

APPLICATION OF TG FOR VALUATION OF SELECTED ALIPHATIC DIAMIDE STABILISATION EFFECT ON LOW DENSITY POLYETHYLENE

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Abstract

Spontaneous structural changes of a polymer that is its ageing due to thermal energy, radiation energy, chemical compounds and micro-organisms lasting at least several season cycles change the characteristics of polymer products. Changes of polymer characteristics found during ageing can be reversible or irreversible. The most substantial changes occur as the result of UV radiation.

Tests of selected aliphatic diamides of terephthalic acid as stabilisers of low density polyethylene (LD-PE) used for the production of gardening films were performed. Accelerated ageing of films for a period of one year was done in the Xenotest Alpha type apparatus. Studies were made for 0.1 mm thick commercial films.

Studies of selected mechanical properties of LD-PE films without stabilisers and of LD-PE sheeting containing an addition of one of the synthesised diamides of terephthalic acid or the standard Tinuvin 783 stabiliser were performed before and after the ageing process.

To determine the effect of stabilisers on the ageing process of LD-PE films, thermogravimetric analysis was applied. This allowed us to determine the decomposition activation energy of the investigated films before and after the ageing process and the influence of stabilisers on the observed changes.

Keywords: activation energy, polyethylene, stabilisation, thermal analysis

Introduction

Ageing is a spontaneous structural change occurring in the whole mass of the investigated material within a time span of several season cycles. This change diminishes the mechanical properties of polymers and is caused by such as: heat, light and chemicals. The changes taking place during the ageing process can be reversible and irreversible. One of the most important irreversible changes is the one caused by UV radiation. From the engineering point of view polyolefines, particular-

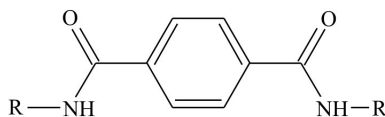
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ly polyethylene, polypropylene and ethylene/propylene copolymers, are of crucial importance. These polymers are characterized by very good mechanical properties, low density, high elasticity in low temperatures, high impact resistance, low water absorption, excellent electroinsulating properties as well as many other expedient usable features. Polyolefins and other macromolecular compounds may, however, lose their precious properties due to thermooxidative degradation, atmospheric conditions, elevated temperature, light, corrosive environment and other factors. During the ageing process olefins become less elastic and fragile than other linear polymers and, in general, exhibit worse mechanical and electric properties [1–13]. Therefore, the struggle vs. those disadvantageous phenomena is of vital importance.

Stabilisation of polymers should prevent premature degradation of usable properties. There are numerous chemical substances applied as single stabilizers and/or co-stabilizers. Substances such as: phenols, thioethers, amines and their derivatives, epoxides, esters and others prevent ageing of different types of polymers, among others, polyolefins [1–3, 8–13]. Stabilizers are frequently used with UV absorbers in order to increase polymer resistance to degradation caused by the solar light. Nowadays, for polyethylene stabilisation the hindered amine light stabilizers (HALS), a type of stabilisers with UV absorber, are frequently used [14, 15]. Organic acid diamides were applied as stabilisers for polymers. Terephthalic acid diamides were obtained in high yields during the investigations of aminolysis processes of poly(ethylene terephthalate) (PET) waste [16]. Hence, the application of these substances (terephthalic diamides) as stabilizers seemed promising. The terephthalic acid diamides have been used as stabilizers for the first time. The method of their synthesis from waste PET materials was developed in our laboratory. Tinuvin 783 was used as a standard stabiliser.

Experimental

Diamides were obtained from PET waste in reaction with aliphatic amines such as: *n*-butylamine, *n*-hexylamine, *n*-octylamine and *n*-dodecylamine. The reactions were carried out in mass with an excess of amines. After crystallization, the obtained diamide was filtered and washed with methanol.



where $R = C_4H_9, C_6H_{13}, C_8H_{17}, C_{12}H_{25}$.

Obtained diamides are solids with appropriate melting points: ($C_4H_9 - D-4$) 228–231°C, ($C_6H_{13} - D-6$) 219–221°C, ($C_8H_{17} - D-8$) 211–2145°C, ($C_{12}H_{25} - D-12$) 205–207°C [16].

Plastic films made of LD-PE with addition of 0.25% of appropriate diamides used in these studies were pressed during the production PE blown films. Films of 0.1 mm thickness were obtained with the following potential stabilizers and the mentioned standard stabilizer:

100% LD-PE	(LD-PE)
99.75% LD-PE, 0.25% N,N'-di- <i>n</i> -butyl-terephthalamide	(LD-PE D-4)
99.75% LD-PE, 0.25% N,N'-di- <i>n</i> -hexyl-terephthalamide	(LD-PE D-6)
99.75% LD-PE, 0.25% N,N'-di- <i>n</i> -octyl-terephthalamide	(LD-PE D-8)
99.75% LD-PE, 0.25% N,N'-di- <i>n</i> -dodecyl-terephthalamide	(LD-PE D-12)
99.75% LD-PE, 0.25% Tinuvin 783	(LD-PE Tin 783)

The amount of the additive (0.25%) is standard for gardening and farming films.

Accelerated ageing of the samples was carried out in the Xenotest Alpha type apparatus.

The ageing process was carried out for LD-PE, LD-PE D-6 and LD-PE Tin 783. Five samples of each plastic film were taken for ageing.

The tests were performed in the following conditions: light source: UV radiation, spectrum 300–400 nm, radiation dose: 100 MJ m⁻², filter: Xenochrome 300 imitates the light in the open air, number of phases: 2, duration of phase I: 102 min without sprinkling, duration of phase II: 18 min with sprinkling, temperature in the chamber: 40°C, temperature of the black thermometer; taken at the level of the samples: 68°C (phase I), 63°C (phase II), relative humidity in the chamber: 65%.

The applied time of accelerated ageing equals one-year of ageing occurring in natural conditions.

Mechanical studies were done in the TIRAtest 2700 instrument. Tensile strength and elongation at break were applied in accordance with Polish standards i.e. PN 85C89037 relevant to PN-EN-ISO4892-2-2001.

Parameters of studies: KA (measure range of the head) – 500N, LO (distance between holders) – 50.00 mm, V₀-V₃ (velocity of expansion) – 500 mm min⁻¹, FO (initially set load) – 0.3N, Le (initial distance between holders) – 50.00 mm.

Thermogravimetric studies were accomplished with Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA. Sample masses ranged between 0.2 to 0.4 mg. The samples were heated up to 650°C with the heating rate of 5, 10, 20, 40 K min⁻¹ in nitrogen atmosphere. The mass of the sample was continuously measured as a function of temperature and the rate of mass loss (DTG) was automatically recorded.

Results and discussion

Studies of the influence of different terephthalic diamides, as potential stabilisers, for the ageing of low density polyethylene were performed. The same dose of diamides and the standard stabiliser were applied for these studies. Mechanical and thermogravimetric measurements of plastic films were carried out before and after ageing processes.

Mechanical studies

Mechanical studies were performed for all types of aged and non-aged plastic films. Five samples of each film were taken for studies.

It was found that changes in the tensile strength and elongation at break values were more advantageous for the polyethylene sheeting with addition of diamides than for the polyethylene films stabilized by Tinuvin 783 (Tables 1, 2).

One can see that the tensile strength of plastic films with Tinuvin 783 and D-12 diamide before the ageing process is higher than for polyethylene film without any additive. The tensile strength of plastic films prepared with the use of other diamides is lower than the one for pure polyethylene film. It was found that the decrease of tensile strength of plastic films after the ageing process is between 32.7 and 43.5% of the initial value in the case of LD-PE films prepared with diamide addition and 11.3% for LD-PE film prepared with Tinuvin 783 addition. It can be seen that the

Table 1 Tensile strength of non-aged and aged films

Sample	RR (non-aged)/ N mm ⁻²	RR (aged)/ N mm ⁻²	Average variation RR/ %
LD-PE without stabiliser	23.1±2	14.3±2	37.9
LD-PE Tin 783	26.2±1	23.2±1	11.3
LD-PE D-4	22.6±2	13.3±2	41.5
LD-PE D-6	21.5±2	14.5±2	32.7
LD-PE D-8	22.1±2	14.8±2	33.0
LD-PE D-12	24.1±2	13.6±2	43.5

RR – tensile strength

Table 2 Elongation at break non-aged and aged films

Sample	AR (non-aged)/%	AR (aged)/%	Average variation AR/%
LD-PE without stabiliser	700.4±40	315.5±40	54.9
LD-PE Tin 783	642.2±20	525.3±20	18.2
LD-PE D-4	746.1±40	457.3±40	38.7
LD-PE D-6	664.2±40	524.7±40	21.0
LD-PE D-8	862.6±40	592.5±40	31.3
LD-PE D-12	758.6±40	443.6±40	41.5

AR – elongation at break

diamides addition only induces a small decrease of tensile strength after the ageing process for plastic films prepared with D-6 diamide and D-8 diamide (32.7 and 33.0%, respectively) in comparison with pure LD-PE film (37.9%). The change of tensile strength of plastic films prepared with the addition of D-4 diamide and D-12 diamide after the aging process is higher (41.5 and 43.5%, respectively) than the one for the pure LD-PE film. It can be seen that diamides have weak stabilising properties. In the case of determining the elongation at break it was found that the addition of diamides: D-4, D-8 and D-12 to the LD-PE film induced an increase of the value of this factor measured before aging, in comparison with the LD-PE film without stabilisers, while the addition of the diamide D-6 and Tinuvin 783 to the LD-PE film induced a decrease of this value. Moreover these two substances induced

almost the same small change of elongation at break for the plastic films after ageing processes i.e. 18.2% for LD-PE Tin 783 and 21.0% for LD-PE D-6, in comparison with data exhibited by plastic films LD-PE D-4 (38.7%), LD-PE D-8 (31.3), LD-PE D-12 (41.5%) and pure LD-PE (54.9%). The change in elongation at break for the films with N,N'-di-*n*-hexyl-terephthalamide did not exceed the value suggested by the Polish standard (i.e. up to 25% of change of elongation at break). It was observed that the addition of the diamides affected the measured mechanical properties of LD-PE films. However, a precise explanation of these changes for instance the influence of the hydrocarbon chain length, require further studies.

The results of thermogravimetric studies were only done for plastic films obtained with the addition of N,N'-di-*n*-hexyl-terephthalamide and Tinuvin 783 as a standard stabilizer. The studies were also performed for pure plastic films.

Thermogravimetric analysis

Thermogravimetric analysis (TG) was applied for evaluation of the stabilization effect in polymers. The indicators of thermostability were determined according to the procedure described previously [17–20].

The curves of LD-PE, LD-PE D-6 and LD-PE Tin 783 films obtained for four different heating rates are presented in Figs 1–3. The starting and finishing temperatures of one stage mass loss decomposition and the temperature of the maximum rate of mass loss were determined (Table 3). The assigned temperature points are indicated in Fig. 4. The accurate assignment of temperatures was easy to perform since there was of only one maximum rate of mass loss on the DTG curves.

From the TG data it can be seen that thermal decomposition starts above 300–350°C for the LD-PE films with and without stabilizers before and after ageing. One loss of mass occurs devolatilisation and decomposition. This process is essentially completed below 500–550°C. Above these temperatures no further mass loss takes place. A shift in TG curves towards higher temperatures with the increase of the heating rate is observed. The shift of thermal degradation was shown earlier [21–23]. It was attributed to the combined effects of the heat transfer at different heating rates and to the kinetics, resulting from delayed decomposition [21, 22]. The heat transfer from the furnace to the sample hinders the determination of the kinetic parameters. Also a close contact between the thermocouple and the sample is desirable [24]. In our investigations the thermocouple measured the temperature of the sample boat. Owing to the facts mentioned above, the observed shift in the curves with increasing heating rate seems to be due to the changes in the kinetics of thermal decomposition.

Kinetic parameters

The use of TG to determine kinetic parameters for the LD-PE films decomposition with and without a stabilizer is possible since only one stabilizer was used as an additive for the preparation of each film sample. It must be emphasised that no char was observed after the decomposition processes. Since during the decomposition

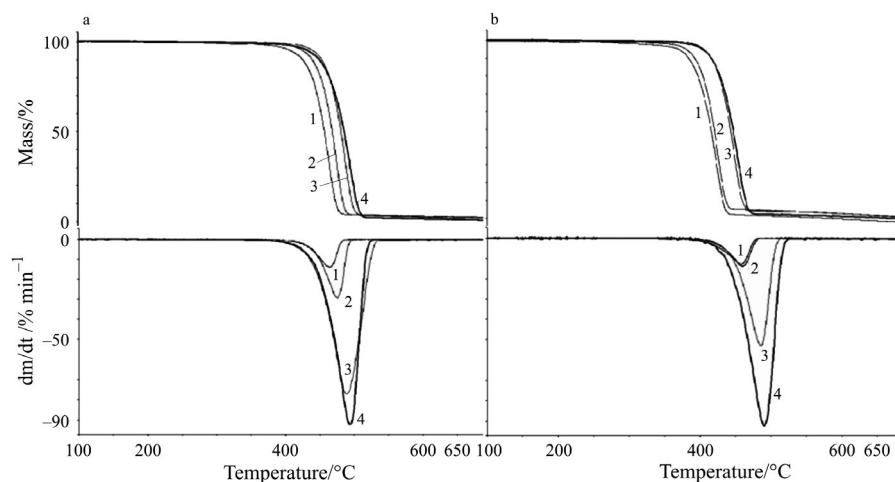


Fig. 1 TG and DTG curves of LD-PE film: a – non-aged, b – aged, at: 1 – 5 K min⁻¹, 2 – 10 K min⁻¹, 3 – 20 K min⁻¹, 4 – 40 K min⁻¹ heating rate

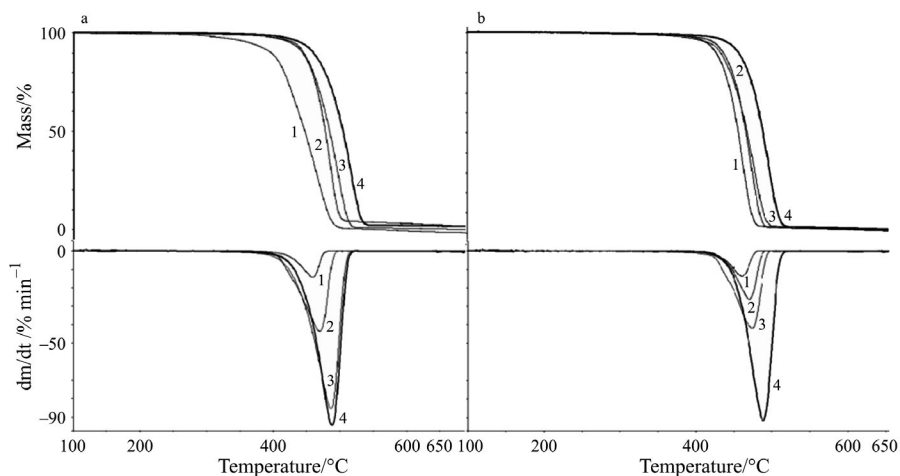


Fig. 2 TG and DTG curves of LD-PE D-6 film: a – non-aged, b – aged, at: 1 – 5 K min⁻¹, 2 – 10 K min⁻¹, 3 – 20 K min⁻¹, 4 – 40 K min⁻¹ heating rate

processes a large number of parallel and series reactions took place, the TG curves show the overall mass loss caused by them. Hence, TG provides only general information on the overall kinetics rather than individual reactions. However, it is useful in providing comparative kinetic data in different reaction conditions such as the heating rate. The approach adopted by many scientists in kinetic analysis of TG data is to assume a first-order reaction for devolatilisation [25–30]. The fact that the sample size is small i.e. eliminates the heat transfer effect, and the assumption of a

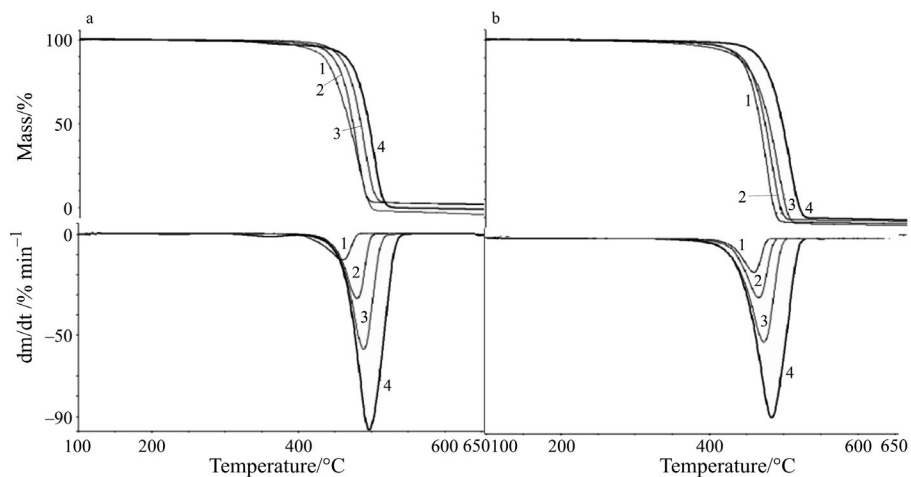


Fig. 3 TG and DTG curves of LD-PE in 783 film: a – non-aged, b – aged, at: 1 – 5 K min⁻¹, 2 – 10 K min⁻¹, 3 – 20 K min⁻¹, 4 – 40 K min⁻¹ heating rate

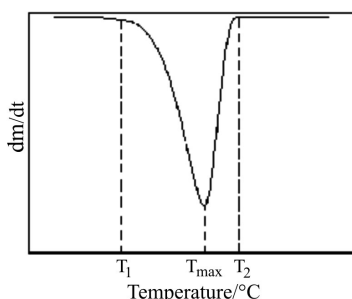


Fig. 4 DTG nomenclature for Table 3

Table 3 Temperature characteristics for the pyrolysis for the samples LD-PE by TG

Sample	Heating rate/ K min ⁻¹	Non-aged			Aged		
		$T_1/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_2/^\circ\text{C}$	$T_1/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_2/^\circ\text{C}$
LD-PE	5	389	464	490	373	458	487
	10	370	474	503	376	462	492
	20	375	480	510	386	485	518
	40	407	488	526	389	486	537
LD-PE D-6	5	349	461	489	370	461	488
	10	351	463	501	380	471	515
	20	355	471	509	387	474	531
	40	363	492	523	395	479	540
LD-PE Tin 783	5	362	463	489	362	463	490
	10	368	471	515	368	471	504
	20	372	477	531	372	477	521
	40	378	479	540	378	479	534

(nomenclature defined in Fig. 4)

Table 4 Kinetic parameters for thermal decomposition of LD-PE films before and after ageing

Sample	Heating rate/ K min ⁻¹	Non-aged		Aged	
		Activation energy/ kJ mol ⁻¹	Pre-exponential factor A/min ⁻¹	Activation energy/ kJ mol ⁻¹	Pre-exponential factor A/min ⁻¹
LD-PE	5	182	1.9·10 ¹²	158	5.9·10 ¹⁰
	10	170	5.2·10 ¹¹	147	1.1·10 ¹⁰
	20	128	2.4·10 ⁹	136	4.2·10 ⁸
	40	122	1.1·10 ⁹	118	2.3·10 ⁷
LD-PE D-6	5	180	8.3·10 ¹¹	219	1.3·10 ¹⁵
	10	169	5.5·10 ¹¹	175	4.1·10 ¹¹
	20	114	8.8·10 ⁷	156	3.1·10 ¹⁰
	40	100	2.7·10 ⁶	132	2.6·10 ⁹
LD-PE Tin 783	5	228	3.3·10 ¹⁵	236	1.6·10 ¹⁶
	10	168	2.1·10 ¹¹	208	1.9·10 ¹⁴
	20	162	2.6·10 ¹⁰	187	3.2·10 ¹²
	40	148	3.8·10 ⁹	169	1.8·10 ¹²

first-order reaction during the sample decomposition, gives us the possibility of using TG data for the calculation of the activation energy [25–27]. A common Arrhenius equation was used for the LD-PE films:

$$k = Ae^{-E/RT} \quad (\text{logarithmic form: } \ln k = \ln A - E/RT)$$

where k – constant value for decomposition reactions [min⁻¹], A – pre-exponential factor [min⁻¹], E – activation energy of the decomposition reaction [J mol⁻¹], R – gas constant [J mol⁻¹ K⁻¹], T – temperature [K].

The used method is based on k -calculation from the equation:

$$dw/dt = -k(w-w_k)$$

where dw/dt – derivative mass [mg min⁻¹], w – mass of undecomposed material [mg], w_k – mass of the residue at the end of the reaction [mg].

The TG continuous record of mass loss vs. time and temperature enables the determination of dw/dt and k . The plot of $\ln k$ vs. $1/T$ gives a straight line of slope $-E/R$ and the activation energy of the decomposition reaction is defined (Table 4).

In general, the activation energy value decreases with the increase of the heating rate. The lowest activation energy value was obtained for the aged LD-PE film samples without stabilisers. For the LD-PE film without stabilisers, the determined activation energy was higher for the non-aged samples than for the aged ones. On the contrary, the activation energy is higher for the aged LD-PE samples with D-6 stabiliser than for the non-aged ones, as in the case of LD-PE with addition of the Tinuvin 783 stabiliser. This fact may suggest that D-6 exhibits some stabilising properties. It was determined that the activation energy value of the non-aged LD-PE Tin 783 samples was higher than for the LD-PE samples.

Conclusions

The results of mechanical properties of the non-aged and aged low density polyethylene films, prepared with or without different terephthalic diamides, obtained from poly(ethylene terephthalate) as potential stabilisers, indicate that these compounds exhibit only small stabilising properties. It was found that the non-aged and aged samples of LD-PE films with addition of N,N'-di-*n*-hexyl-terephthalamide gave the change of value of elongation at break below the one admissible by the Polish standard. This diamide could be used as a stabiliser but it needs further detailed studies, i.e. on the influence of amount of this stabiliser, prepared from the polymer materials waste, on the properties of the LD-PE films.

In TG examination of thermal decomposition of the non-aged and aged LD-PE film samples, with or without stabilisers, a shift towards higher temperatures of thermal degradation is observed with the increase of the heating rate. The determination of the kinetic parameters (pre-exponential factor and activation energy) was also possible.

It was found that value of the activation energy of LD-PE D-6 film samples is similar to the activation energy value of LD-PE film samples with Tinuvin 783 used as a standard.

From the determined kinetic parameters, one might suppose that N,N'-di-*n*-hexyl-terephthalamide possesses good stabilising properties however, mechanical properties of LD-PE film samples with this compounds did not confirm this assumption.

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