Mechanochemical Activation of Mixtures for Low-Melting Glasses Production
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Mechanochemical Activation of Mixtures for Low-Melting Glasses Production

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Abstract

Mechanochemical activation in high-energy devices (micronizers) as a way of giving mechanical energy to solid-state materials has become very popular. During the mechanochemical activation various structural changes of material and at the same time changes of its properties (chemical, electrical, thermal, mechanical etc.), as well as reactivity increase are taking place. Whereas numerous chemical reactions are happening during the glass production, investigating of the influence of previous mechanochemical treatment on those reactions and on the glass production at once is very attractive. Because of the great interest for low-melting glasses, PbO-B_2O_3-SiO_2 system, with following chemical composition: 40 mol% (69,4 wt%) of PbO, 34 % (18,4 wt%) of B_2O_3 and 26 mol % (12,2 wt%) of SiO_2 was chosen for investigation in this research. In the experimental work, minium (Pb_3O_4), boric acid (H_3BO_3) and quartz sand (SiO_2) were used as raw materials for preparation of glass mixtures. Five glass mixtures were prepared. Mechanochemical activation was a realized in high-energy vibro mill with rings. Following times of mechanical activation were used: 7 min., 14 min., 28 min., and 49 min. The referent, non-activated glass mixture and four mechanochemically activated glass mixtures were subjected to differential thermal analysis (DTA). Applied method for the quantification of mechanochemical activation results showed that the effects of mechanochemical activation on the properties of glass mixtures for obtaining low-melting glasses were considerable. Mechanochemical activation had a significant influence on temperature changes in the investigated system, during heating. Differential thermal analysis showed the existence of qualitative changes in thermal properties of prepared glass mixtures depending on the time period.

Keywords: mechanochemical activation, low-melting glass, DTA

1. Introduction

Material activation as a process for introduction of additional energy to the system applies worldwide. Mechanical activation in high-energy devices (micronizers) that is used for introduction of mechanical energy to the solid-state material becomes more and more actual. During the treatment, various structural changes of the material are taking place. These structural changes of the material cause its properties changes (chemical, electrical, thermal, mechanical, etc.) as well as its reactivity improvement. Former researches show that the various compounds could be synthesized by mechanochemical activation, that is solid-state reactions are carried out in this way.
Since during the glass melting particular chemical reactions are taking place, it is very important to investigate influence of previous mechanical treatment of glass mixtures on the reactions development as well as on the conditions of glass obtaining.
According to previous researches, mechanically treated materials are more reactive and they roughly, sometimes explosively, react with other materials, their melting temperatures are lower and they give products of higher quality by sintering.
With regard to the fact that the high temperature is the main problem in glass production and considering the mentioned researches, the idea in this work was to enable better utilisation of energy necessary for obtaining glass by previous mechanical activation.
Because of the great importance of low-melting glasses, just because of its low production temperature, three-component PbO-B_2O_3-SiO_2-system was chosen for investigation.
The correct choice of methods for possible effects quantification is required in analyzing of mechanochemical effects of mixtures for glass production. The idea was to analyze mechanochemical activation macro effects. Differential thermal analysis (DTA), as an indirect method that doesn't offer mechanisms of changes in the system, but the effects noticeable on macro level was applied. It means that those effects were considered by changes of thermal properties of activated mixtures.

2. Experimental

Five glass mixtures of the same composition were investigated in this research. On the basis of previous results, the glass with the composition shown in the Table 1 was chosen.

Table 1. Composition of glass mixtures

Component	Content (mol %)	Content (mas %)
PbO	40	69,4
B_2O_3	34	18,4
SiO_2	26	12,2

In a vitrification ability diagram for the system PbO-B_2O_3-SiO_2, this glass is in the range of transparent glass.

Minium, boric acid and quartz sand were used as raw materials for the preparation of glass mixtures with the particular composition.
Five glass mixtures of defined composition were prepared. The referent glass mixture was not mechanochemically activated. Other four glass mixtures were mechanochemically activated. Four time periods of activation were selected: 7min, 14min, 28min and 49min.
Mechanical activation of prepared glass mixtures was performed in the high-energy vibro mill with the torsion spring and ring working elements, produced by KHD Humboldt Wedag A.G., Germany, and type MH 954/3. Mechanism with the elastic shaft, off-center flywheel and torsion springs is placed in the operating part of mill. It converts uniform rotations of electromotor with the power of 0,8 kW into the vibrations that are directly transferred on the working vessel of mill (mechanochemical activator). The main part of mill consists of specially constructed bearing and closing device of horizontally placed working vessel of mill. The vessel is made of stainless steel. It is in the shape of cylinder with the internal diameter of 17 cm and the depth of 4 cm. The cover of the mill is also made of stainless steel, with particular dimensions. It is lined around the rim with felt seal. Two concentric stainless steel rings with the total weight of 3 kg are placed in the working vessel. They occupy one third of mechanochemical activator working volume.
According to the properties of mechanochemical activator, the most reliable results in regard to the reproducibility were obtained when the total weight of treated substance was in the range of 50 and 150 g. On that basis it was decided to use 80 g of the substance, which should be activated.
Glass mixtures, the referent, non- activated one and four mechanochemically activated, were subjected to differential thermal analysis (DTA).
Differential thermal investigations of glass mixtures were made by apparatus type SHIMADZU-DTA 50. The analysis were done on further conditions:
-temperature range of measurement- from room temperature to 1100°C ;
-heating rate of 20°C/min;
-nitrogen atmosphere;
-Pt- crucible for samples.

3. Results and discussion

Differential thermal curves of investigated mixtures are presented in the Figure 1.

It is obvious that two groups of those curves can be distinguished. DTA curves of mixtures activated for 7 and 14 min minimally vary from DTA curve of the referent, non-activated mixture and they belong to the first group of curves. DTA curves of mixtures activated for 28 and 49 min belong to the second group of curves and they indicate qualitative and quantitative deviation from DTA curve of the referent, non-activated mixture.

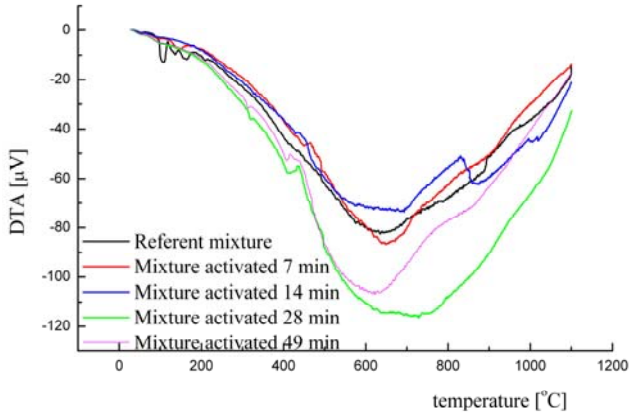
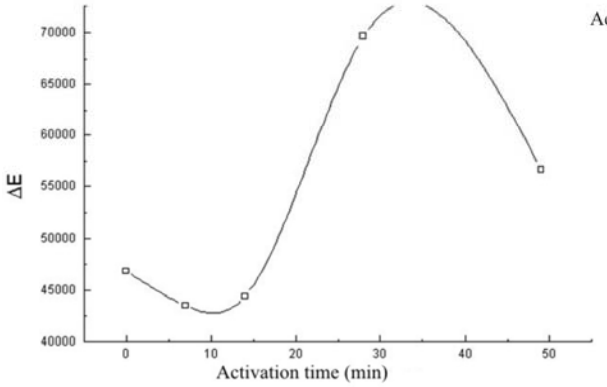


Figure 1: Differential thermal curves of referent and activated mixtures

The mechanochemical activation effects on behaviour of the mixtures during heating were analysed through total accumulated energy of the activated mixtures in relation to the referent mixture (Figure 2). The content of energy accumulated in mixture was obtained by calculation of differential thermal curve area.
Differential thermal curve area of the referent mixture i.e. its accumulated energy was defined as unit and accumulated energies of the other mixtures were compared with it (legend in Figure 2).



Activation time (min)	Energy
0	1
7	0.93
14	0.95
28	1.49
49	1.21

Figure 2: Thermal transformation energy change depending on activation time

According to this analysis, it is obvious that the mixture activated for 7min accumulates cca 8% of energy less than the referent mixture, during heating, while the mixture activated for 14 min accumulates cca 5% of energy less than the referent mixture. From engineering point of view, it can be considered that mixtures activated for 7 and 14 min act approximately like the referent mixture (differential thermal curves comparable!) and thereby activation time of 14 min doesn't induce remarkable changes in the system.
The mixture activated for 28 min accumulates almost 50% of energy more than the referent mixture, during heating. That means that during the activation period from 14 to 28 min the most significant changes are happening. The mixture activated for 49 min accumulates only 20% of energy more than the referent mixture, during heating.

Therefore, the activation after 28 min, doesn't produce any noticeable quality of the mixture, so the mixture modifies and returns to the initial state.
Analysing of DTA curves minimum variation of the activated mixtures compared to the referent mixture leads to the similar results (Figure 3).

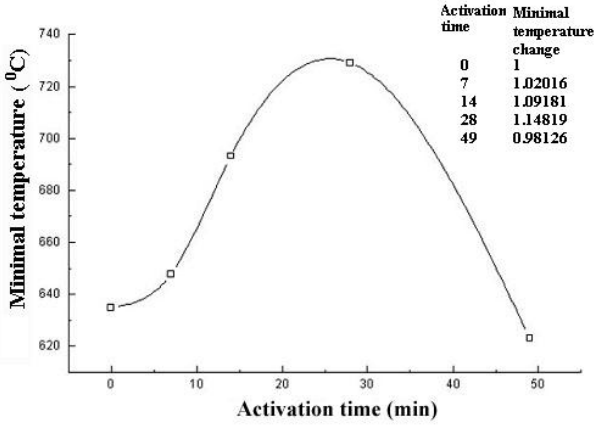


Figure 3: Variation of thermal transformation minimal temperature depending on activation time

Results of comparison of the referent and the activated mixtures are shown in the legend in Figure 3.
It can be concluded that relatively slight variations of DTA curves minimum (2% and 9% respectively) are present for the mixtures activated for 7min and 14min, while the variation for the mixture activated for 28min is almost 15%.
These temperature variations for three mentioned mixtures are positive, i.e. minimal temperatures are ”moving” towards higher numerical values. The temperature variation of the mixture activated for 49min is approximately 2% but negatively, i.e. towards lower temperatures and almost 17% towards lower values comparing to the mixture activated for 28min which is more important.
Those results signify that the greatest changes in system, meaning the greatest mechanochemical effects on thermal sensitivity of mixture are taking place for the activation period of 28min. Further changes are happening for the activation period between 28min and 49min, whereby the macro effect of the changes shows apparent ”return” of the system closer to the starting position.

4. Conclusion

The mechanochemical activation effects on properties of mixtures for low- melting glass production i.e. on temperature changes in the investigated system during heating are significant. The method chosen for quantification of those effects, differential thermal analysis was sensitive and reproductive enough to indicate the existence of corresponding effects.
It can be concluded that mechanochemical activation provides better utilization of thermal energy necessary for glass forming, whereby a small amount of this energy is

spent on melt formation. So the main effect of activation is reducing of energy necessary for melt formation, i.e. for viscosity change of the system.
Presented analyses point out that activation period of 28min has the greatest effect on the investigated mixtures. Activation after 28min also brings important transformations in the system and approaching to non-activated state, which looks like degradation of the quality obtained for the activation period of 28min.
It means that the amount of energy necessary for maximal ”moving” of the system from its initial state is defined and further energy introducing has the opposite effect on the system.

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