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THERMOOXIDATIVE DEGRADATION OF POLY(VINYL CHLORIDE) AND CHLORINATED POLYETHYLENE WITH DIFFERENT Ca/Zn CARBOXYLATES

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Abstract

The thermooxidative degradation of poly(vinyl chloride) (PVC), chlorinated polyethylene (CPE) and PVC/CPE blend 50/50 was investigated by means of dynamic and isothermal thermogravimetric analysis in the flowing atmosphere of air. To estimate the thermooxidative stability of the samples the characteristics of thermogravimetric (TG) curves were used. Kinetic parameters (the apparent activation energy E and preexponential factor Z) were calculated after isoconversional method for the first stage of dynamic degradation where dehydrochlorination (DHCl) of PVC and/or CPE is the main degradation reaction. Despite the chemical resemblance, the degradation mechanisms of CPE and PVC are different, as a consequence of differences in microregularity of the corresponding polymer chains. The addition of Ca/Zn carboxylates as well as the ratio of Ca and Zn carboxylates have considerably different influence on the investigated polymers.

Keywords: Ca/Zn carboxylates, chlorinated polyethylene, poly(vinyl chloride), thermogravimetric analysis, thermooxidation

Introduction

Poly(vinyl chloride) (PVC) is often mixed with other polymers to modify its physical properties in a desired manner. Chlorinated polyethylene (CPE) is impact modifier of PVC in PVC/CPE blends which are used for the production of geosynthetics, marine and hydroisolation foils and the like. Both polymers, PVC and CPE, can be subjected to thermooxidative degradation either during their processing or application. Although these polymers are chemically similar, CPE has superior thermal stability to PVC [1]. Moreover, the investigated polymers have different degradation mechanism. The dehydrochlorination (DHCl) is the main reaction of the PVC thermal degradation and also a dominant reaction of the CPE degradation. DHCl of PVC is a fast ‘zip’ reaction, while DHCl of CPE is a slow random HCl elimination [1]. In the presence of oxygen, thermal degradation is accelerated and becomes more complex [2].

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Adding of heat stabilizers is necessary in all PVC formulations to prevent the decomposition of PVC by heat and shear during processing. These stabilizers fall mainly into three categories: metallic soaps, organic compounds and organotin compounds. Lead salts and soaps, once very popular, have been replaced by barium/cadmium (Ba/Cd) and calcium/zinc (Ca/Zn) soaps [3]. The latter ones are more expensive and less effective than many others, but they are interesting because of their physiological harmlessness. The stabilizing action of these carboxylates is usually explained by the esterifying displacement of labile chlorine atom in the polymer chain, according to the mechanism first proposed by Frye and Horst [4]. The allylic chlorine-carboxylates exchange reaction results in a significant reduction of the DHCl rate of PVC and the induction period is elongated. However, in the case of Zn carboxylate an abrupt increase, after the end of the induction period, in the DHCl process has been reported [3, 5]. This problem is solved by synergistic effect of combining alkaline earth (Ca) carboxylates with covalent metal (Zn) carboxylates. Alkaline earth carboxylates undergo ester exchange reactions with covalent metal chlorides, thus regenerating the covalent metal carboxylates. $ZnCl_2$ catalyzes the degradation reaction by forming a stable complex $H^+ZnCl_3^-$ and creates a labile allylic chlorine in the PVC chain [6]. Unlike the covalent metal chloride, alkaline earth chlorides do not promote dehydrochlorination. The alkaline earth carboxylates do not react as primary stabilizers of PVC but serve to regenerate the active stabilizer and remove the potentially destructive effect of the covalent metal chloride [4]. The complexation of the two stearates, i.e. forming of the $CaStZnSt_3$ complex, during the heating of the stabilized PVC sheets, has been observed [7, 8]. In addition, the optimization of the Ca/Zn ratio is very important in order to maximise the synergistic effect between the Ca and Zn carboxylates. This ratio effects not only the thermal stability of the system but also the processing conditions, because metal carboxylates are lubricants of PVC in their own right [4].

The addition of the stabilizers in PVC formulation has influence on the impact modifier, too. The recommended heat stabilizers for CPE are similar to those used for stabilizing PVC, although their effectiveness is not directly comparable. Therefore, in the present paper the effect of two different Ca/Zn carboxylates on thermooxidative degradation of PVC, CPE and PVC/CPE blend 50/50 was investigated by means of thermogravimetry (TG). The kinetic parameters of the thermooxidative degradation of the investigated samples were determined from the dynamic TG curves by applying isoconversional method.

Experimental

Material

The investigation was done with the suspension grade PVC (chlorine content=56.0%; *K*-value=58±1) supplied by BorsodChem, Hungary, CPE (chlorine content=42%, melting temperature=108.64°C, enthalpy of fusion=4.1 J g^{-1}) supplied by DuPont Dow Elastomers, Belgium, and two different Ca/Zn carboxylates: STAB. I – Ca/Zn oleate in organic solvent (Ca:Zn=1.2:1) and STAB. II – Ca/Zn stearate (powder) (Ca:Zn=2.1:1).

PVC, CPE and PVC/CPE blends 50/50 were prepared by mixing the polymer powders in mixer and then on a laboratory roller mill at 135°C for 8 min. The drawn-out foils (thickness 0.15±0.05 mm) were pressed at 120°C under pressure of 6 N mm^{-2}. The polymer samples were prepared in the same manner with addition of 2 mass% of Ca/Zn carboxylates.

Methods of analysis

The thermooxidative degradation of PVC/CPE blends was investigated by means of thermogravimetry using Perkin Elmer TGS-2 thermobalance with TADS 3600. The studies were carried out in synthetic air flow (30 cm^3 min^{-1}) and at the heating rates of 2.5, 5, 10 and 20°C min^{-1} in the temperature range 50–650°C (dynamic conditions) and at temperature 240°C (isothermal conditions). Before starting the experiment, the sample (2±0.2 mg) was placed on a platinum pan and held at 50°C for 30 min. During the isothermal experiment the sample was heated from the start to the selected degradation temperature at the heating rate of 80°C min^{-1} and then held at that temperature for 120 min.

To evaluate the thermooxidative stability of the polymers different criterion can be used. From the derivative thermogravimetric (DTG) curves the following characteristics of the first degradation step were determined: the temperature for a 5% degree of conversion ($T_{5\%}$), the temperature at the maximal rate of DHCl (T_{max}), the maximum rate of mass release by DHCl (R_{max}) and the mass losses for the corresponding degradation steps (Δm).

The apparent activation energy (E) and preexponential factor (Z) for the first degradation step were calculated according to linear isoconversional method [9].

$$\ln\frac{\beta}{T^2}=\ln\frac{ZR}{Eg(\alpha)}-\frac{E1}{RT} \tag{1}$$

where β is the heating rate, T is temperature read off from the dynamic TG curve for selected conversions, $\alpha=(m_0-m_t)/m_0$ (m_0 and m_t are the masses at zero and t times), Z is the preexponential factor, R is the gas constant, E is the apparent activation energy and $g(\alpha)$ is the kinetic model.

Results and discussion

Dynamic thermogravimetry

The results obtained from the dynamic thermooxidative study of investigated samples at the temperature interval 50–650°C are shown in Figs 1–3 and Table 1. From TG and DTG curves it is evident that thermooxidative degradation of all investigated samples proceeds in the two basic degradation steps. In the first degradation step only the PVC/CPE blend 50/50 shows two maxima, the former corresponds to the mass loss of PVC and the latter corresponds to the mass loss of CPE. By the addition of 2% Ca/Zn carboxylates these two maxima are merged into one.

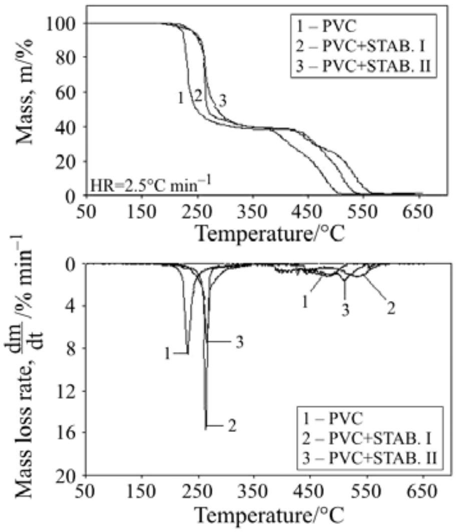

Fig. 1 Dynamic TG and DTG curves for non-stabilized and stabilized PVC

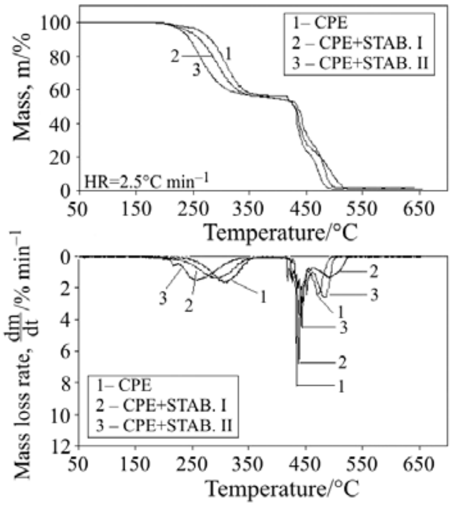

Fig. 2 Dynamic TG and DTG curves for non-stabilized and stabilized CPE

At the temperatures up to cca 400°C DHCl of PVC is the main degradation reaction followed by several secondary processes: cyclization of polyenes, crosslinking and benzene formation [2]. The presence of oxygen additionally accelerates the process of PVC degradation. The mass loss at the end of the first degradation step (61.67%) is greater than chlorine content in PVC (56%) and indicates that besides the HCl, some other volatile products have been developed.

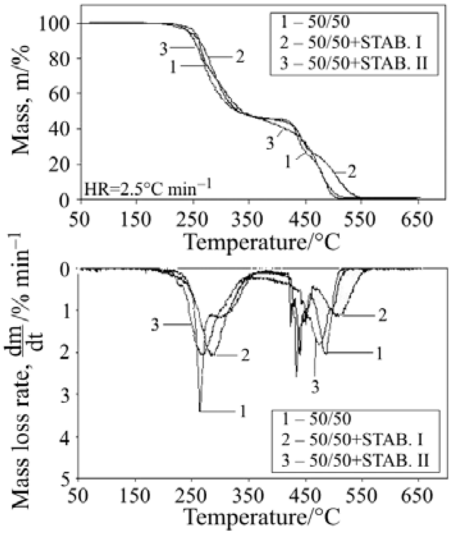

Fig. 3 Dynamic TG and DTG curves for non-stabilized and stabilized PVC/CPE blend 50/50

The first degradation step of the CPE is characterized by HCl evolution mainly, whereas in the second, destruction of the basic polymer chain occurs. Apart from HCl other volatile substances are released such as H_2, CO, CO_2, CH_3OH etc. These gases were formed as by products from the initial oxidation of the polymer following its melting [10].

The temperature $T_{5\%}$ (Table 1) indicates that thermooxidative degradation of PVC starts at lower temperature than of CPE. This temperature for PVC/CPE blend 50/50 is between the temperatures of 'pure' polymers. Addition of Ca/Zn carboxylates (STAB. I or STAB. II) does not affect the $T_{5\%}$ of PVC, but lowers the $T_{5\%}$ of CPE for 22°C (STAB. I) and for 32°C (STAB. II), respectively. The maximal rate of PVC dehydrochlorination is achieved at lower temperature than of CPE and 50/50 blend. This rate for PVC is 5 times greater than for CPE, and 2.5 times greater than for 50/50 blend. Both stabilizers shift the T_{max} of CPE to lower values, but they retard the maximal DHCl rate. At the same time, the T_{max} of PVC and 50/50 blend increases. STAB. II slightly retards, and STAB. I accelerates DHCl of PVC. This behaviour could be explained by the lesser amount of costabilizers (Ca carboxylate) in STAB. I, and hence, greater influence of $ZnCl_2$ released during heating of sample. $ZnCl_2$ is acting as an effective degradation catalyst and its increased amount increases the degradation rate [11]. It is obvious that degradation mechanism of PVC and CPE is different and that the effect of Ca/Zn carboxylates on thermooxidative degradation of PVC and CPE is different, too. According to Ahmad and Manzoor [6] the DHCl process, occurring in stabilized PVC, is influenced by the following factors: the structural defects in PVC and in structures containing oxygen, random DHCl elimination, the catalytic effect of HCl and the catalytic effect of $ZnCl_2$.

Table 1 The characteristics of the thermooxidative degradation curves (heating rate 2°C min^{-1}) and kinetic parameters of the dehydrochlorination of all investigated samples

Sample	1st degradation step								2nd degradation step	
	T_{range}/°C	$T_{5\%}$/°C	T_{max}/°C	R_{max}/ % min^{-1}	Δm_1/%	E/ kJ mol^{-1}	ln$Z$/min^{-1}	E/ln$Z$	T_{range}/°C	Δm_2/%
PVC	180–390	242.05	252.46	8.63	61.63	130.2	26.17	4.98	390–515	37.83
PVC+STAB. I	180–440	242.13	264.04	16.29	61.47	128.3	25.65	5.00	440–575	37.76
PVC+STAB. II	195–425	241.23	264.97	7.37	60.32	121.0	23.69	5.11	425–545	38.05
CPE	190–415	262.04	309.25	1.79	42.63	131.6	24.18	5.44	415–485	54.88
CPE+STAB. I	190–420	240.99	289.32	1.48	46.38	174.4	35.02	4.98	420–525	52.29
CPE+STAB. II	195–430	230.61	255.61	1.50	43.85	137.8	27.49	5.01	430–500	51.43
50/50	225–420	252.81	262.61	3.38	54.72	117.3	21.75	5.39	420–510	44.10
50/50+STAB. I	225–430	243.55	285.57	2.22	55.23	136.5	26.56	5.14	430–550	43.65
50/50+STAB. II	200–365	241.03	266.84	2.15	51.89	140.2	27.67	5.07	365–520	41.89

The shape of DTG curves at the temperatures above 400°C indicates the complexity of the degradation processes of all investigated samples.

Kinetic parameters (Table 1) were calculated only for the first degradation stage, where DHCl of PVC and/or CPE is the dominant reaction. In the case of heterogenous reactions, as the thermooxidative degradation of PVC and CPE is, apparent activation energy could not be the criterion of the system stability without the corresponding Z and $g(\alpha)$ [12]. On the assumption that $g(\alpha)$ is the first order reaction, Z was calculated and connected with E through the compensation ratio $E/\ln Z$ [13]. According to this criterion the greater ratio value means the greater stability of the system.

Isothermal thermogravimetry

For the purpose of better understanding of the PVC and CPE thermooxidative degradation processes the isothermal experiment was conducted, too. The chosen isothermal temperature of 240°C is close to the temperature of the beginning of DHCl of the investigated samples. The isothermal TG curves of PVC and PVC+STAB. I (Fig. 4) have S-shape, which confirms the autocatalytic effect of the released HCl and/or $ZnCl_2$. PVC+STAB. I shows a slower mass loss rate than PVC in the first 35 min. After that time the mass loss rate increases, which can be explained by catalytic effect of $ZnCl_2$. PVC+STAB. II shows a convex TG curve, which confirms that greater ratio of Ca:Zn in STAB. II diminishes the catalytic effects of HCl and $ZnCl_2$. DHCl of PVC is almost completed after 120 min and the mass loss is 53.45%. Addition of STAB. I and STAB II. slightly decreases the mass loss at the end.

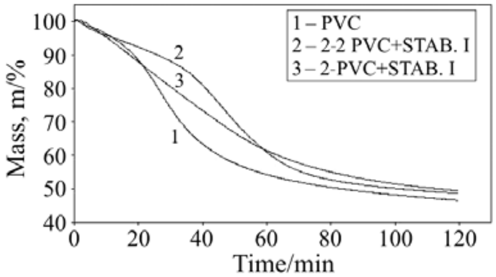

Fig. 4 Isothermal TG curves for non-stabilized and stabilized PVC

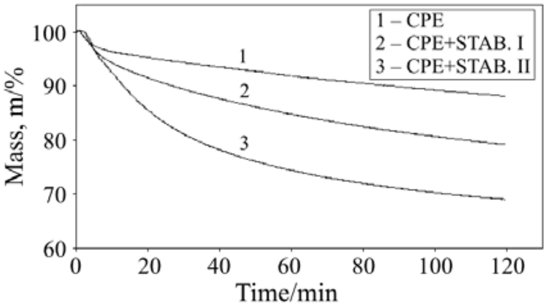

Fig. 5 Isothermal TG curves for non-stabilized and stabilized CPE

The CPE and CPE with STAB. I and STAB. II show convex TG curves (Fig. 5). After 120 min CPE loses 11.83% of the initial mass, therefore the DHCl is partial. Ca/Zn carboxylates considerably increase the mass loss of CPE during the thermooxidative degradation. The shape of CPE curves indicates that there is no catalytic effect of degradation products during the CPE thermooxidation. The isothermal degradation of PVC/CPE blend 50/50 shows the behavior similar to that of CPE (Fig. 6).

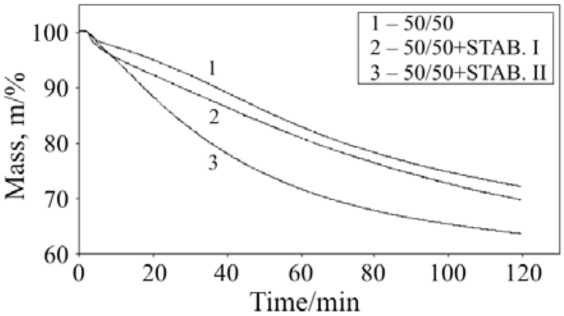

Fig. 6 Isothermal TG curves for non-stabilized and stabilized PVC/CPE blend 50/50

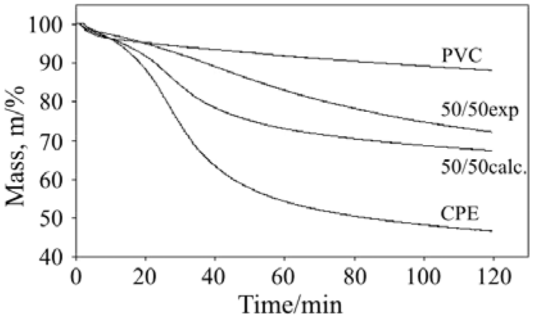

Fig. 7 Isothermal TG curves for PVC, CPE, PVC/CPE blend 50/50 and calculated TG curve for PVC/CPE blend 50/50, at temperature 240°C

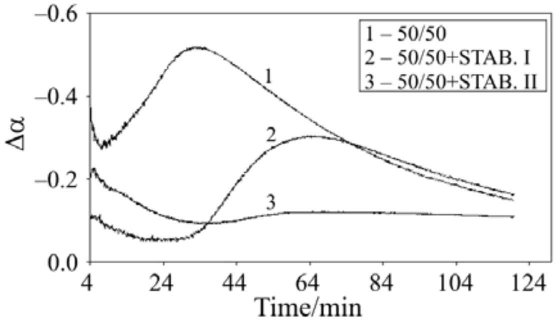

Fig. 8 Comparation of the interaction Δα of 'pure' PVC/CPE blend 50/50 and PVC/CPE blend 50/50 stabilized with different Ca/Zn stabilizers

From PVC and CPE isothermal TG curves it can be concluded that thermooxidation of CPE occurs more slowly than of PVC at the investigated temperature of 240°C. CPE with chlorine content 42% is immiscible with PVC (data not presented in this paper). By comparing the experimental TG curve of 50/50 blend with the TG curve calculated according to additivity rule, it can be concluded that interaction does exist between these polymers (Fig. 7). The calculated TG curve indicates the stabilizing effect of CPE on PVC. The values $\Delta\alpha=(\Delta\alpha_{exp}-\Delta\alpha_{calc})/\Delta\alpha_{calc}$ calculated for 50/50 blend and blends with STAB. I and STAB. II, are shown in Fig. 8. For all samples $\Delta\alpha$ is lesser than zero ($\alpha_{exp}<\alpha_{calc}$), which means greater thermooxidative stability than can be predicted on the basis of individual polymers. Ca/Zn carboxylates diminish that effect in the blend with 50% of CPE.

Conclusions

From the TG curves and the corresponding DTG curves it is evident that the thermooxidative degradation of PVC and CPE occurs through two basic degradation steps in the investigated temperature range. In the first step the main degradation reactions are the dehydrochlorination of PVC and CPE. The PVC dehydrochlorination is a several times faster process than the CPE dehydrochlorination. The second degradation step consists of several substeps, which indicates the complexity of degradation process in that temperature region. The shape of isothermal TG curves confirms that the dehydrochlorination of PVC is a fast, autocatalytic process, while the dehydrochlorination of CPE is a slow process of HCl elimination. Although PVC and CPE are chemically similar, they have different degradation mechanisms, which could be explained by differences in microregularity of the corresponding polymer chains.

The addition of Ca/Zn carboxylates effects on the shape and thermal characteristics of TG curves as well as on the kinetic parameters of PVC and CPE dehydrochlorination in a completely different manner. Investigated Ca/Zn additives act as stabilizers for PVC only. In the case of CPE, those additives promote thermooxidative degradation significantly. Moreover, no pronounced effect on the thermooxidative stabilization is observed with the PVC/CPE blend.

The importance of Ca:Zn ratio in additive was confirmed, too.

Despite the immiscibilty of PVC and CPE, the interactions between these polymers were found. These interactions are diminished by the influence of Ca/Zn carboxylates. The reduced degree of dehydrochlorination for PVC/CPE blends is caused probably by the insertion of CPE macromolecules (or their aggregates) between the PVC ones under the experimental conditions employed, thus affecting the zipper-mode of PVC dehydrochlorination.

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