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An isoperibolic self-made calorimeter for the measurement of redox-initiated polymerization reactions

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Abstract

An isoperibolic calorimeter for testing of medical suitable polymerizable materials was developed and constructed. The calorimeter enables in an effency way the simultaneous recording of sample temperature, evolved heat and thermal flow between sample and water bath. By this relevant parameter with the respect to practical use, like sample temperature, monomer conversion and retardation time of polymerization, are easy and exactly available.

1. INTRODUCTION

The use of polymers in medicine and dental medicine increases more and more. For dental composites e.g. dimethacrylates are used as polymer matrix. Particularly for this purpose a number of demands must be taken into consideration:

- the polymerization has to take place nearly at room temperature,
- a retardation is necessary for manipulation,
- a high degree of conversion in short time is desirable.

For the selection and the study of the used redox-initiator-systems calorimetric measurements are suitable. In this way we are able to get information on

- the temperature inside the sample,
- the total heat for the calculation of the monomer conversion,
- the retardation time and in this way information on the kinetics of the initiator system.

We found, that commercial calorimeters for watching this processes are unsuitable, particularly because of their high preparation time. Moreover they need several experiments to get all this results.

2. DESCRIPTION OF THE INSTRUMENT

For that reason we constructed a self-made calorimeter, suitable for measuring all effects in one experiment. The calorimeter is characterized by a rather simple construction

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and service and enables to measure a great number of samples in short time. The working temperature of this isoperibolic calorimeter is + 30°C. The construction of the calorimeter cell is shown in figure 1. The reacting product (6) (about 1 ml) is included in a thin glass tube within a metallic block (3), which immerses in a 100 ml water bath (1). The metallic block is fixed heat-insulated on the calorimeter cover. The temperature within the sample can be measured by a thermocouple, protected by a glass capillary. A metallic tube, which contains a platinum resistance thermometer (Pt 100) for the registration of the temperature - time - progress, is also arranged within the water bath (2). For measuring the heat exchange between the reacting system and the water bath a further resistance thermometer (4) is placed within the metallic block. If the heat generation rate in the sample is greater than the heat transmission rate, the temperature is rising /1/. The water bath is well mixed by a propeller stirrer (7). The water bath is separated from the thermostated mantle by an air slit.

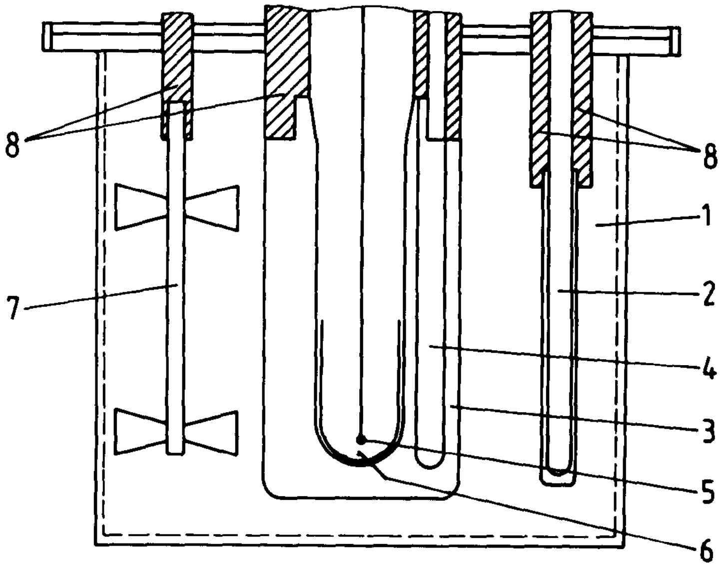

Figure 1: Measuring cell of the calorimeter
1 - water bath
2 - Pt 100 for measuring of evolved heat
3 - metallic block
4 - Pt 100 for recording the heat exchange
5 - thermocouple for recording the sample temperature
6 - reacting system in a glass tube
7 - stirrer
8 - thermo-insulating material

For testing the quality of thermal insulation we determine the "water value" of the calorimeter in dependence on time of heating with aid of a resistance combination and a quartz timer. An electric heater is arranged lateral on the metallic block (part 3 in figure 1). In five different time-steps (from 60 to 960 s) nearly the same thermal energy is developed by the heater. Table 1 shows, that no significant time-dependence of the "water value" exists. A "water value" of 612 Joule/K secures, that the temperature-increase owing to a polymerization reaction of 1 ml monomer is less than 1 K.

Table 1
Decision of the water value of the calorimeter

heating step	heating time (s)	heat evolved (Joule)	ΔT (K)	water value (Joule/K)
1	60	486,6	0,794	612,8
2	100	525,4	0,859	611,6
3	240	554,1	0,905	612,2
4	480	572,3	0,945	605,6
5	960	656,3	1,065	616,2

average value: 611,7 Joule/K
standard deviation: ± 0,63 %

The good thermal insulation of the calorimeter requires a special equipment for fast return to the starting temperature of the calorimeter system. We have solved this problem by a thermal coupling between water bath and thermostated mantle according figure 2. This coupling mechanism consists of a metallic piston in contact with the thermostated mantle. During the measurement the piston is arranged in the lower position (figure 2 above). For temperature compensation the piston is pressed to the bottom of the water bath by the help of a lever system (figure 2 below). In this way we realise a "thermal short circuit" between the measuring cell and the thermostated mantle and the time necessary for the temperature compensation decreases by a factor of 5. The effect of the coupling mechanism is shown in figure 3.

3. RESULTS

The curves obtained with the described calorimeter are shown in figure 4. In both examples TEDMA (triethylenglycol-dimethacrylate) was polymerized.

Reaction 1 was initiated by an usual redox system and reaction 2 by an initiator system consisting of the same redox

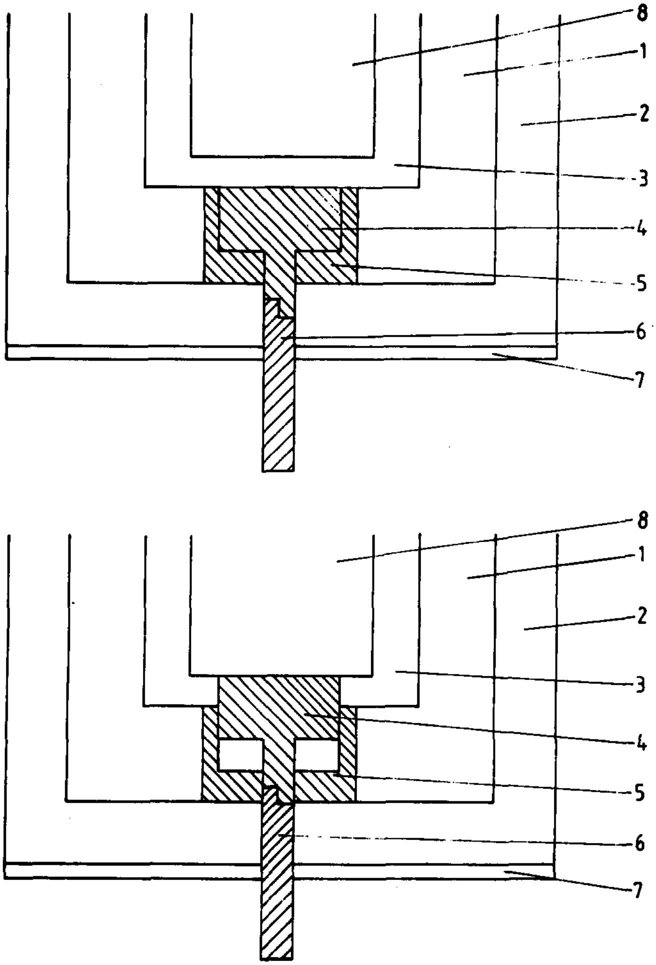

Figure 2: Thermal coupling mechanism
above: during measurement
below: during temperature compensation

1 - thermostat mantle
2 - insulating material
3 - air slit between measuring cell and thermostated mantle
4 - adjustable piston, made from a good diathermic metall
5 - metallic casing, connected with the thermostated mantle
6 - rod, made from poor diathermic material
7 - basic plate
8 - measuring cell of the calorimeter (compare figure 1)

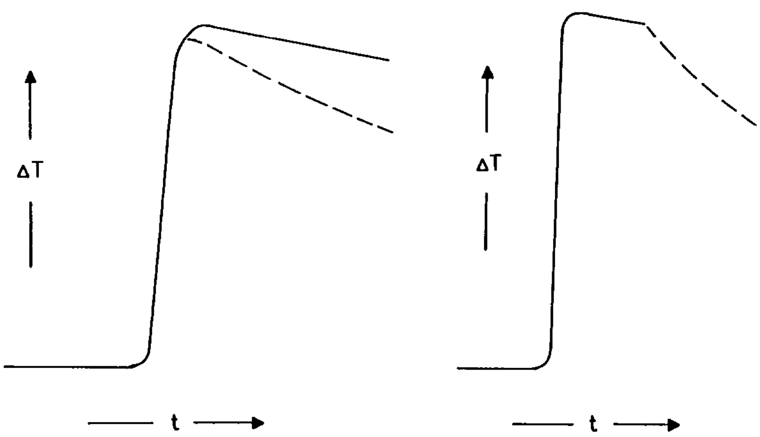

Figure 3: Influence of the coupling mechanism on the form of the cooling curves in the case of equal electric heat (marked with little lines: coupling mechanism in action).

initiator and azobis-isobutyronitrile. The smaller amount of the redox initiator in example 2 is not sufficient for a complete polymerization. The further reaction due to the effect of the azo-initiator at higher temperature is visible only in the lower curve (measuring point 4). The amount of heat calculated from the middle curves is -360 respectively -368 Joule/g. This correspond to a monomer turnover of 88 and 90 % /2/. In /2/ it was ensured by extensive measurements, that a complete polymerization of TEDMA is connected with a heat of -408 Joule/g. The desired temporal retardation of the reaction start is good visible in the lower curves.

The calorimeter is suitable to measure all effects simultaneously, which are necessary for valuation of initiators and monomers with respect to their use in medicine and dental medicine. The results are described in /3/.

The simultaneous recording of sample temperature, evolved heat and retardation time enables an efficient application of this calorimeter.

4. REFERENCES

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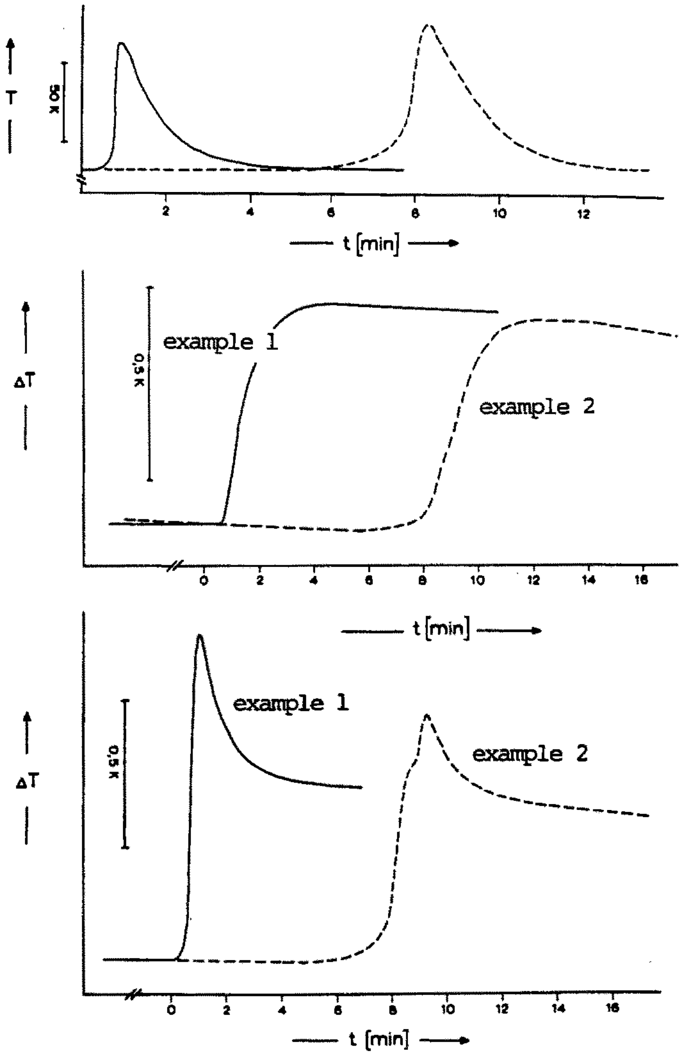

Figure 4: Curves, obtained on 3 measuring points of the calorimeter
above: Change of the sample temperature (measuring point 5, figure 1)
middle: Change of the temperatur within the calorimetric system (measuring point 2, figure 1)
below: Change of the curve concerning the heat exchange (measuring point 4, figure 1)