

# Determination of Phase Transition Temperatures of Polymer Binding Agents by Differential Scanning Calorimetry

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**Abstract**—A method for determination of phase transition temperatures for binding agents on a differential scanning calorimeter is considered. Differential scanning calorimetry (DSC) curves of different types of polymer binding agents that are used in production of items from fiber-glass and carbon-fiber plastics are presented. It is shown how to determine the optimal curing regimes using the resulting DSC curves. By the example of epoxy polymer binding agents, the effect of disperse fillers on polymerization process kinetics is demonstrated.

**Keywords:** differential scanning calorimeter, polymer binding agent, phase transition, glass transition point

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Differential scanning calorimetry (DSC) is widely used to develop curing modes for polymer binding agents and study their properties. This method, as are differential thermal analysis (DTA), thermogravimetric analysis (TGA), and so on, is a thermoanalytical method that allows one to determine the change in any parameter depending on heating temperature and rate. In its shape, a DSC curve is similar to a DTA curve, but the accuracy of determination of phase transition temperatures in DSC is essentially higher, which, in the end, has led to actual displacement of DTA in investigations of polymer binding agents [1, 2].

The word “differential” in the names of the DTA and DSC methods means that during investigation of materials by these two methods, a difference in the properties of a sample and reference is measured.

The heating regimes can be set up depending on a particular problem: thus, for example, heating (cooling) can be carried out at a constant rate, the given time range can be held at a constant temperature, temperature can be changed in the cyclic manner with differing amplitude and frequency, and any combinations of these regimes can be used.

The goal of the present study is to determine phase transition temperatures of polymer binding agents depending on the heating process kinetics.

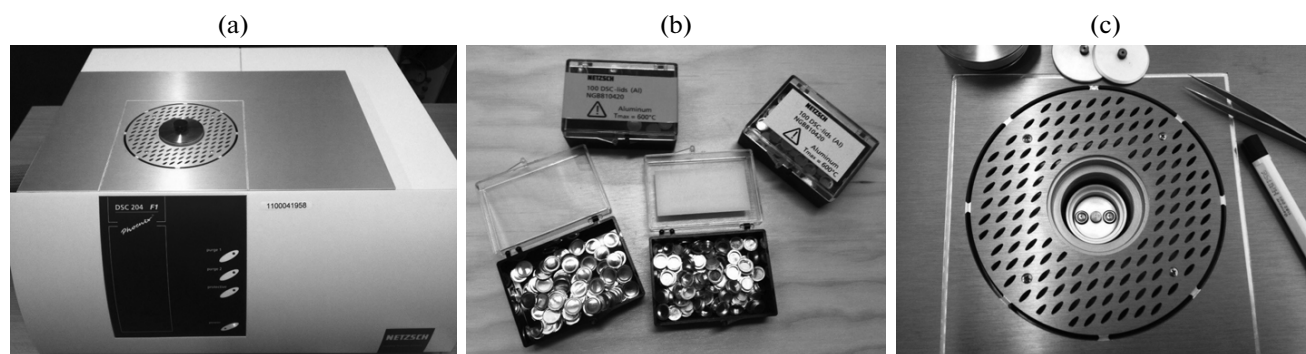
Phase transitions (or phase transformations) are transitions of a material from one thermodynamic phase to another. It is a peculiarity of curing processes of thermosetting polymer binding agents (epoxy, phe-

nol-formaldehyde, etc.) that there is a sequential transition from one aggregate state into another, i.e., from liquid into gel-like and solid, and each change in the aggregate state is characterized by a particular phase transition.

Knowledge of phase transition temperatures is of great practical importance [3–5]; for example, in development of new compositions of polymer binding agents, it allows one to determine the optimal curing regimes. Knowledge of the kinetics of temperature variation of phase transitions allows one to determine the degree of polymerization of a binding agent. The change in the temperature of phase transitions is used to quantitatively determine the effect of one or another component (e.g., solvent, plasticizer) on the operational properties. One of the most important operational characteristics of a composite material is the glass transition point, since it determines the upper, maximum allowed range of working temperatures, and the DSC method allows its most precise determination.

A DSC 204 F1 Phoenix differential scanning calorimeter (Fig. 1a) was used in the present study to carry out investigations. Despite the fact that this unit allows controlling the temperature in the range of from  $-80$  to  $+600^{\circ}\text{C}$ , all the studied polymer binding agents were not heated above  $250^{\circ}\text{C}$ , since the main phase transition temperatures lie precisely in this interval, which greatly reduced the investigation time.

The principle of operation of DSC units is based on measurement of the difference of heat flows of the



**Fig. 1.** Photographs of (a) a DSC 204 F1 scanning calorimeter, (b) crucibles, and (c) a measuring cell.

materials under study and the reference. The reference was an empty crucible that allowed one to avoid the appearance of processes connected with heat release and absorption. A reference sample with well-known characteristics can also be placed into the crucible. However, in any case, it is necessary to measure a base line for the result accuracy; therefore, for the sake of simplicity, the empty crucible is chosen as a reference in which no exo- or endothermal processes occur.

The rate of heat flow in the sample and that in the reference are registered as functions of temperature using a symmetrical (double) measuring system. The measured values are the absolute temperature of the sample and the temperature difference that arises between the reference and sample and is proportional to the difference of heat flows between them. This allows one to quantitatively determine the thermal effects.

Prior to investigations, unit calibration is performed, which consists in the determination of the sensitivity index.

In the following step, the sample under study is weighed. The weight of the material being investigated is restricted by the crucible volume and can vary depending on the problem that has been set. For the unit in use, this change can lie in the range of 4–35 mg. The higher the sample weight, the more intense the signal detected by the calorimeter and, correspondingly, the lower the error introduced by external factors. However, as the weight drops, the accuracy in determination of released heat and, consequently, the accuracy in determination of phase transition temperatures increase, whereas, at the higher substance quantity, an essential difference in temperatures appears in dependence on its volume.

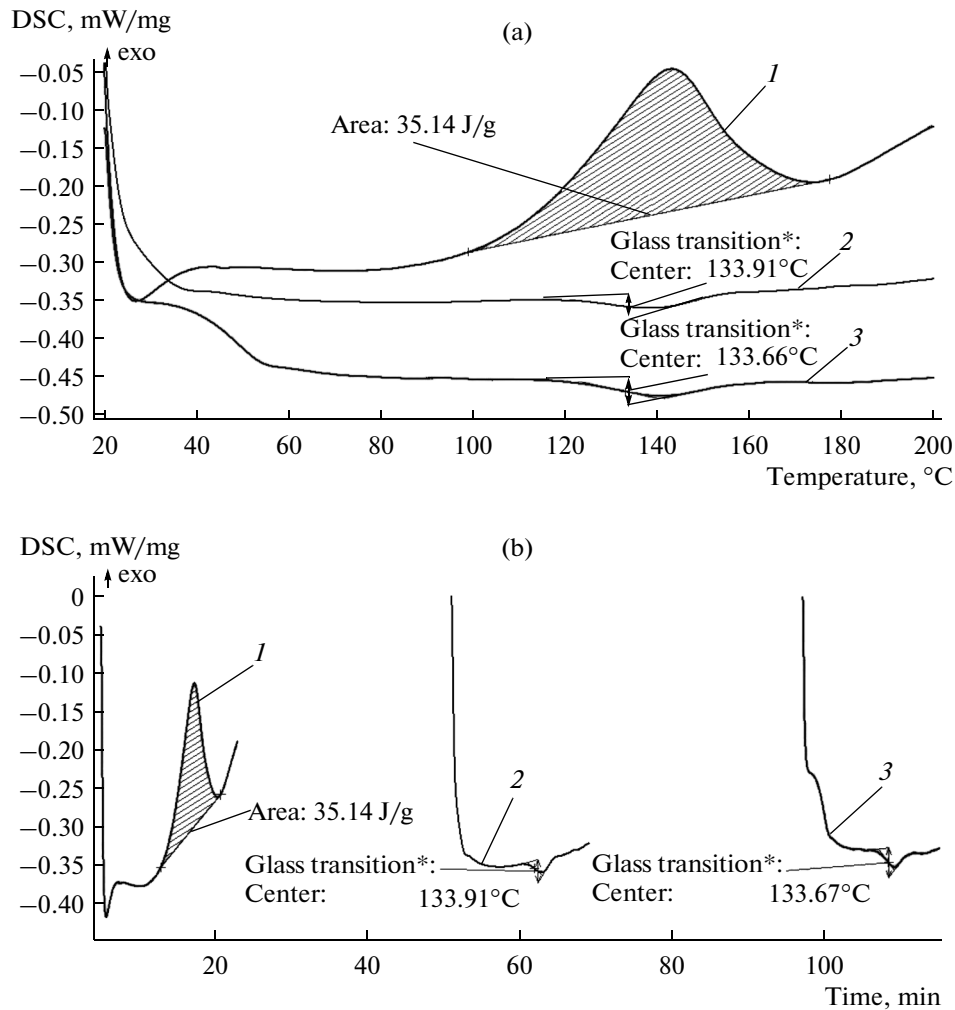
To obtain comparable results, all investigations with different types of polymer binding agents were carried out at a sample weight of 15 mg. Subsequently, the weighed sample was closed with a cover that was pressed using a special device. At this stage, particular

attention should be drawn to the quality of mutual disposition of the crucible surfaces after pressing. If they have distortions, it will lead to a reduction in the thermal contact between the heat flow sensor and sample, which will increase the measurement accuracy.

After pressing, a small hole is made in the crucible cover, the main purpose of which is to avoid deformation and crucible degradation due to the enhanced internal pressure that can occur upon the release of a great amount of volatile products during curing. A crucible prepared in this manner was placed into a measuring cell along with the reference (Figs. 1b, 1c).

The rate of the heating process has a strong effect on the DSC results. The unit allows one to change it from 0 to 100 K/min. High rates of heating give rise to a delay in heating of unit parts and sample, since heat is not transferred intermediately. For example, upon rapid heating, the sample can melt before it is decomposed, but, at low rates, the substance decomposes before melting. Therefore, the samples must be heated at low rates for the system to be close to equilibrium. In addition, at low heating rates, a DSC signal can be obtained on which the processes occurring in the substance are clearly defined; the lower the rate, the more clearly they are distinguished. In contrast, at high heating rates, some processes can combine and it would be impossible to determine the characteristic temperatures of these phenomena (for example, the combination of two peaks with similar temperatures). However, it should be noted that separation of processes is not always necessary and, in many cases, to save time, an optimal heating rate of 10 K/min can be chosen.

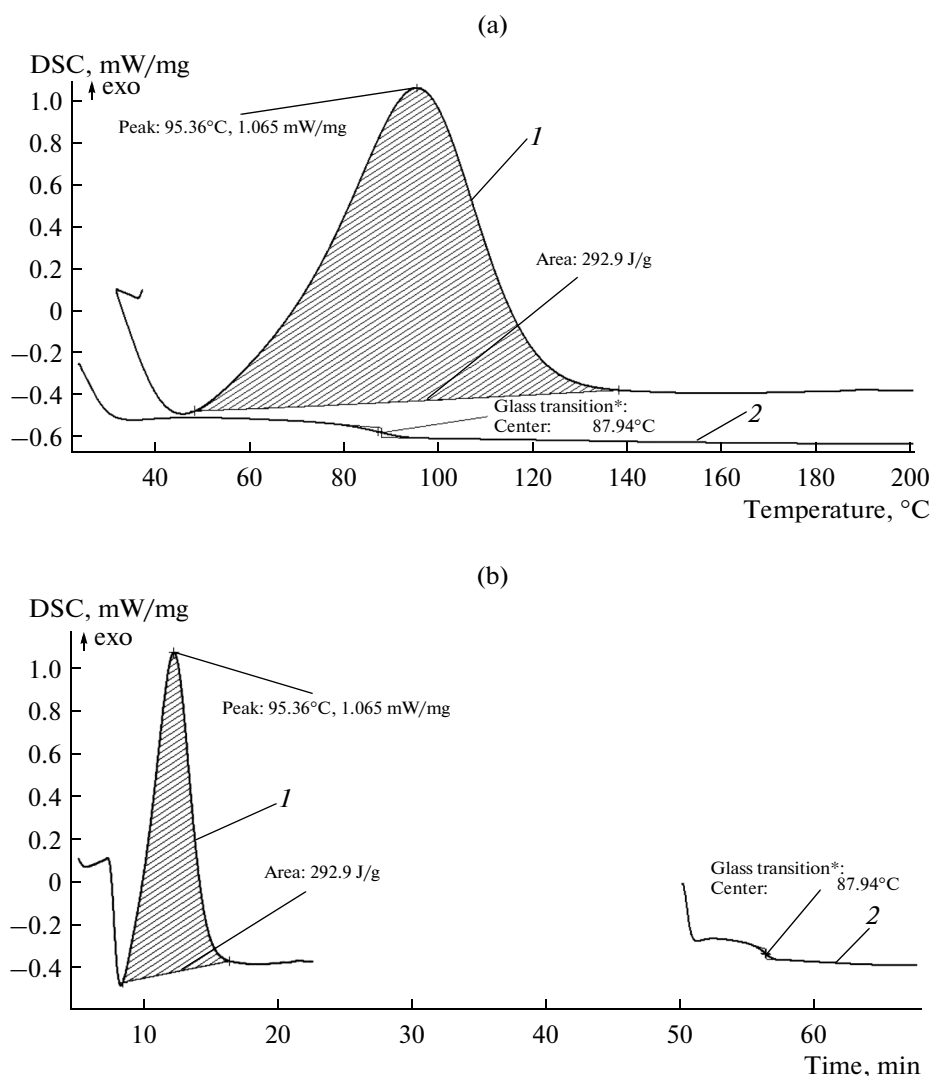
Figure 2 shows DSC curves obtained for an epoxy-furan binding agent [6] upon its heating with the constant rate of 10 K/min from 20 to 200°C. Curve 1 was obtained for the initial composition of the binding agent, which, upon curing at elevated temperature, transforms from the liquid aggregate state into the solid one. This transition is accompanied by a high



**Fig. 2.** DSC curves for epoxy-furan binding agent upon (1) first, (2) second, and (3) third heatings depending on (a) temperature and (b) time [6].

exothermal effect that is caused by the peak area and comes to 35.14 J/g. The exothermal peak lies in the temperature range of from 95–100 to 175–180°C with a maximum at 135°C. The presence of the maximum on this curve testifies to the fact that it is at this temperature that the reaction occurs at the greatest rate and, therefore, must be taken as the temperature of the curing process. However, it is impossible to accurately determine the duration of the curing process by this DSC curve alone. Nevertheless, if the rate of heating (10 K/min) and the temperature range of the exothermal peak (from 95–100 to 175–180°C) are known, it can be assumed that curing of this binding agent requires about 8 min. Moreover, the unit program package allows one to determine the dependence of the DSC signal on time, from which it is obvious that the exothermal effect starts at 13–14 min and ends at 22–23 min. Hence, it can be stated without reservation that the process takes 8 min.

Curves 2 and 3 (see Fig. 2) were obtained for the same binding agent, but the initial state of this material differs from that upon the initial heating, since the first heating caused it to be cured. These DSC curves allow one to determine the glass transition point the magnitude of which is taken to be equal to the bending point, which has a value of 133.91°C upon the second heating and 133.6°C upon the third heating. As a rule, the glass transition point upon the third heating is always lower than that upon the second, since there are post-curing processes; however, this value can slightly veer toward both higher and lower values, as has been shown in the present study. For the binding agent being considered, the glass transition point upon the second and third heating has only an insignificant difference of 0.3 K, which can be neglected. Nevertheless, we believe that the third heating allows for more precise determination of the glass transition point.



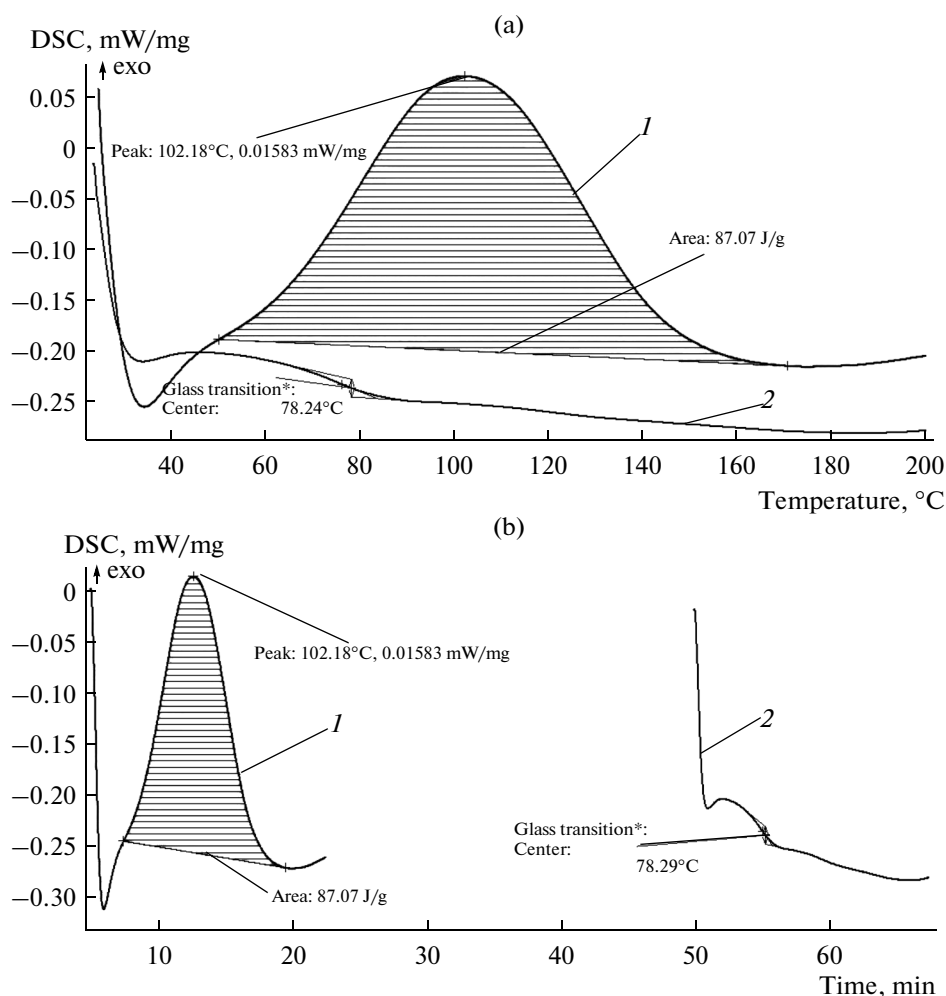
**Fig. 3.** DSC curves for (1) initial and (2) cured epoxy binding agent containing 20 wt % of shungite depending on (a) temperature and (b) time [7].

Analogous results have been presented in paper [7], the authors of which studied the DSC curves for an epoxy binding agent that included a disperse filler on the same calorimeter (Figs. 3 and 4). These polymer materials have found application as repair compositions for removal of defects of heat-loaded elements of machines and equipment [8].

Curve 1 (Figs. 3a and 4a) was obtained for the initial binding agent which during heating was cured, curve 2 (Figs. 3a and 4a) was obtained for the already cured one. The first heating allows one to determine the optimal curing temperature, while the second one permits finding the glass transition point. Fragments of the curves with endothermic peaks equal to the amount of heat released during curing and the fragments of the DSC curves that show the values of glass

transition points are shown in Figs. 3b and 4b. As the DSC studies showed, introduction of a filler leads to a change in the temperature at which the maximum of exothermal reaction is observed, which means that curing of these materials needs to be carried out in different technological regimes.

Hence, as a result of the studies that have been carried out, it was established that the DSC method in use is a simple and informative method for investigation of the properties of polymer binding agents. Upon the first heating, it allows one to determine the starting and final temperatures of exothermal reaction and, therefore, to establish the optimal curing temperature. The second and third heatings allow the glass transition point to be determined.



**Fig. 4.** DSC curves for the (1) initial and (2) cured epoxy binding agent containing 40 wt % of shungite depending on (a) temperature and (b) time [7].

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