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DEVELOPMENT OF EXPERIMENTAL DEVICE WITH DATA ACQUISITION FOR THERMOMECHANICAL CHARACTERIZATION OF POLYMERS

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Abstract. *The aim of this paper is to present a handmade laboratory device with data acquisition for estimating the thermomechanical characteristics (caused by dimensional changes in height) of polymeric materials. This experimental device is able to perform penetration tests, monitoring the expansion of the samples and based on experimental tests, the thermal expansivity or coefficient of thermal expansion (CTE) can be determined. A data acquisition instrument, which register (i) the deformation of the specimen, by using two displacement transducers (an inductive proximity transducer and an transmission type photoelectric linear encoder) as well as registers (ii) the temperature (at the base of the specimen and in the vicinity of the point of contact with the penetrator) is used. In order to test the device and to highlight its qualities, preliminary tests were carried out on a thermosetting polymeric material in various stages of polymerization.*

1. Introduction

Thermomechanical analysis (TMA) is one of the essential tools needed to estimate the behavior of polymeric materials under heating conditions. The TMA is based on monitoring the dimensional variations of the material when is heated, in the absence of a load (expansion mode) or under loading conditons (penetration or tension modes) [1]. Analyzes have to be performed with respect of following specifications ASTM E831 (Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis) [2] and ASTM E1545 (Standard Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis) [3] .

Regardless of the standard test modes and the different construction variants of the thermomechanical test devices, the testing on this experimental device (developed by our team), consisted of determining the dimensional variations of a sample depending on the heating temperature.
If the sample has the initial length l_0 at room (ambient) temperature T_0, l_T is the length of the sample at temperture T (to which the material is heated) and $\Delta l = l_T - l_0$ is expansion of the sample in the temperature range $\Delta T = T - T_o$.

For temperatures higher than room (ambient) temperature, T_o, , all these parameters are related by the relations:

$$l_T = l_0 + \alpha \cdot l_0 \cdot (T - T_0) \qquad (1)$$

or

$$\Delta l = \alpha \cdot l_0 \cdot \Delta T \qquad (2)$$

where the coefficient of linear expansion, α, is calculated as an average coefficient on ΔT temperature ranges.
In our preliminary experiments, we monitoring this expansion of the samples or

$$\Delta l = l_T - l_0 = f(T)$$

or relative expansion of the samples

$$\frac{\Delta l}{l_o} = \alpha \cdot \Delta T \qquad (3)$$

and we can also calculate the average coefficient of linear expansions, as:

$$\alpha = \frac{\Delta l}{l_o} \cdot \frac{1}{\Delta T} \qquad (4)$$

In the representation of relative expansion as a function of temperature, the shape of the curve is not a straight line and the slope of this interdependence has the significance of the coefficient of thermal expansion.

The reason why the real curve Δl = f (T) is not a straight line is related to the heating rate of the samples. In order to obtain a linear dependence between expansion and temperature it is necessary to maintain a constant heating rate. The errors depend very much on the length of the test samples and the uniformity of its heating. In general, smaller errors can be obtained on shorter specimens because the homogenization of the temperature in the sample is easier [4].

2. Description of the thermomechanical analysis device

2.1. Device construction

The schematic diagram of the thermomechanical analysis device is shown in Figure 1.

In experimental penetration tests we used cylindrical samples of 8-12 mm in diameter and different lengths.

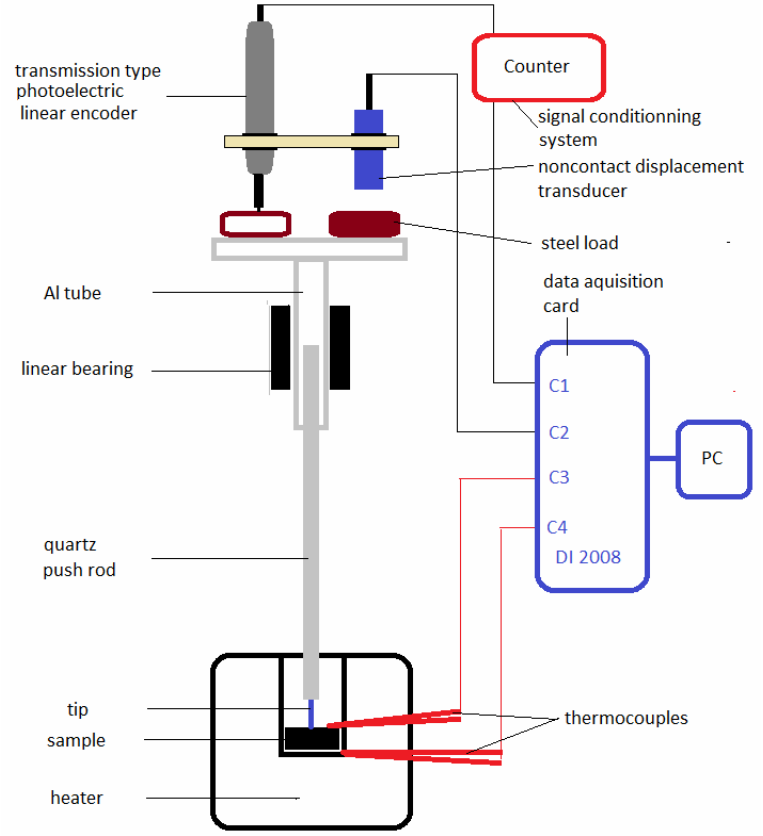


Figure 1. Block diagram of the thermomechanical analysis device

The normal pressing force, in the penetrating mode, is controlled by applying metal discs with known mass to the support disk secured to the aluminum tube. One of these metal disks (mandatory made of steel) is required as a reference element for the inductive proximity transducer.

Non-contact transducers are usually used to measure the deformation of the test samples in order to not induce additional forces into the measuring chain. Thus, an inductive proximity transducer AM1 / D2-5A with a resolution of 1 µm is used (detection range is between 0 - 6 mm and the analog signal output in the range 0-10 V, proportional to the distance between sensor and a steel block (detected object) which closes the magnetic field lines generated by the detector).

Another precision transducer (Mitutoyo LGK 0110) transmission type photoelectric linear encoder with a measuring range of 0-10 mm and selected accuracy up to 0.1 µm is used for real-time visual monitoring of the dimensional changes of the specimen. The transducer is coupled to a counter (Mitutoyo LH 101P) with the role of setting the parameters of measurement, displacement display and signal conditioning so that it is possible to use an analog output signal in the range of 2.5-4.5 V corresponding to a selectable displacement in ranges (0-200 mm, 0-2 mm or 0-20 mm).

The temperature is measured with two K-type thermocouples located in the vicinity of both ends of the specimen. The sensors position can be seen in Fig. 2 which shows the overview of the device.

The signals transmitted by the transducers are monitored and recorded by using the DI 2008 data acquisition card, produced by DataQ Instruments. The DI 2008 data acquisition instrument is a data recording module that communicate with PC through USB port.

The main features are following:

1. 8 input analog differential channels with programmable measurement ranges of (±10 mV ..... ±50 V) or thermocouple types
2. built-in cold junction compensation in case of temperature measurement with thermocouples
3. 16 bit measurement resolution.
4. free software download-able from the DataQ Instruments web site



(a) (b)

Figure 2. The handmade laboratory device (a) overall image (b) details

The data acquisition instrument it is controlled by computer software via the WinDaq Dashboard program, and for setting of data acquisition parameters it has been used the WinDaq Waveform Browser software. Files obtained from an experiment can be saved in ".csv" format and imported into Excel for graphical representations and post processing data (values of transformation points or coefficients of thermal expansion estimation).

Due to the fact that, in theory, any element in the measuring chain could be a source of measurement errors, two-step calibration tests were performed:

1. Compatibility of the signals transmitted by the two displacement transducers
2. Experimental determination of the own expansion of the measuring system

The elements - sources of error - in the measurement stages could be:

(i) the quality of the contact (between penetrator and sample, between thermocouple and sample, between the displacement transmission system and the probe of the incremental photoelectric transducer), (ii) the accuracy of the transducers, (iiiI) the accuracy of the signal conditioning systems or (iv) the accuracy of the plate data acquisition.

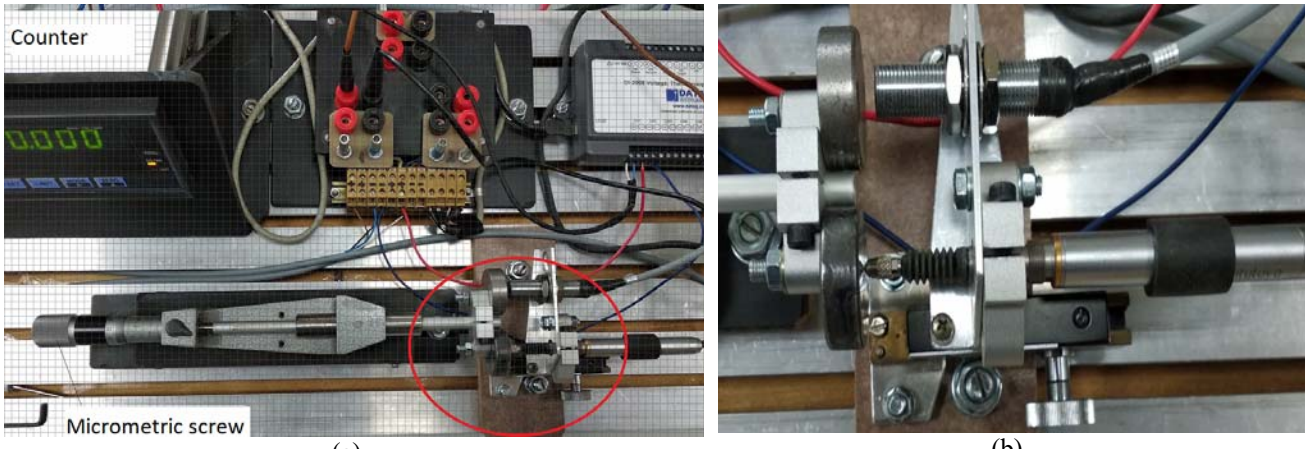
2.2. Calibration of the measuring device

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(a) (b)

Figure 3. Displacement transducers calibration: (a) overall image of the displacement transducers; (b) details.

Calibration of the displacement transducers was performed on a stand (Fig. 3) in which the displacement of the system was simulated (quartz rod support tube, weight placement disc to achieve the desired penetration force) by using a micrometric screw.

The visual output of counter, witch use signal from transmission type photoelectric encoder, has been seted to shows real values, by proper setting of counter parameters.

In case of cylindrical inductive sensor with analog output AM1/D2 -5A the data characteristic of the same displacements with both displacement transducers were recorded and a deviation from linearity was found. This slight nonlinearity is reported also by producer, as shown in Fig. 4 [5] .

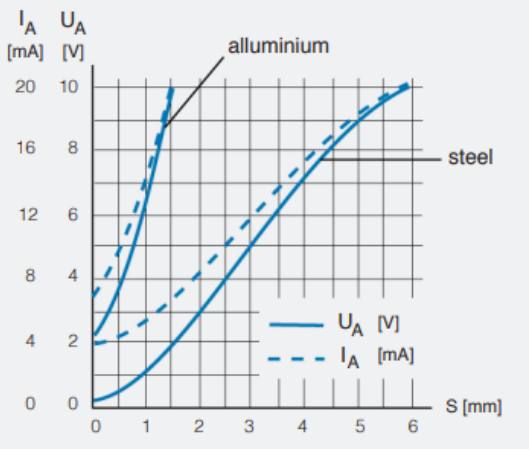


Figure 4. The output of AM1/D2 -5A as function of distance between transducer and detected object [5]

This inductive sensor with analog output AM1 / D2 -5A can be used without problems to highlight the glass transition temperature. However, due to the static operating characteristic of the transducer (this is not linear for any distance from the detected object displacement values), the measurements are inaccurate and thus, the coefficient of linear thermal expansion cannot be accurately calculated.

3. Testing of device functionality

3.1. Materials used in experiments

By using unsaturated preaccelerated thixotropic polyester resin ENYDYNE H68372 TA, which contain styrene monomer as crosslinking agent and 1,5% MEKP50 (methyl ethyl ketone peroxide) as catalyst had been made samples according to different polymerisation stages.

3.2. Experimental procedure

According to the producer prescriptions [6] , the polymerization cycle consists in maintaining 16 h at 40^0C followed by a maintenance of 2h at 90^0C. Three plates were made (Fig. 5), exposed to different polymerization conditions, shown in Table 1.

Table 1. Plate polymerization conditions

Cycle	C1	C2	C3
Polymerization conditions	T amb	16 h at 40^0C	16 h at 40^0 + 2h at 90^0C

To perform the tests, the cylindrical specimens with a diameter of 12 mm and a height of approximately 4.5 mm were cut from the plates.



Figure 5. Polymeric materials after the polymerization process

4. Experimental results

In order to test the reproducibility of the data (precision of the measuring system) were tested two specimens taken from the polymerized plate according to the C2 polymerization cycle (16 h at 40^0C) corresponding to the notations 16h S1 and 16h S2 in Fig.6.

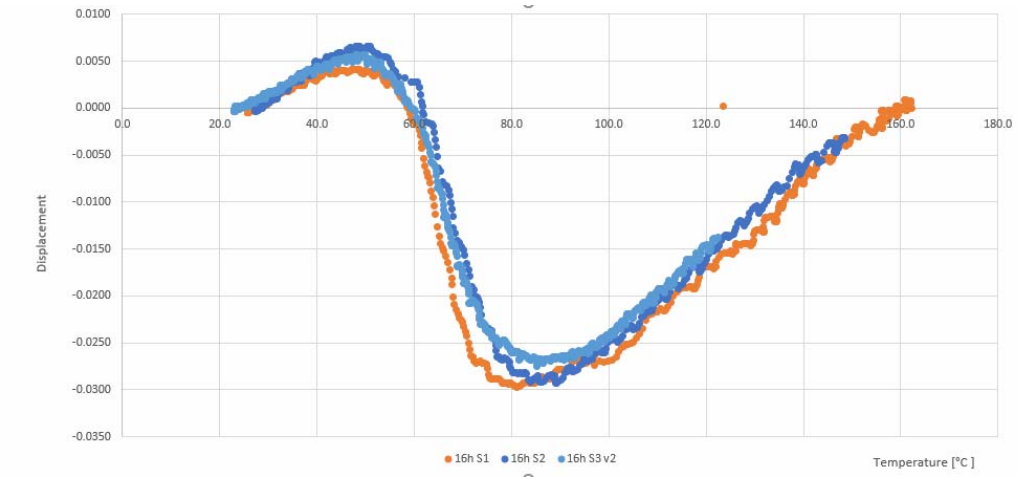


Figure 6. Reproducibility of data and influence of heating speed

The test tubes were heated to a speed of 6^0C / min and the test was performed at a load of 2000 mN. As can be seen, the differences between the two curves are very small, which could lead to the assertion that they correspond to the natural scattering of experimental data and for the whole measurement chain, reproducibility is ensured.

A preliminary test was also carried out to determine the influence of the heating rate on the test results, by testing an identical test tube (16h S3 v2), under the same loading conditions, but with a heating speed of three times lower (2^0C / min). It is observed that, except that the total penetration is slightly lower, the shape of the curve and the transformation temperatures do not appear to change.

One of the advantages of processing experimental data through Microsoft Excel is that it allows the determination of the trend lines equations. By proper selection of data series, the trend lines intersections represent the respective start and end temperatures of the transformation (Fig.7).
The average of these two temperatures resulting from the simple solution of the two systems of equations formed by Eq1 and Eq2, respectively Eq2 and Eg3, can be associated with the glass transition temperature of the polymerized material.

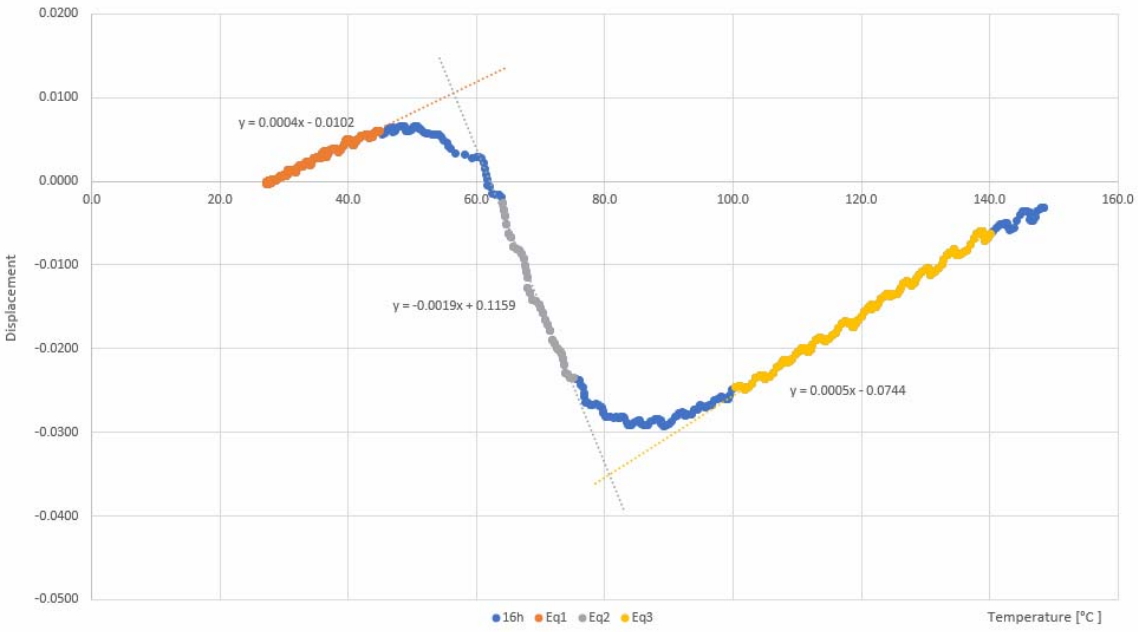


Figure 7. Determination method of the start and end temperatures of the transformation

The three relations mentioned above (Eq 1, Eq2 and Eq3) are the equations of the trend lines of the linear data series selected in Fig. 7.
Moreover, if the components (top shape , quartz rod and Al support of the quartz rod) corresponding to the proper expansion of the measuring system are extracted from the displacement-temperature dependence curve, the initial and final slope of the curve (corresponding to similar equations Eq1 and Eq3) is proportional to the coefficients of linear thermal expansion of the polymer before and after the glass transition. Assuming that the proper expansion of the measuring system is strictly directly proportional to the temperature, for ENYDYNE H68372 TA type resin, the coefficient of thermal expansion before Tg is lower than at higher temperatures Tg.
To highlight the influence of polymerization conditions on the thermomechanical characteristics, Fig.8 shows the thermomechanical analysis curves of the specimens taken from the plates according to the polymerization cycles C1 (ambient temperature Tamb, symbolization), C2 (symbolized 16h) and C3 (symbolized 16h 2h).

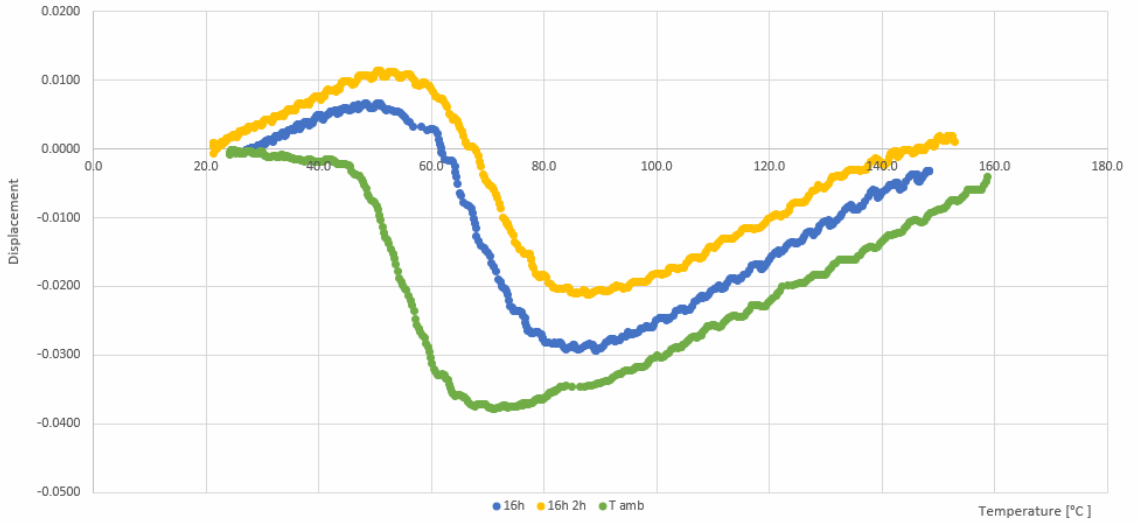


Figure 8. The curves characteristic of the three polymerization cycles

The characteristic curve of the specimen maintained at ambient temperature (Tamb in Fig. 8) shows an initial zone in which the dimensions do not increase (the initial zone of expansion preceding the glass transition does not appear). This shows that the polymerization process continues as the sample heats up, styrene is released and the size is reduced (it is known that significant shrinkage occurs when polymerizing polyester resins).
In the case of samples in which the polymerization stage is advanced, it can be seen that the glass transition temperature is higher.
The transformation takes place in the range 50-80^{0}C specified by other authors in the case of thermomechanical analysis of composite materials using as matrix unsaturated polyester resin [7].

5. Conclusions

1. The accuracy of the displacement measurement provided by the incremental photoelectric transducer (0.1µm) is sufficient to accurately lift the thermomechanical curves.
2. The measuring device ensures the reproducibility of the results
3. The variation of the heating rate does not lead to significant differences in the appearance of the thermomechanical analysis curves or to the transformation temperatures, which would lead to the conclusion that small variations in the heating rate during the experiments do not have a significant influence on the results.
4. The acquisition of data after acquisition in Microsoft Excel allows the precise determination of the start and end temperatures of transformation and implicitly the association of the glass transition temperature. Moreover, if the influence associated with the proper expansion of the measuring system is eliminated numerically, the coefficients of linear thermal expansion of the material before and after the glass transition can be determined.
5. The thermomechanical behavior of the unsaturated polyester resin in various stages of polymerization is different. Thus, the more advanced the stage of polymerization of the material, the higher the value is highlighted by the thermomechanical analysis.

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