Aspects of Hot Stability of High Density Polyethylene (PEHD)

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PEHD plastic materials are more and more used in applications. Their possible physical and chemical changes, depending on the temperature changes and time, in a given atmosphere, can be made by simultaneous measurement of the sample mass and its temperature. It is achieved by the use of thermogravimetry (TG). The thermogravimeter Mettler Toledo presents thermograms or thermogravimetric curves as well as their differentials. Results obtained in this way can be starting points for next researches.

Keywords: PEHD, thermogravimetry, thermogravimetric differentials, quantitative analysis

Their increasing applicability, as well as the problems they arise during the service life, elaboration problems, but also welding and control problems, issuing of standards to regulate different aspects including those related to testing, justified the development of professional organizations having this preoccupation respectivelly the option for each application is determined by the results of experiments that evince their behaviour depending on temperature[1-14].

Plastic material pipes and especially those made out of PEHD are preferred to the metallic ones, in the most diverse fields.

Network of water pipelines forms the first application field of PEHD pipes, due to the multitude of advantages they present: elasticity, flexibility, resistance, no possibilities to appear rust, irrigation networks in the following variants: sprinkler irrigation, fertilizations, possibility to automate this field; gas grids, sewage systems, underwater network systems, relining, which allows the replacement of old pipelines by a simple interposition; installations in buildings; industrial installations, by which the resistance to chemical agents is increased, rapid assembling and easy maintenance, reliability, transport applications, sewage systems and technological process, pressure vessels; waterproof networks, due to the reduced conductivity, delay a possible water freezing, high elasticity, aerial installations etc.

Table 1
COMPARATIVE PROPERTIES OF PEHD AND STEEL

Properties	PEHD	Steel	Measure units
Density	> 0,954	7.8	g/cm^3
Tensile resistance	20÷ 30	500	N/mm^2
Elongation	400 ÷ 800	20	%
Elasticity module	700 ÷ 1000	210000	N/mm^2
Impact resistance	no fracture	90	J
Crystallisation radius	130 ÷ 135	1200 ÷ 1450	°C
Thermal dilatation coefficient	2×10^{-4}	0.12×10^{-4}	K^{-1}
Conductivity	0.43	50	W/mK
Electric resistance	$> 10^{13}$	0.10	Ω

Table 2
MECHANICAL CHARACTERISTICS OF MAIN PLASTIC MATERIALS

PM	Abbreviation	Density <g/cm^3)	Young modulus (GPa)	Tensile resistance (MPa)	Fracture elongation (%)	Glass transition temperature (°C)	Maximum temperature (°C)	Melting temperature (°C)	Solidification contraction (%)
Polyethylene - low density PE	PELD	0.92-0.94	0.2-0.5	9-12	400-800	-110	60	115	1.3-3.5
- high density PE	PEHD	>0.95	1.0-1.2	30-35	700-1000	-110	100	130	2-4
Poly propylene	PP	0.90	1.1-1.6	20-40	200-1000	-10	-	170	1.0-2.5
Rigid PVC	PVC	1.38	2.4	50	10-50	75-105	70	160	0.1-0.5
Polystyrene	PS	1.04	3	40	4	90	70	-	0.1-0.7
Expanded PS		0.02-0.06	-	0.02-0.04	-	-	70	-	-
Acrylobutadyen -styren	ABS	1.03-1.08	2.5	30-60	20-60	110	-	-	0.4-0.9
Methyl polymetacrylate	PMMA	1.18	3.3	65	4	120	85	225	-
Polytetrafluoroethylene	PTFE	2.14-2.18	0.35-0.75	20-40	250-500	125	260	330	-
Polyamides	PA								
PA 6-6		1.14	3	83	60	3	140	250	1.5
PA 6-12		1.50	-	60	100	-	-	210	1.5

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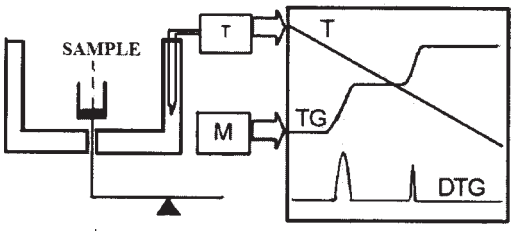

Fig. 1 Principle scheme for recording T and TG curves

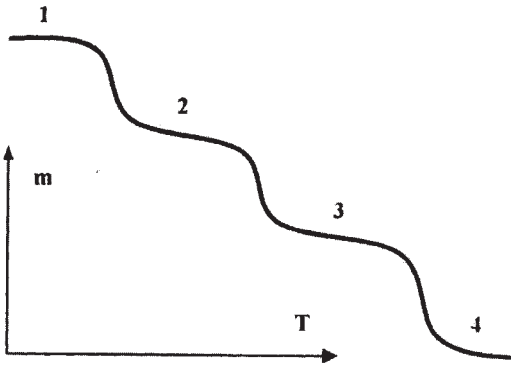

Fig.2 Aspect of the thermogravimetric TG curve for calcium oxalate

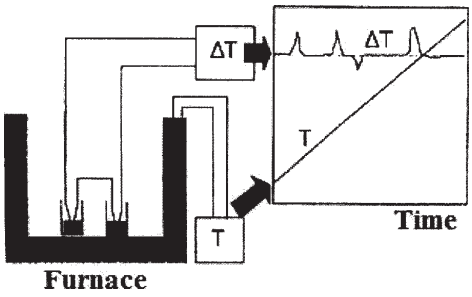

Fig. 3 Principle scheme for obtaining DTA curves

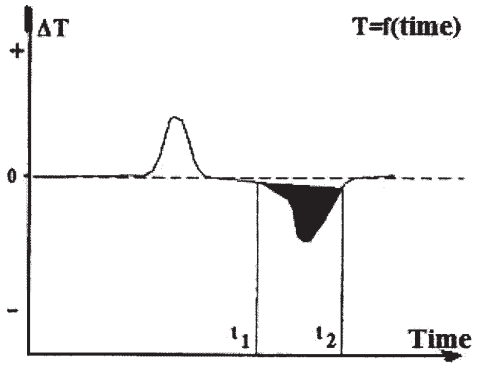

Fig. 4 Analytic signal in DTA

Approaching this field, for each country, there exists specifications such as AD MERKBLATT for Germany, WIS (Water Research Centre) for England - ISO/ CD 13953, INSTA (Inter Nordic Standardisation Work), NF A 89-803 for France, JIS Z 3831-89 for Japan or professional organizations IIW/IIS documents - Commission XVI, CEN TC 248 SC3 or ISCIR Technical Prescriptions.

Comparative properties of PEHD and steel are given in table 1.

Among the specific properties of PEHD products, it is worth mentioning that they are flexible, supple, insipid, inodorous and not toxic. The polymers soften around the temperature of 115°C, become brittle under -25°C and decompose themselves around the temperature of 300°C.

The most important resistance characteristics of the PEHD pipes are:

- long time resistance (for example PEHD pipes, performance class PE 100, have the minimum necessary resistance, MRS 10, namely minimum 10MPa at 20°C, for 50 years);
- high resistance at crack's slow propagation and indirectly higher resistance for long time loading, insensibility when crack propagation increases, respectively;
- high resistance when crack rapidly propagates.

A global image of the main mechanical characteristics of thermoplastic type plastics presented comparatively with the thermo-hardnable ones are obtained analysing the date presented in table 2.

Thermogravimetry (TG) can be defined as the study of changing the mass of materials depending on temperature, time and a given atmosphere. TG is a technique by which the sample mass is measured when the temperature increases. This method is useful in determining the sample purity as well as the concentration of material components, and generally to study any thermal decomposition reaction.

Therefore, by heating (or cooling) at constant speed a combination or a base material, it can suffer a series of transformations both physical and chemical, which can be evinced by simultaneously measurement of the sample mass and its temperature. The mass modifications lead to graphic representations named thermograms or thermogravimetric curves (TG) as well as their differentials (DTG) that can be seen in figures 1 and 2. The equipment used is described in the same figure (fig. 1). It can be noticed that the PEHD sample is heated in oven, which temperature is measured, the heating speed being controlled, so that it increases continuously, as linearly, as possible. It is worth mentioning that, simultaneously, the PEHD sample is weighted.

Thermograms (TG curves) are true imprint for the samples allowing even quantitative analyses using the standard addition method.

The thermo-differential analyses (DTA) are based on measuring the temperature difference between the sample and a reference substance, when the whole system is heated. This method is sensitive to endo and exothermal processes (fig. 3) [1, 2, 8, 10].

The DTA curves, obtained when applying the mentioned above method, record the temperature difference, AT, that appears between the probe and a reference substance, situated in the same oven in a heating process. It is an old technique, introduced by W. C. Roberts-Austen in1899. A differential thermocouple is used for example, as that presented in figure 4.

Therefore, the sample and the reference material are in the same temperature conditions T, heating or cooling or kept to an in time constant value of temperature.

At a certain temperature only the smple suffers a transformation, which depending on its nature, is with heat absorption or yield of heat. The ΔT curve – depending on T is the thermo- differential curve or the DTA. Exothermic phenomenon (ΔT<0) or endothermic ones, can be evinced resulting a characteristic curve for a certain base material (for example, soils, minerals, metals, different plastic materials etc.) For the simple case, when the thermal conductibility of the sample, k coincides with that of the standard sample, inherent from the structure modifications point of view, under the action of temperature, between the sample mass, m and ΔT the following equation can be written (1) :

$$\Delta T = \frac{m}{k} \cdot \frac{dH}{dt} \qquad (1)$$

where dH/dt represents the heat elimination quantity (consumed, respectively) of 1 moll substance in the time unit, at a given moment, t in the time interval , as the endothermic transformation last (fig.5) the following equation can be written (2):

$$m \int \frac{dH}{dt} = k \int \Delta T dT \qquad (2)$$

For the above transformation, the result of the first integral – ΔH- being a constant, and the moll number N=m/M, the equation (3) can be written:

$$N = \frac{k}{\Delta H} \int \Delta T dT \qquad (3)$$

where the integral represents the aria under the curve. Therefore, knowing the thermal effect of the reaction (ΔH) and determining the aria under the curve, quantitative analyses can be realized with this technique, assessing the number of molls, n in a substance on the bases of a previous standard calibration.

The equipment recording simultaneously the curves T, TG, DTG and ATD on the same sample are named derivatographes [1, 2, 8].

Experimental part

These experiments were made in order to determine the purity of the sample , as well as the heat decomposition reactions appearing when temperature increases. From the differential analyses one can observe the solid state reaction, as well as the exothermic and endothermic phenomena [1-10].

Figures 5 present results obtained following the respective analysis [1, 2, 8].

Determinations were made using a thermal analyses device METTLER, and the process of weight decrease as a function of the temperature is presented by means of DTG.

Testing of the PEHD sample has been made for 100 minutes, at 500 Celsius degree, and the speed (rate) of 5 °C/min.

It can be noticed, the reduction of weight, as it follows. Up to 262 °C the situation is stable, without modifications from the thermal point of wiew. Starting with 262°C the reduction of weight starts, with an inflexion from 262.71°C.The decrease is slow up to the temperature of 384.48°C. Then a very rapid decrease follows which leads to failure. A strong exothermal reaction appears at 416°C. It is worth mentioning the existence of inflexion points at 446.2 and 463.25 °C with exothermal drops at 416.2 and 463.25 °C [1, 2, 8].

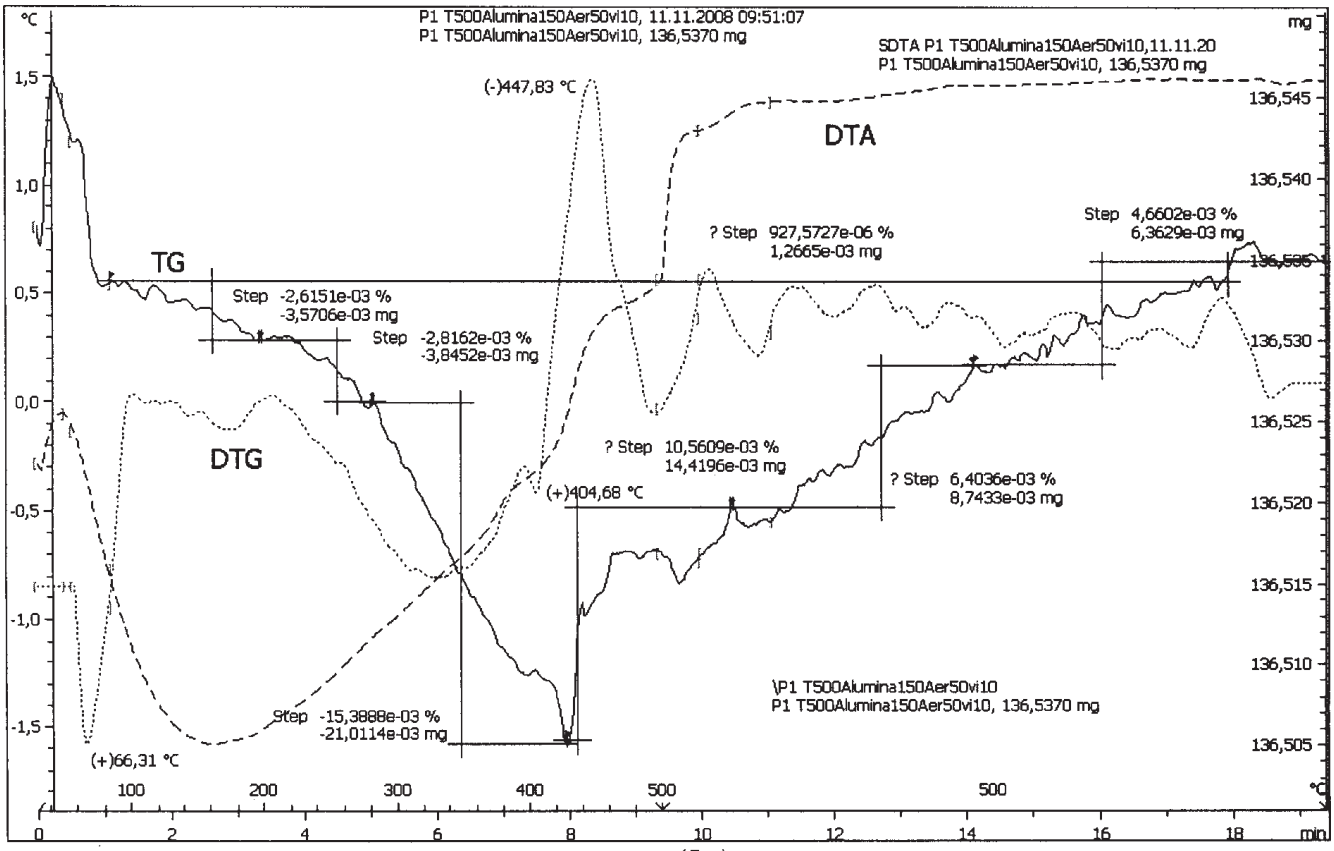

Fig. 5a

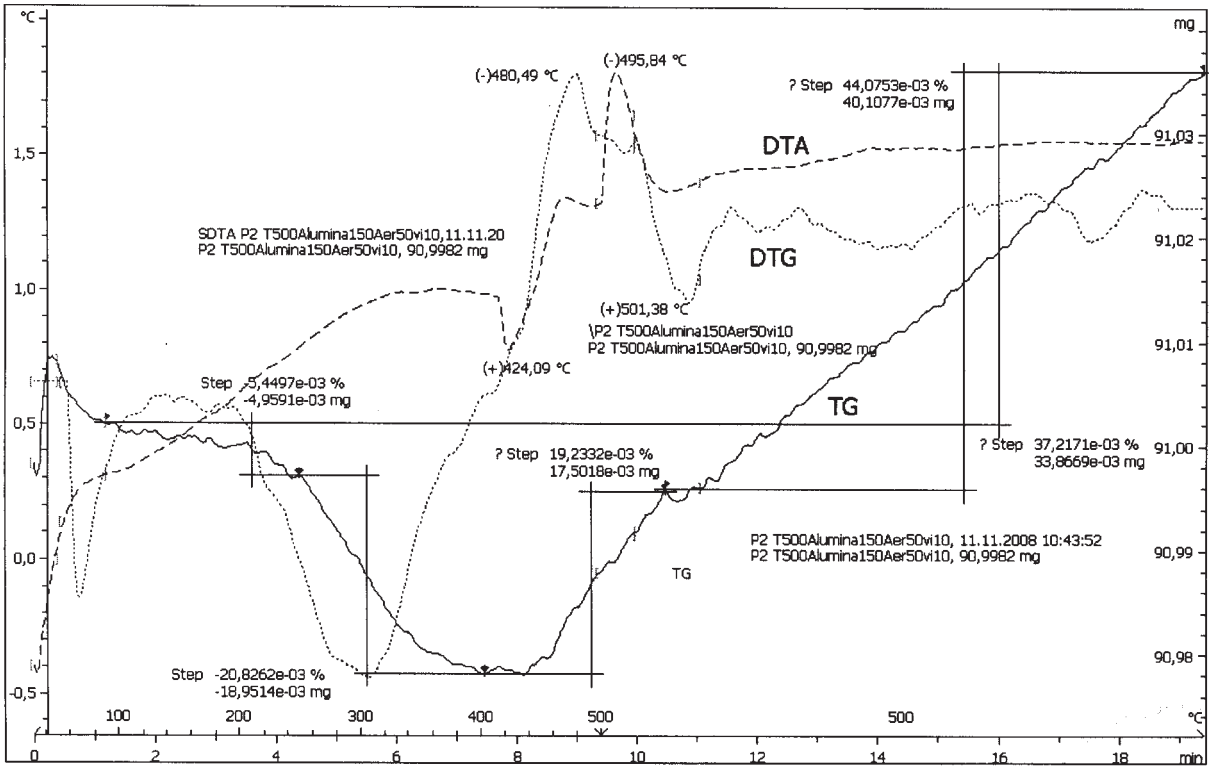

Fig. 5b. Symbols in figure 5a and 5b are as follows: – TG (TGA)- Thermo gravimetric analyses
- DTG - derivate TG - DTA – Differential analyses

Conclusion

Results obtained following the experiments with the Metler-Toledo installation evinced a good behaviour of PEHD for temperatures .

The results of the thermogravimetric analysis are given related to the PEHD behaviour as a function of temperature, at the weight decreasing module up to failure at temperature over 262°C.

References

1. ERSTESVAG V., Application Polymer Degradation and Stability, Journal of Thermal Analysis and Calirimetry, 1998, vol. 59, p. 85
2. JFORREST, M., Analysis of Thermoset materials, Precursors and Products, 2003, vol. 14, nr. 6
3. LEONE, G., La crescita del PE nelle reti di distribuzione gas ed acqua in pressione, Revista Italiana della Saldatura, 2003, an LV, nr. 4, p. 479
4. POPESCU, M., Materialele plastice si imbinarea lor, Ed Politehnica Timisoara, 2009
5. POPESCU, M., ARGESANU, V., JULA, M., Rev. Chim. (Bucharest), **43**, no. 4, 2006, p. 381
6. POPESCU, M., MARTA, C., MOCUTA, E.G., CANEPARU, A., GABRIAN, A.,When welding PEHD pipelines, Scientific Bulletin of the POLITEHNICA University of Timisoara, 2008, tom. 53(67), fasc. 3, p. 76
7. POPESCU, M., BERGER, E., MUSAT, L., CARBUNARU, T., Tendances dans l'elargissement d'utilisation des tuyaux en polyethylene dans le transport d'eau et du gas naturel, rapports au tendances existents dans le monde,Annals of the Oradea University, Fascicle of Management and Technological Engineering, 2004, mai, p. 144
8. SCHUBNELL, M., Determination of polymer crystallinity with DSC measurements ,User Com Mettler Toledo, 2001, nr. 1, p.12
9. TARNOGRODSKY, V.P., PONOMAREREVA, E.YU., Methods to improve the strength of welded joints of thermoplastic pipes, Avtomaticeskaja Svarka, 2003, vol. 600, nr. 3, p. 41
10. MITELEA, I., VĂRZARU, N., BORDEAŞU, I., POPESCU, M., Mat. Plast., **46**, no. 1, 2009, p.101
11. VODA, M., BORDEASU, I., MESMACQUE, G., CHITAC, V., TABARA I., Mat. Plast., **44**, no.3, 2007, p. 254
12. CIUCA, D. BOLCU, D., STANESCU, M. M., VERMESAN, D., PREJBEANU, R., PETRE, C.C., CARAIANE, AURELIANA, RIZESCU, S., Mat. Plast., **46**, no. 4, 2009, p. 444
13. GHITA E., GILLICH GR., BORDEASU I., Mat. Plast., **44**, no.2, 2007, p. 158
14. MITELEA, I., VĂRZARU, N., POPOVICI, D., POPESCU, M., BORDEAŞU, I., Mat. Plast., **45**, no.3, 2008, p. 289
15.MITELEA, I., VĂRZARU, N., BORDEAŞU, I., SCURTU, D., Mat. Plast., **46**, no. 4, 2009, p.439

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