Glass Transition in Dehydrated Amorphous Solid

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Glass is considered as a kind of rigid, non-crystalline material. Usually glass is obtained by supercooling of liquid and therefore this condition is invariably adopted in its numerous definitions.

Non-crystalline solids can be, however, prepared by other unusual methods.[1] Dehydration process of some hydrated crystals also yields amorphous anhydrides.[2] Then a question arises as to whether these non-crystalline solids can be called glasses or not. One approach to this problem is to find out glass transition phenomena in these amorphous materials. This phenomenon is always accompanied with usual glass and characterizes boundary between glassy and supercooled liquid states.

Magnesium acetate tetrahydrate was dehydrated in solid state under vacuum (10^{-3} mmHg). The anhydride is known to give only one broad band in the low angle range of its X-ray diffraction pattern indicating an amorphous material, which transforms spontaneously into crystalline anhydride at about 250°C on heating.[3] About 20 mg of the anhydride was packed into an aluminum pan and mounted on sample holder of Perkin-Elmer DSC-1B scanning calorimeter. In order to keep a constant condition, sample was first heated up to 500°K, kept for a short time, and finally quenched to 400°K. Measurements were then carried out with heating rates between 1.25 and 80 deg·min^{-1}. The results are shown in Fig. 1.

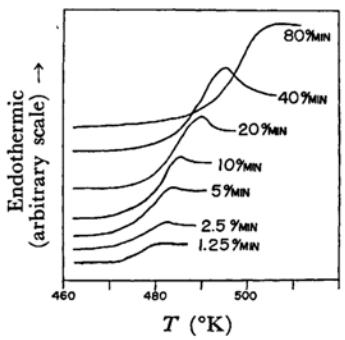

Fig. 1. DSC curve for the glass transition of magnesium acetate.

An endothermic anomaly always appears just before an exothermic effect due to crystallization. The shape and the temperature of the anomaly strongly depend on the heating rate employed. These results clearly show that the anomaly is due to glass transition phenomenon of the amorphous anhydride. Activation plot of the type developed by McMillan[4] is given in Fig. 2. From the slope of the bestfit straight line, apparent enthalpy of activation governing relaxation process becomes 131 ± 5 kcal·mol^{-1}.

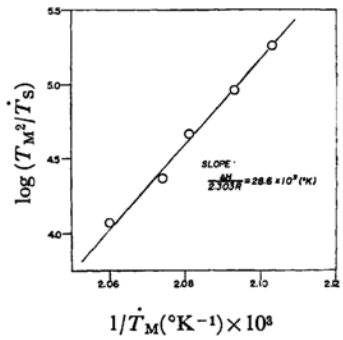

Fig. 2. Activation plot for the glass transition of magnesium acetate (T_M, inflection point; $\dot{T}_S$, heating rate).

We have discovered the first example of the non-crystalline solid prepared by dehydration exhibiting a glass transition phenomenon. This fact coincides with our previous observations[5] that the non-crystalline solid deposited on the chilled substrate from vapor state shows the same phenomenon. These observations lead to the conclusion that amorphous solids prepared by unusual methods other than supercooling of liquid can be firmly regarded as glasses. The details of the results will be given in due course.

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