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**Dynamic Mechanical Measurements During Cooling Process  
in Poly( methyl methacrylate )**

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**Abstract** : Dynamic mechanical measurements have been done during cooling process in PMMA . Results show that at a slow cooling condition , cooling rate doesn ' t affect the value of  $\alpha$  internal friction peak temperature (  $T_\alpha$  ) . It suggests that even if  $T_\alpha$  is not very different from  $T_g$  at low frequency , both temperatures differ in their nature :  $T_\alpha$  is nearly not dependent on cooling rate ( at least at a slow cooling process ) , while  $T_g$  is dependent on cooling rate strongly . At a rapid cooling condition , the dynamic mechanical behavior of PMMA has also been investigated tentatively .

**Key words** : poly( methyl methacrylate ) ; cooling process ; dynamic mechanical measurements

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**Introduction**

Glass transition is one of the most important phenomena for amorphous polymers , however , a clear picture of the nature of the transition has not yet emerged . The classic methods for the experimental determination of the glass transition temperature are dilatometry and calorimetry . One of the general facts observed is that the glass transition temperature (  $T_g$  ) determined by calorimetry or dilatometry depends on thermal history and heating ( or cooling ) rate strongly . In addition to above methods , dynamic mechanical analyzer has also been extensively employed . Under dynamic experimental conditions , the storage moduli commonly decrease by about three orders of magnitude in the vicinity of the  $T_g$  , on the other hand , the internal friction (  $\tan\delta$  ) exhibit maxima in the glass transition region . Frequently , the  $\alpha$  internal friction peak temperature (  $T_\alpha$  ) is taken as the  $T_g$  but it is clear that they will not be identical and that in general it will yield higher value than those obtained by dilatometric or thermodynamic methods .

The differences of  $T_g$  and  $T_\alpha$  were only explained as differences in the time scale<sup>[1]</sup> . As for whether  $T_g$  and  $T_\alpha$  are from the same physical nature received little attention .

However , how to compare the results obtained from different probes has recently become an open question for glass transition . And it has been suggested that one difficulty in understanding glass transition phenomena is that the different experiments probe different aspects of molecular motion , and different ' probes ' are involved in those experiments . In this paper , we will study the correlation between  $T_g$  and  $T_\alpha$  .

On the experimental side , it has been investigated extensively that the effects of thermal histories on dynamic mechanical properties of amorphous polymers ( i . e . , samples were cooled at different rates from well above  $T_g$  or aged a certain time at a temperature below  $T_g$  , then internal friction or storage modulus versus temperature was measured at constant heating rate )<sup>[2~5]</sup> . However , in order to carry out a direct comparison with the behavior of  $T_g$  , it is necessary to test the internal

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friction of amorphous polymers during cooling process. It is generally accepted that higher cooling rate causes higher  $T_g$ . This reason leads us to give a systematic experimental study of the influence of cooling rate on the  $T_g$  and  $T_\alpha$  of amorphous polymers. We select poly (methyl methacrylate) for the study.

## 1 Experimental

The PMMA was prepared by radical bulk polymerization of a monomer, using 0.06% AIBN as initiator. First, the monomer was pre-polymerized at 70 °C for 40 min, then poured into a glassy mould, kept at 40 °C for 30 hrs, 80 °C for 2 hrs and 100 °C for 2 hrs to finish the polymerization, finally, the sample was dried in vacuum stove till the weight does not vary. Its calorimetric  $T_g$  results to be 105 °C.  $T_g$  were taken to be the midpoint in an upwards temperature scan at 20 °C/min (measured immediately after cooling at -20 °C from rubbery state); Its  $m_\gamma$  is  $1.02 \times 10^6$ .

A dynamic mechanical analyzer, Dynastat (Imass, Inc.), was used to measure the dynamic mechanical properties. The internal friction (or storage modulus) was obtained during cooling process. Sample size were about  $2 \times 10 \times 15 \text{ mm}^3$ .

## 2 Results and Discussion

The internal friction versus temperature for PMMA, measured during two different cooling rates, 0.017 °C/min and 0.2 °C/min, is shown in Fig. 1. The prime reason for choose the above two slow cooling rates was to ensure the thermal lag between sample and temperature sensor in the sample room can be negligible. The results described in Fig. 1 were found to be readily reproducible. The variation in internal friction between supposedly identical samples was about  $\pm 0.003$ . As shown in Fig. 1, at slow cooling condition, cooling rate doesn't affect the peak temperature of loss tangent ( $T_\alpha$ ). This is quite different from the results measured by dilatometry or calorimetry, which is well known that the more slowly the liquid is cooled, the lower the  $T_g^{[1]}$ .

In order to understand above observation, we try to begin with a schematic plot, Fig. 2 shows the change in enthalpy (or volume) of a glass-forming polymer during cooling through the transition region. For conve-

nience, the supercooled liquid or rubbery state above the glass transition temperature range is referred to as the equilibrium state, to distinguish it from the non-equilibrium glassy state. As the temperature drops, the time required to establish the equilibrium configuration of the liquid increases, and eventually the structural change cannot keep pace with the rate of cooling. As the structure falls out of equilibrium, the liquid is said to enter the glass transition region. As shown in Fig. 2, at a normal experimental condition,  $T_\alpha$  is higher than  $T_g$ . The results of Fig. 1 can be understood as, during slow cooling process,  $T_\alpha$  measured at 1 Hz is well above the  $T_g$  obtained at the same cooling condition (i. e.,  $T_\alpha$  is appeared at thermodynamic equilibrium state), therefore cooling rate doesn't affect  $T_\alpha$ .

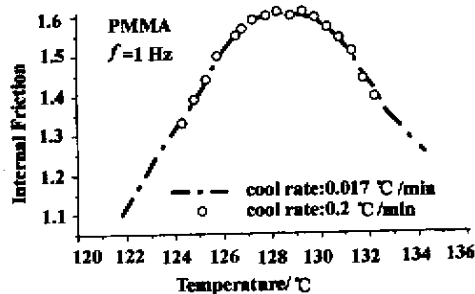


Fig. 1 Internal friction versus temperature for PMMA during two slow cooling processes

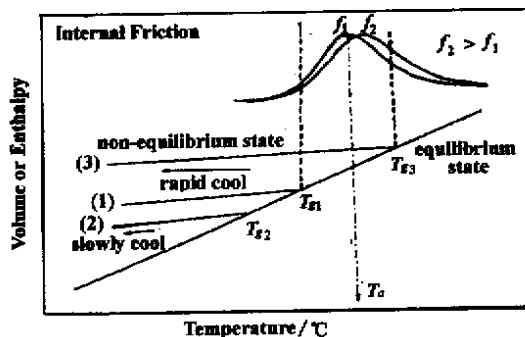


Fig. 2 Schematic plot of the change in enthalpy (or volume) of a glass-forming polymer during cooling through the glass transition region, and the relation between  $T_g$  and  $T_\alpha$

Nevertheless, results shown in Fig. 1 are obtained at slow cooling condition, at which  $T_\alpha$  is higher than  $T_g$ . If the dynamic mechanical behavior is measured during rapid cooling process (for example, at condition of (3) in Fig. 2, at which  $T_g$  is higher than the normal  $T_\alpha$ ), what phenomena should be observed? For this purpose, we managed to measure the  $\alpha$  internal friction peak and

the storage modulus of the PMMA at a cooling rate of  $100\text{ }^{\circ}\text{C}/\text{min}$ . The temperature of sample was calibrated at a reference process, for the serious thermal lag between sample and temperature sensor. A tentative results are presented in Fig.3, where the  $\alpha$  internal friction peak and the storage modulus of the PMMA are very 'smeared out' in temperature. The results in Fig. 3 is only basically repeated, because of the actual difficulty to reach a well repeated experimental condition between supposed identical samples. However, at each measurement during rapid cooling process, we can firmly observed that  $\alpha$  peak becomes lower and broader, and storage modulus is no longer sharp, compared with the results at usually cooling condition.

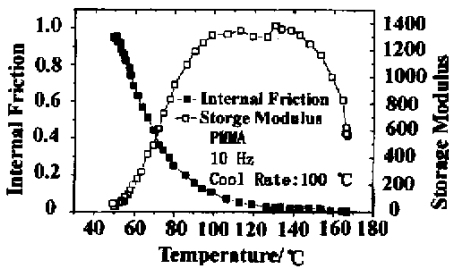


Fig.3 Internal friction and storage modulus versus temperature for PMMA during rapid cooling process

Intuitively, the differences of apparent behavior between  $T_g$  and  $T_\alpha$  are due to the fact that, only one variable, temperature, is involved, while during dynamic

during calorimetric( or dilatometric ) measurement, mechanical measurement, the variables are temperature and a sinuous force. Therefore, during dynamic mechanical measurement, maybe two processes, thermal relaxation and mechanical relaxation are involved.

Above is only some preliminary results. A detailed theoretical analysis of these observations and their implications along with further measurements of the dynamic mechanical behavior of other polymers are currently being carried out in our laboratory.

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## 降温速率对聚甲基丙烯酸甲酯内耗行为的影响

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摘 要 : 玻璃化转变是非晶高聚物的重要现象之一 , 如何比较不同测量手段所得的结果 , 已成为玻璃化转变的一个公开问题 . 研究了降温速率对聚甲基丙烯酸甲酯动态力学行为的影响 . 结果表明 : 在缓慢降温的测量条件下 , 降温速率并不影响  $\alpha$  内耗峰的峰温  $T_\alpha$  . 由此可推断 , 即使在低频测量时 ,  $T_\alpha$  和用示差扫描量热法测得的玻璃化转变温度  $T_g$  在数值上相差不大 , 但是这两个温度在本质上是不同的 :  $T_\alpha$  几乎不依赖于降温速率 ( 至少在缓慢降温的情况下 ) , 而  $T_g$  具有强烈的降温速率依赖性 . 最后尝试研究了快速降温条件下聚甲基丙烯酸酯的动态力学行为 .

关键词 : 聚甲基丙烯酸甲酯 ; 动态力学行为 ; 降温测量