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INDUCTION PERIOD OF CRYSTALLIZATION OF $\text{Li}_2\text{O} - \text{SiO}_2 - n \text{TiO}_2$ GELS

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ABSTRACT: In order to evaluate thermal stability of gels against crystallization, a new criterion based on the length of induction period of crystallization is suggested. It is discussed that the end of the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts. Four gels in system $\text{Li}_2\text{O} - 2 \text{SiO}_2 - n \text{TiO}_2$ ($n = 0.00; 0.03; 0.062$ and 0.1) were prepared and the validity of the criterion was tested by applying it to these gels. Was obtained thermal stability decrease with amount of TiO_2 in gels.

KEY WORDS: induction period, gels, DTA

1. THEORETICAL ANALYSIS

For any mechanism, the rate of a process can be described by the general rate equation [1]

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where α is the conversion of the process and $f(\alpha)$ is the conversion function. Temperature's dependence on the rate constant k is usually expressed by the Arrhenius equation

$$k = A_k \exp\left[-\frac{E_a}{RT}\right] \quad (2)$$

where A_k is the preexponential factor, E_a is the activation energy, T is absolute temperature and R stands for the gas constant.

Since Eq. (1) is general, we assume that it also describes kinetics of the processes occurring during the induction period. Existence of these processes is not detected by the experimental technique used; however, they have to take place as a preparatory stage preceding the main process. Combination of Eqs. (1) and (2), after the separation of variables, gives following result:

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i} A_k \exp\left[-\frac{E_a}{RT}\right] dt \quad (3)$$

The conversion α_i in Eq.(3) is the conversion of the processes occurring during the induction period and corresponding to the end of the induction period, i.e., to the start of the main process detected by the apparatus, and t_i is the length of the induction period. It is further assumed, that the conversion α_i is the same for any temperature. Then, after integration of the left side of Eq. (3) one can get:

$$F(\alpha_i) - F(0) = \int_0^{t_i} A_k \exp\left[-\frac{E_a}{RT}\right] dt \quad (4)$$

Since conversion α_i , which corresponds to the end of the induction period is assumed to be independent of temperature, the value of the integrated function $F(\alpha)$ at the point α_i , $F(\alpha_i)$, is also constant. Therefore, Eq.(4) can be rewritten as:

$$1 = \int_0^{t_i} \frac{d t}{A \exp \left[\frac{B}{T} \right]} \quad (5)$$

where the constants A and B are given as:

$$A = \frac{A}{F(\alpha_i) - F(0)} \quad (6)$$

$$B = E/R$$

Physical meaning of the denominator in Eq. (5) can be simply demonstrated for a special case of isothermal processes, where denominator is a constant equal to the induction period at the given temperature. Thus, the temperature's dependence on the induction period can be expressed as

$$t_i = A \exp \left[\frac{B}{T} \right] \quad (7)$$

For linear increase of temperature in DSC measurements, the furnace's temperature can be expressed as

$$T_F = T_0 + \beta t \quad (8)$$

where T_F is the furnace temperature, T_0 is the starting temperature of the measurement and β stands for the heating rate. If one assumes that the temperature of the sample equals to that of a furnace, combination of Eqs. (5) and (8) gives the result [2]

$$\beta = \int_0^{T_x} \frac{dT}{A \exp \left[\frac{B}{T} \right]} \quad (9)$$

where T_x is the temperature of the end of induction period, i.e. the onset temperature of the crystallization peak. Starting temperature in Eq. (9) is set as $T = 0$ K, since the rate of the process at the starting temperature is negligible. When deriving Eqs. (3) and (4), the assumption is implied, that the conversion function $f(\alpha)$ holds during the induction period. That means that no change of the mechanism occurs. As Eq. (9) indicates, when increasing the rate of heating, the onset temperature also increases.

2. EXPERIMENT

2.1 Preparation of gels

For silica acid sols' preparation, the solution of sodium silicate prepared for 2 hours in boiling flask by 120 °C by the reaction of SiO_2 with the solution of NaOH; ratio of $\text{Na}_2\text{O} : \text{SiO}_2$ was 1 : 3, SiO_2 content in the solution was ~25 wt. %. For the preparation of silica acid sol this solution was diluted to about 9 wt. % SiO_2 .

Pure silica acid sol was prepared by ion's exchange by the use of an acid ionoexchanger Amberlite. After the transition of solution through the ionoexchanger layer, substitution of sodium ions by hydrogen ions was reached. LiCl and TiOSO_4 were added to silica acid sol. TiOSO_4 was prepared by the reaction of TiO_2 and H_2SO_4 . Prepared samples were dried in the drier at the temperature of 120 °C for the duration of 4 hours. Gels prepared in this way were dried and burned, respectively, from laboratory temperature to 200 °C (heating rate 1°C/min) and from 200-900 °C (heating rate 1 °C/min), for 2 hours. Samples were thereafter burned in a platinum crucible at 1400 °C for 2 hours.

3. RESULTS AND DISCUSSION

Typical curves of $\text{Li}_2\text{O} - 2\text{SiO}_2 - n\text{TiO}_2$ gels at the heating rate of $10^\circ\text{C}/\text{min}$ are shown in Fig. 1. Onset temperature, T_X , and the maximum peak temperature, T_p , were directly determined from DTA curves. Inflection point temperature, T_i , was determined from the maximum peak temperature on DDTA curves [3,4]. As shown in Fig. 1, as the crystallization proceeds, an exothermic peak is observed since the crystallization is accompanied by a rapid heat evolution. Crystallization occurs in several stages. The point of the steep increase of DTA record due to crystallization is taken as the onset temperature.

Parameters A and B in Eq. (9) have been obtained by minimizing the sum of squares between experimental and theoretical values of the onset temperature T_X for various heating rates by simplex method. Theoretical values of onset temperature are given by Eq. (9). Integration indicated in Eq. (9) has been carried out by Simpson's method. Standard deviations of A and B were calculated by assuming a quadratic surface near the minimum. The agreement between experimental and calculated values of onset temperatures for various heating rates is shown in Fig. 2. The resulting values of A and B are listed in Tab. 1. It can be seen from Tab. 1 that the adjustable parameter B is approximately constant for the gel samples under study. Difference in the stabilities can be accounted for by the difference in the values of parameter A . Since the onset temperature is determined as a point of the steep increase of DTA record due to crystallization, the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts.

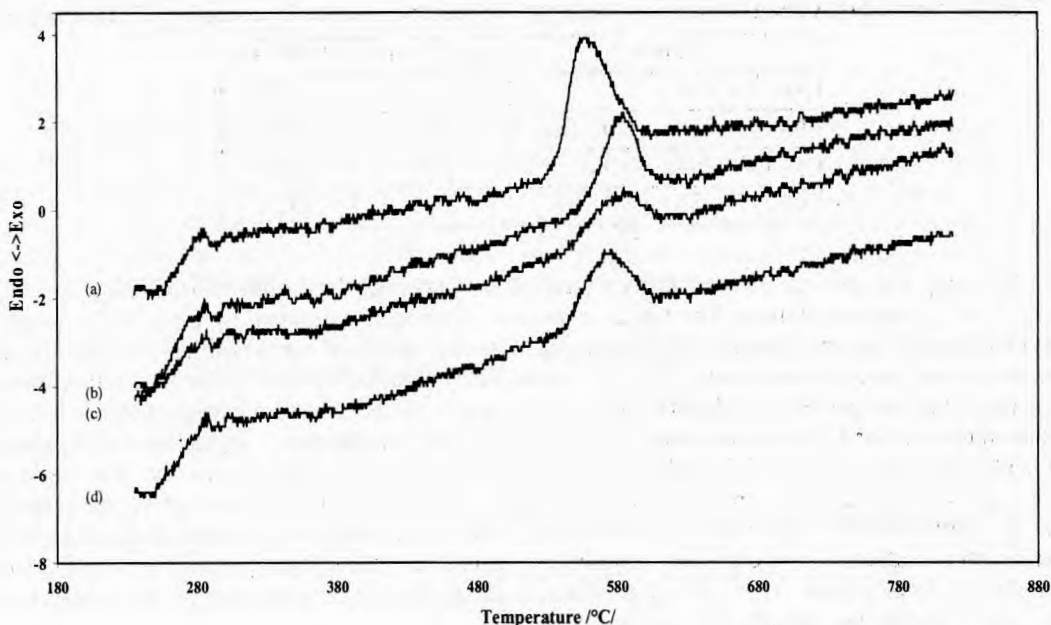


Fig.1: DTA curves of $\text{Li}_2\text{O} - \text{SiO}_2$ (a), $\text{Li}_2\text{O} - \text{SiO}_2 - 0.03 \text{TiO}_2$ (b), $\text{Li}_2\text{O} - \text{SiO}_2 - 0.062 \text{TiO}_2$ (c), $\text{Li}_2\text{O} - \text{SiO}_2 - 0.1 \text{TiO}_2$ (d) gels samples at the heating rate $10^\circ\text{C}/\text{min}$

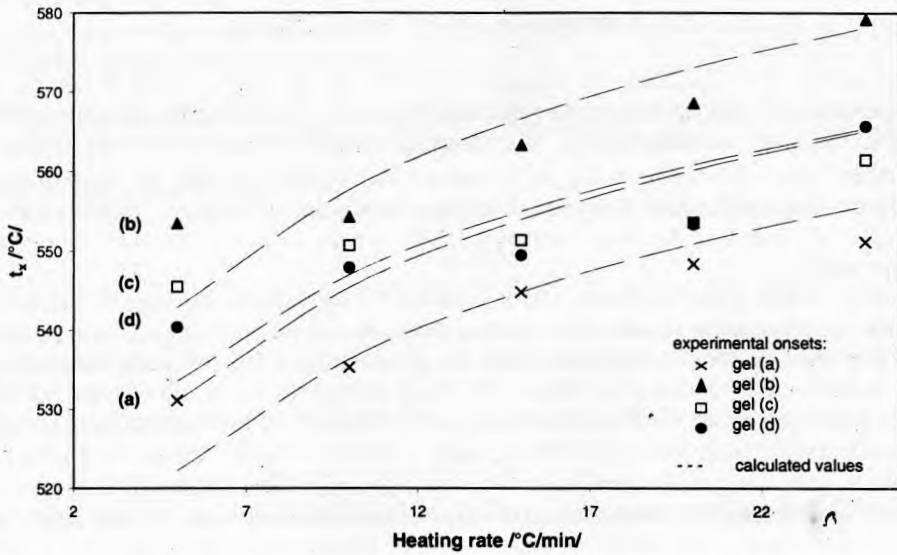


Fig. 2: Experimental and calculated values of onset temperatures of gel crystallization for various heating rates

Tab. 1: Parameters A and B describing the length of induction period by using Eq. (7) for the gels

Sample	A / 10^{-16} min/	B / 10^{-3} K/
a) $\text{Li}_2\text{O} - 2\text{SiO}_2$	1.65	30.00
b) $\text{Li}_2\text{O} - 2\text{SiO}_2 - 0.03 \text{TiO}_2$	4.41	30.03
c) $\text{Li}_2\text{O} - 2\text{SiO}_2 - 0.062 \text{TiO}_2$	0.11	32.56
d) $\text{Li}_2\text{O} - 2\text{SiO}_2 - 0.1 \text{TiO}_2$	1.77	30.29

By using the new criterion, stability of gels is evaluated as the length of isothermal induction period for a given temperature. The length of induction period is calculated by Eq. (7). The range of temperatures for the calculation of the lengths of induction period of crystallization was chosen from interval where have the onset temperatures of crystallization been observed. Hence, it can be expected that the values of calculated induction periods are quite realistic, since no extrapolation outside the temperature region of the measurement has been carried out. Temperature's dependence of the lengths of isothermal induction period for individual gels is shown in Fig. 3. It can be seen, that the stability of gels against crystallization is in the temperature region of 530 - 620 °C and it is in the order $a < d < c < b$, i.e., the thermal stability gels against crystallization with TiO_2 decrease. Eq. (5) enables us to calculate the length of induction period for any temperature regime and, thus, to evaluate the order of thermal stabilities for that regime. The order of stabilities evaluated by the new criterion is in agreement with the order based on the characteristic temperatures.

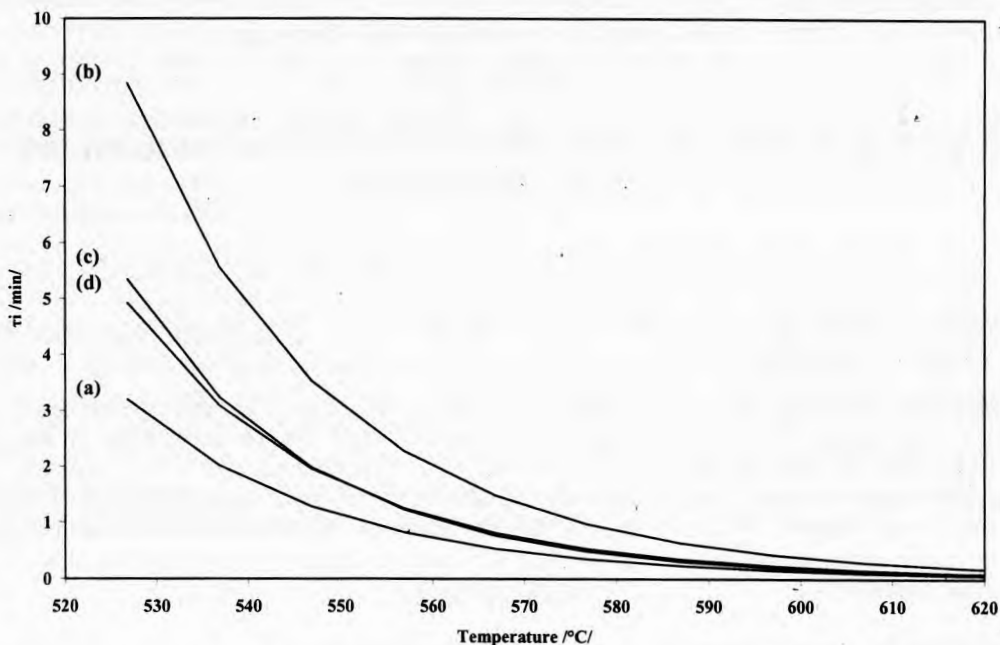


Fig. 3: Induction period of crystallization for individual gels samples calculated by Eq. (7)

4. CONCLUSIONS

The length of isothermal induction period of crystallization is suggested as a new criterion for evaluation of the thermal stability of gels. Lengths of induction periods are calculated by using Eq. (7), where are parameters A and B obtained from the treatment of the dependence of onset temperature of the crystallization peak on the heating rate in the nonisothermal DTA measurements. For a set of gels, the order of stabilities obtained by the new method coincides with the order determined by stability criteria based on the characteristic temperatures.

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