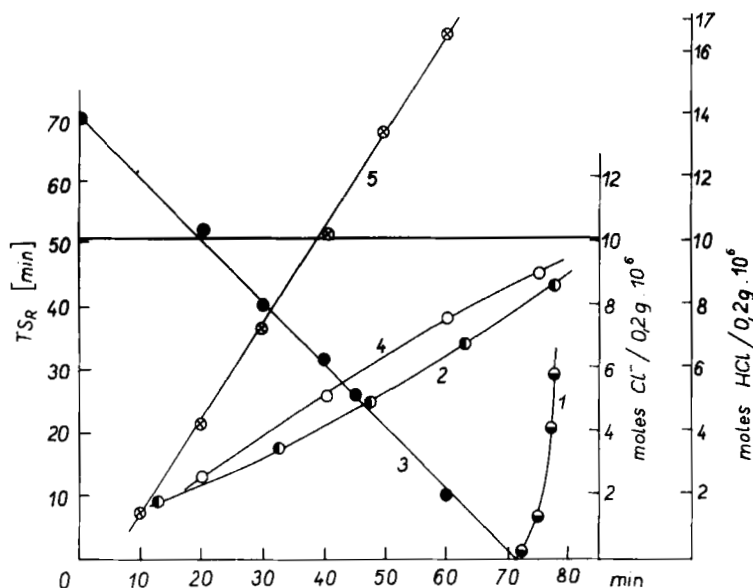


FIG. 1. Effect of static conditions of thermal treatment at 180°C on the thermal stability of poly(vinyl chloride) mixture with stabilizer 2: (1) time dependence of hydrogen chloride evolution during thermal treatment in the degradation apparatus; (2) time dependence of chloride formation during thermal treatment in the degradation apparatus; (3) time dependence of TS_R during pressing; (4) time dependence of chloride formation during pressing; (5) time dependence of hydrogen chloride evolution from the original unstabilized polymer during thermal treatment in the degradation apparatus.

chloride) mixture. The consumption of the stabilizer is equal to 85% on degradation in the degradation apparatus and 80% on degradation in a press.

On the basis of the measurements with stabilizers 2 and 4, as well as with other two types of stabilizers (1 and 3), we note (see Table 1) that the times necessary to reach the zero residual thermal stability are in agreement for both types of apparatus. Their absolute values depend on the amount of cations in the mixture and on the rate of hydrogen chloride evolution from the original unstabilized polymer [9]. From the point of view of the color changes [7], the samples degraded longer than the time corresponding to $TS_R = 0$ were already dark.

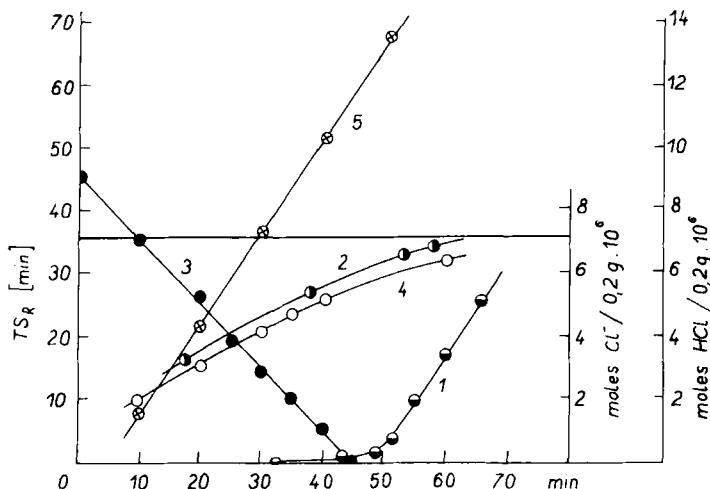


FIG. 2. Effect of static conditions of thermal treatment at 180°C on the thermal stability of poly(vinyl chloride) mixture with stabilizer 4: (1) time dependence of hydrogen chloride evolution during thermal treatment in the degradation apparatus; (2) time dependence of chloride formation during thermal treatment in the degradation apparatus; (3) time dependence of TS_R during pressing; (4) time dependence of chloride formation during pressing; (5) time dependence of hydrogen chloride evolution from the original unstabilized polymer during thermal treatment in the degradation apparatus.

Figures 3 and 4 show the time dependence of the torque (curves 1), of the temperature in the mixture (curves 2), of the formation of chlorides (curves 3), of the residual thermal stability TS_R (curves 4) obtained in investigations of the dynamic thermal treatment of poly(vinyl chloride) mixtures containing stabilizers 2 and 4, respectively. The solid lines indicate the amount of hydrogen chloride equivalent to the stabilizer present in the sample.

In the case of stabilizer 2, zero residual thermal stability ($\text{TS}_R = 0$) occurred in 57 min and in the case of stabilizer 4, in 52 min. The consumption of stabilizers 2 and 4 was about 90 and 80%, respectively, based on the amount of the original stabilizer. The time dependence of the torque shows that the field of its second increase, generally considered the start of intense degradation and crosslinking of the mixture, is in good agreement with the value of $\text{TS}_R = 0$ found.

TABLE 1. Consumption of Stabilizers during Thermal Treatment under Different Conditions and the Times Necessary to Reach the Zero Residual Thermal Stability

Thermal treatment	Equipment	Consumption of Stabilizers							
		Stabilizer 1		Stabilizer 2		Stabilizer 3		Stabilizer 4	
		Amt (%)	TS _R = 0 (min)	Amt (%)	TS _R = 0 (min)	Amt (%)	TS _R = 0 (min)	Amt (%)	TS _R = 0 (min)
Static	Degradation apparatus	73	80	80	71	84	40	85	45
Dynamic	Press	72	81	85	71	84	38	78	45
	Mixing cavity of Brabender Plastograph	82	52	91	57	78	36	80	52

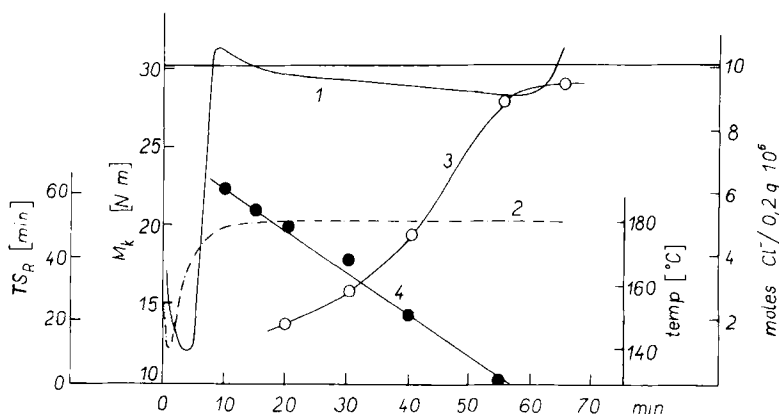


FIG. 3. Effect of dynamic conditions of thermal treatment at 180°C on the thermal stability of poly(vinyl chloride) mixture with stabilizer 2: (1) time dependence of torque; (2) time dependence of temperature in the mixture; (3) time dependence of chloride formation during mixing in Brabender Plastograph; (4) time dependence of TS_R during mixing in Brabender Plastograph.

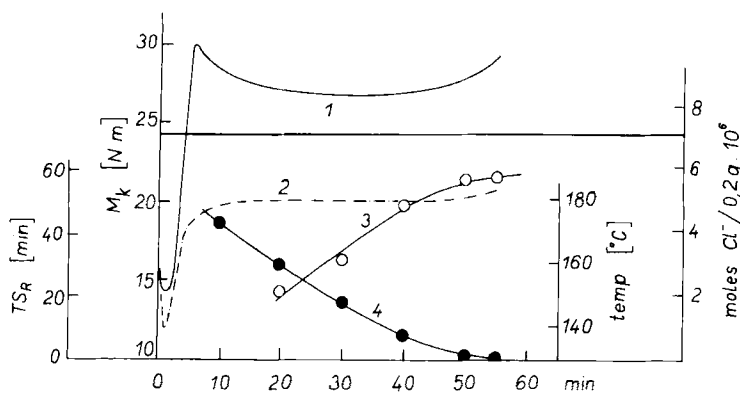


FIG. 4. Effect of dynamic conditions of thermal treatment at 180°C on the thermal stability of poly(vinyl chloride) mixture with stabilizer 4: (1) time dependence of torque; (2) time dependence of temperature in the mixture; (3) time dependence of chloride formation during mixing in Brabender Plastograph; (4) time dependence of TS_R during mixing in Brabender Plastograph.

Analogous results were obtained in the case of the other two types of Cd/Ba stabilizers (see Table 1). On dynamic thermal treatment of the investigated mixtures, the absolute values of the residual thermal stability depend not only on the amount of the cations in the mixture but probably also on the rheological character of the mix.

DISCUSSION

The aim of the present investigation was to ascertain the effect of different conditions of thermal treatment of nonplasticized poly(vinyl chloride) mixtures on the efficiency of the stabilizers used. Table 1 shows that in both cases, under static and dynamic thermal treatment, the stabilizer was not consumed completely. At $TS_R = 0$, sudden color changes appear [7], and there is no further increase in the consumption of a stabilizer, it is evident that there is a direct connection between the two dependences discussed. The values of the residual thermal stability show that under the dynamic conditions of the thermal treatment, stabilizers are consumed faster than under static conditions excluding Ca/Zn stabilizer. In the case of Cd/Ba stabilizers and dynamic conditions of the thermal treatment, zero residual thermal stability ($TS_R = 0$) values are not proportional to the amount of efficient compound in the stabilizer. This finding can be explained in accordance with other investigations [10] on the basis of a different lubricant ability of the stabilizers investigated. The measurements show further that the results obtained under static conditions of the thermal treatment cannot be applied to mixtures which would be processed under dynamic conditions.

For the formation of chlorides by the reaction of a stabilizer from which hydrogen chloride is evolved significantly more slowly than from the original unstabilized polymer and for which evolution of hydrogen chloride from the stabilized sample is practically nil during the time interval TS , it is evident that the stabilizers slow down the evolution of hydrogen chloride from the polymer.

REFERENCES

- [1] J. Štěpek, P. Lalet, and Č. Jirkal, *Plast. Mod. Elast.*, **20**, 126 (1968).
- [2] G. Briggs and N. F. Wood, *J. Appl. Polym. Sci.*, **15**, 25 (1971).
- [3] G. Ocskay, Z. Nyitrai, F. Várfalvi, and T. Wein, *Eur. Polym. J.*, **7**, 1135 (1971).
- [4] K. S. Minsker and G. T. Fedoseeva, *Destruktsia i Stabilizatsia PVC*, Khimia, Moscow, 1972.

- [5] J. Štěpek, Z. Vymazal, and E. Czako', Preprints International Symposium on Polyvinylchloride, Lyon, 1976, p. 265.
- [6] Z. Vymazal, E. Czako', and J. Štěpek, Plasty Kauc., 11, 331 (1974).
- [7] E. Czako', Z. Vymazal, and J. Štěpek, Plasty Kauc., 12, 259 (1975).
- [8] Z. Vymazal, E. Czako', B. Meissner, and J. Štěpek, Plasty Kauc., 11, 260 (1974); J. Appl. Polym. Sci., 18, 2861 (1974).
- [9] E. Czako', Z. Vymazal, and J. Štěpek, unpublished results.
- [10] G. Menzel and A. Polte, Kunststoffe, 65, 149 (1975).