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THE USAGE OF DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRIC ANALYSIS FOR OPTIMIZATION OF PLASTICS PROCESSING

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Original scientific paper

Plastics have various thermal stabilities that are depending on the structure of polymers chains. Therefore it is very important to know these properties, which influence temperature regime processing equipments. This contribution presents differential scanning analysis (DSC) and thermogravimetry analysis (TG) of selected plastics in protective atmosphere of Ar as well as in oxidative atmosphere of synthetic air. These analyses serve for proposition of temperature regime of processing.

Keywords: *differential scanning calorimetry, plastics, polymers, processing, thermogravimetric analysis*

Primjena diferencijalno skenirajuće kalorimetrije i termogravimetrijske analize u optimizaciji obrade plastike

Izvorni znanstveni članak

Plastični materijali imaju različitu toplinsku stabilnost koja ovisi o strukturi polimernih lanaca. Stoga je veoma važno poznavati ta svojstva, koja utječu na temperaturni režim tijekom obrade. Ovaj rad predstavlja analizu diferencijalno skenirajuće kalorimetrije (DSC) i termogravimetrijsku analizu (TG) odabranih plastičnih materijala u zaštitnoj atmosferi Ar i oksidirajućoj atmosferi sintetičkog zraka. Te analize služe kao prijedlog temperaturnog režima obrade.

Ključne riječi: *diferencijalno skenirajuća kalorimetrija, obrada, plastični materijali, polimeri, termogravimetrijska analiza*

1 Introduction

The importance of plastics lies in distinct advantages that they offer. These advantages include: light weight, good thermal and electrical insulation properties, resistance to corrosion effects, chemically inert, high strength and dimensional stability, absorption of mechanical shocks, good dyeability, potential for decorative surface effects, low production costs [1].

Future progress in plastics technology may depend mainly on the same factors that had caused their recent fast growth. Some of the main factors include [2]:

- Improved understanding of plastics characteristics, especially long-term and under combined stresses (that is, under combined mechanical, thermal, and chemical effects).
- Development and utilization of new materials and combinations of materials, especially in reinforced plastics or composites.
- Steady reduction in materials costs relative to competing materials, taking advantage of low energy requirements for processing, and economies of scale.
- Invention and commercialization of new processes.
- Continued improvement in quality, in part due to further automation and in-line measurement and control.
- Advancement in recycling technology to reduce environmental consequences of wider use of nondegradable materials.

One of the first steps in plastics product design is selection of candidate materials by the design engineer, in cooperation with production engineers, toolmakers, and marketing personnel. Therefore, an understanding of the chemistry of polymers as the base of plastics, and the additives used to modify their properties, is essential for good communication among all of the key personnel involved. This is especially true in the evaluation and exploitation of a new polymer of polymer alloy, where the user must consider chemical composition, as it reflects on the performance of any product that is being promoted for public use. The user must also consider the effects of chemical composition on safety in processing, waste disposal, and durability in all sorts of environments. A similar relationship between product and material exists in all technologies, e.g. a machine shop supervisor must know enough about metallurgy to recognize when there is a metallurgical problem and be able to exchange information intelligently with metallurgical experts [2].

During their production, processing and application, plastics are often subjected to temperature-dependent structural changes. Thermal analysis for characterization of plastics is widely practiced today in research and industry [1].

There are three different basic thermal analysis techniques: differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and thermomechanical analysis (TMA) [2].

DSC instruments are widely used for the thermal characterization of plastics [3]. DSC is a technique that measures heat flow into or out of a material as a function of time or temperature. The required sample size is relatively small and very little sample preparation is required which translates to fast analysis time. In a DSC measurement, information about thermal and mechanical history (processing influences, crystallinity and curing, service temperature) is revealed by the first heating curve and for forensic comparison of chemically similar samples thermal history plays an important role because subsequent controlled cooling creates a "new" known specimen history, which gives same characteristic properties to all materials [4]. The advantage of DSC compared with other calorimetric techniques lies in the broad dynamic range regarding heating and cooling rates, including isothermal and temperature-modulated operation [5]. DSC is a useful tool for characterizing thermoplastics by determining the glass transition temperatures. This technique is especially useful in the characterization of copolymers and blends where this information may be directly applied to determining the formulation changes required to improve physical properties [6, 7].

2 Method

Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements were employed in this study. Both measurements were performed on a Netzsch STA 409CD Simultaneous Thermal Analysis Apparatus (Fig. 1). This instrument is able to record both measured values (DSC and TG) at the same time.

Instrument was calibrated in temperature range from room temperature up to 600 °C using certificated melting standards of In, Sn, Bi and Zn. Temperature and sensitivity calibration were performed at the same condition as sample measurement, i.e. heating rate was 10K/min and calibration measurements were done in Ar as well as in air atmosphere.

Figure 1 Netzsch STA 409CD – Simultaneous Thermal Analysis Apparatus

The samples were tested at non-isothermal conditions at the same scanning rates of 10 K/min in two steps: heating and cooling. The temperature range of measurement was from room temperature to 350 °C. Each specimen, i.e. Polyactic Acid (PLA), High Density Polyethylene (HDPE) and Polyamide 66 (PA 66) was measured in inert and also in oxidizing atmosphere.

First measurements were conducted in protective atmosphere of pure Ar (99,9999 vol. %). The evacuation and purification of furnace by Ar was done before measurements. The gas flow of Ar during measurement was 0,00006 m^3/s.

Measurements in oxidizing atmosphere were conducted in static air in furnace without active gas flow. Samples were loaded onto an aluminium pan covered by aluminium lid. The weight of samples varied between 2,0 mg and 6,5 mg. The thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and solidification temperature (T_s) were measured. The thermal stability of the samples was investigated with a TG (dashed lines).

3 Results

Fig. 2 presents the DSC-TG result of PLA sample (6,5 mg) tested in Ar protective atmosphere. The mass of PLA sample for DSC-TG measurement in the static air atmosphere was 3,9 mg. In Fig. 3 is DCS-TG record (heating and cooling) of this sample in axis of TG (left), DCS (right) plotted against Time.

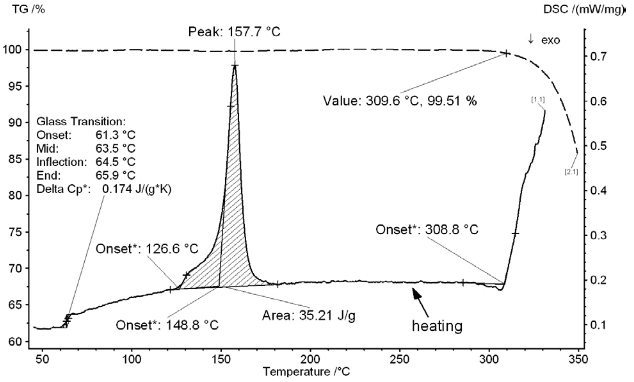

Figure 2 DSC-TG record of PLA (6,5 mg) measured in argon

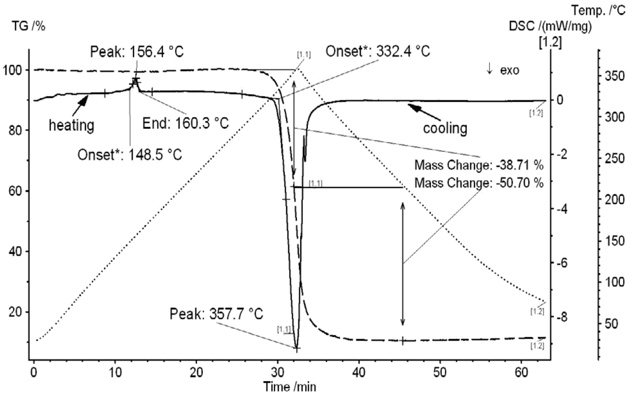

Figure 3 DSC-TG record of PLA (3,9 mg) measured in air

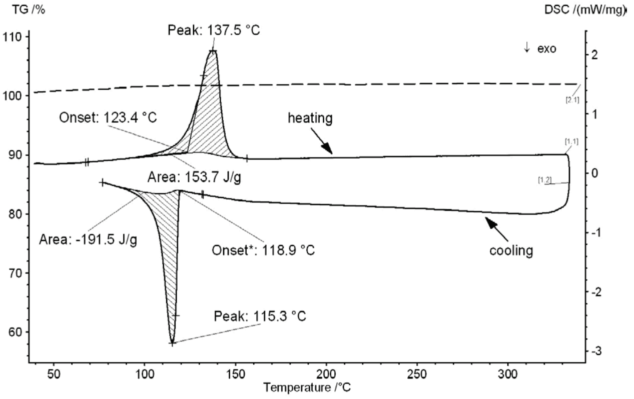

Figure 4 DSC-TG record of HDPE (4,5 mg) measured in argon

The DSC-TG result of HDPE sample (4,5 mg) tested in Ar protective atmosphere is presented in Fig. 4. The weight of HDPE sample for DSC-TG measurement in the static air atmosphere was 3,8 mg. The DCS-TG record (heating and cooling) is shown in Fig. 5. Axes are again in the TG (left), DSC (right) versus Time coordinates.

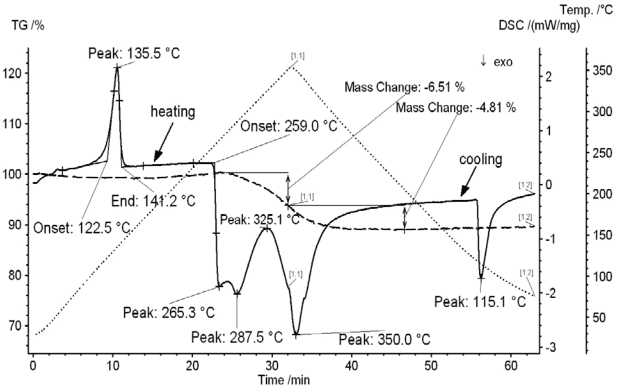

Figure 5 DSC-TG record of HDPE (3,8 mg) measured in air

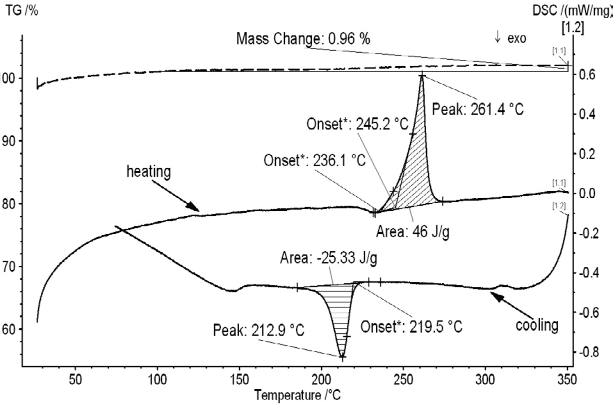

Figure 6 DSC-TG record of PA-66 (4,6 mg) measured in argon

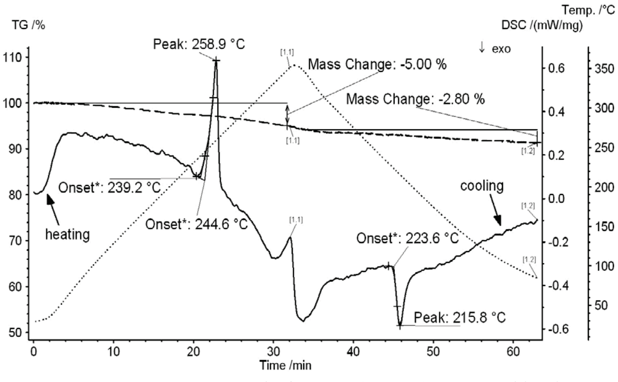

Figure 7 DSC-TG record of PA 66 (2,0 mg) measured in air

Fig. 6 displays the simultaneous DSC-TG measurement of PA 66 sample (4,6 mg) performed under Ar protective atmosphere. DSC-TG measurement of the same PA 66 sample, however in air atmosphere is shown in Fig. 7. Mass of this sample was 2,0 mg.

4 Discussion

Heating DSC curve (PLA sample in Fig. 2) shows only endothermic changes in sample during heating (10 K/min). Glass transition occurred around 61,3 °C and complete transformation finished at 65,9 °C. The sample started to melt at 126,6 °C, however the shape of melting peak indicated that the major components of the sample started to melt at higher temperature 148,8 °C. The sample was completely melted at around 180 °C. The specific heat required for melting was 35,21 J/g. The melted sample was stable during further heating until the temperature of 308,8 °C was reached. After this temperature the sample showed endothermic reaction which seems to be unfinished. Dashed heating curve represents TG signal with correction to the empty pans. TG detected mass loss of 0,5 % at about 310 °C. After this point the sample lost mass rapidly. These results suggest that decomposition of this sample started at about 310 °C. During cooling no exothermic or endothermic reactions were recorded.

The temperature in Fig. 3 can be read at any time on the dotted linear lines (heating and cooling). Melting of the main composition of the sample occurred at similar temperature (148,5 °C) as in previous measurement in the Ar dynamic atmosphere. Over 310 °C the sample started slightly to lose its weight, but at 332,4 °C it started losing weight dramatically, followed by huge exothermic reaction, which was probably burning of the sample. This exothermic reaction has not finished during heating, but continues also at cooling while almost the whole sample is burnt out. After that the DSC and TG signals return to the straight lines till the sample is cooled down to the room temperature. The total mass loss of the sample is 89,41 %.

Heating DSC curve in Fig. 4 (HDPE sample) shows again only endothermic change in sample during heating (10 K/min). The sample started to melt about 100 °C; however the major components of the sample started to melt at higher temperature, 123,4 °C and the sample was completely melted at 137,5 °C. The specific heat required for melting was 153,7 J/g. The melted sample was stable during further heating. During cooling exothermic reaction occurred at 115,3 °C. No mass changes were observed during both program steps.

In Fig. 5 is shown that melting of this HDPE sample started at 122,5 °C at measurement in air atmosphere. However at 259 °C exothermic reactions occurred at least in three steps related with mass loss of about 11,3 %. In DSC cooling curve exothermic reaction is shown representing solidification at 115,1 °C. This measurement shows that during heating at air atmosphere occurred both, melting reaction and oxidative degradation of HDPE sample.

Fig. 6 shows DSC-TG measurement of PA 66. In melting peak at heating curve can be evaluated two extrapolated onsets at 236,1 °C and 245,2 °C. The specific heat consumed by melting of the sample is 46 J/g. Bottom curve represents DSC signal at cooling. Extrapolated onset of sample solidification is shifted to lower temperature due to undercooling. Thermogravimetric curve (dashed) shows negligible mass chance during heating.

The simultaneous DSC-TG record of PA 66 sample measured in air atmosphere is plotted against time (Fig. 7). During heating and cooling also appeared endo- and exo-thermic peak related to melting and solidification, respectively. Moreover at heating curve between 300 °C up to 350 °C exothermic reaction is visible. Total mass loss during whole measurement is up to 8 %.

5 Conclusions

In this contribution we show that simultaneous TG-DSC measurements can be utilized for determination of melting temperatures as well as for determination of thermal degradation in protective atmosphere and thermal oxidation in air atmosphere during heating.

These measured values can determine optimal temperature parameters of plastic processing technologies, i.e. extrusion, injection moulding, blow moulding and rotation moulding.

It was found that PLA degrades in both measurements, in Ar protective atmosphere as well as in air oxidizing atmosphere. On the other hand the HDPE is much more stable, during heating in Ar atmosphere did not occur any exo or endo reaction or mass loss. The melting temperature of PA 66 is the highest among these plastic materials, moreover no significant difference in mass change was detected during heating in Ar atmosphere. The mass loss of PA 66 during measurement in air atmosphere is the lowest, up to 8 %, in comparison with HDPE (over 11 %) and PLA (almost 90 %).

The difference of those three plastics is connected with their diverse macromolecular structures.

The results showed that this method is suitable for further evaluation of rheological properties, especially the temperature range of plastics thermal stability. Through this method the influence of additions to the temperature tracking could be determined. The present measurement results are an important parameter for the next treatment of plastics.

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6 References

[1] Netzsch, Analyzing and testing: Thermal Characterization of Polymers. http://www.netzsch-thermal-analysis.com/download/Polymers_E_0312_en_571.pdf (12. 5. 2012).

[2] Belofsky, H. Plastics: Product Design and Process Engineering. Hanser/Gardner Publishers Cincinnati, Ohio, 1995, 648 p., ISBN 3446174176.

[3] Ehrensttein, G.; Riedel, G.; Trawiel, P. Thermal analysis of plastics, Theory and Practice. Hanser/Gardner Publishers Cincinnati, Ohio, 2004, 359 p., ISBN 156990362X.

[4] Sajwan, M.; Aggarwal, S.; Singh, R. B. Forensic characterization of HDPE pipes by DSC. // Forensic Science International, 175, July 2007, pp. 130-133.

[5] Schick, C. Differential scanning calorimetry (DSC) of semicrystalline polymers. // Analytical and Bioanalytical Chemistry, vol. 359, Oct. 2009, pp. 1589-1611.

[6] Measuring the Glass Transition of Amorphous Engineering Thermoplastics. TA Instruments. http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Applications_Briefs/TA309.PDF (7. 5. 2012).

[7] Gallagher, P. K. Handbook of Thermal Analysis and Calorimetry. Elsevier, 1998, 1032 p., ISBN: 9780444820884.

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