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Melting behavior of confined Ga particles studied by internal friction

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Abstract

Gallium (Ga) particles dispersed in polymethyl methacrylate were prepared by ultrasonic vibration and sedimentation method, and the melting behavior of Ga particles was studied by internal friction method via dynamic mechanical analyzer (DMA). Four internal friction peaks, related to phase transitions from solid α-, β-, γ- and δ-Ga phases to liquid are observed, and the mechanism of internal friction peaks was discussed.

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Keywords: Internal friction; Melting; Ga particles; DMA

1. Introduction

Melting behavior is a common phenomenon in material research. The melting behaviors of confined small particles dispersed in a continuous matrix have been extensively studied by means of various methods, such as electron microscopy [1], differential scanning calorimetry [2], low energy electron diffraction technique [3], extended X-ray absorption fine structure (EXAFS), single-energy X-ray absorption detection (SEXAD), energy-scanning X-ray diffraction [4–7] and so on. Although great efforts have been made, however, a complete understanding of the melting has yet to be achieved. Internal friction method is useful method for studying character and character change of materials [8–11]. Comparing with other methods, internal friction method is convenient for investigating the mechanical behavior of materials and also it is nondestructive to specimens. Recently, the internal friction method via dynamic mechanical analyzer (DMA) has been used to study the surface melting behavior of nanoscaled metal particles dispersed in continuous matrix [12–15]. It has been proved that the internal friction method is sensitive to solid-liquid transitions.

Ga is a unique system which has four orthorhombic crystalline structural phases, α-, β-, δ- and γ-phases with respective melting points of 29.9 °C, −16.2 °C, −19.4 °C and −35.6 °C. In these phases, only α is a stable phase, and all others are metastable ones. The physical property of Ga has been studied widely [16–18]. In this study, Ga particles with a gradient size distribution were dispersed in poly(methyl methacrylate) (PMMA) matrix by means of ultrasonic vibration and sedimentation method, and the melting behavior of confined Ga particles was studied by DMA.

2. Experimental

The procedures of samples preparation were as following: 15 g methyl methacrylate (MMA) monomer was first rinsed with five percent of caustic soda solution in delivery flask until the color of MMA became achromatous and then rinsed by distilled water to make MMA neutral, following with desiccating by anhydrous sodium sulfate. 3 g Ga (purity: 99.9999%) was then put in the MMA and then ultrasonically vibrated at

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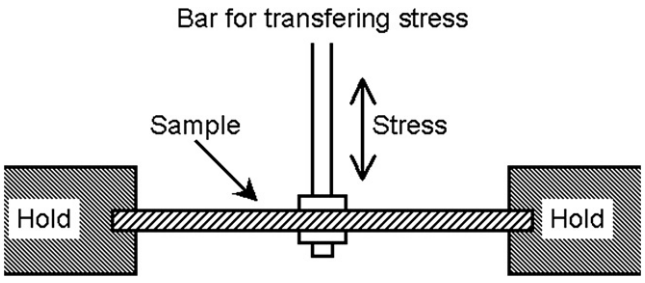

Fig. 1. A sketch map of dynamic mechanical analyzer (DMA).

40–60 °C for about 60 minutes, resulting in the formation of many Ga droplets dispersed in the MMA monomer liquid. After the addition of some Dibenzoyl Peroxide, the mixed solution was stirred in a thermostatic bath. With the bath temperature increasing to 80 °C, the viscosity of the mixture increases gradually. When the viscosity was about duplication of glycerin, the mixture was injected into a glass mold with the size of $75 \times 45 \times 2.5\ \text{mm}^3$. Finally, the mixture was annealed at 60 °C and then at 80 °C for one hour in the air, respectively. After removing the mold, the solid PMMA with well-dispersed Ga droplets was obtained. The volume fraction of Ga particles in the composite is about 3.1%. Here we defined the distance from the bottom of Ga/PMMA composites samples as D. The dimension of the samples for DMA measurement is of $50 \times 4.0 \times 2.0\ \text{mm}^3$, and we cut it from different D.

The characterization of the Ga particles dispersed in PMMA was performed by transmission electron microscope (TEM) (JEOL 2010) and the specimen with thickness of 80–100 nm for TEM observation was made by an ultramicrotome.

The DMA measurements were carried out with a Perkin–Elmer Pyris Diamond DMA equipment with a bend mode (Fig. 1). During DMA testing, a periodic sinusoidal stress is applied to the sample through the probe, and the responding strain developed in the sample is measured, so the internal friction $\tan\delta$ can be determined, where the angle δ is the phase angle by which the responding strain lags behind the applied load stress. Before DMA measurement, the specimen was cooled down to −150 °C and kept at this temperature for ten minutes to allow the solidification of all the Ga particles. In our experiment, the oscillatory frequency of 0.5 Hz was chosen throughout the heating measurement with a heating rate of 0.5 °C/min. For a comparison, pure PMMA was also measured with the same procedure.

3. Results and discussion

The ultrasonic vibration was used to prepare the samples and it is believed that the cavitation and implosion play an important role in the formation of Ga droplets [18]. In the process of preparing samples, the ultrasonic vibration may generate a large amount of bubbles in the liquid and the continuous cavitations result in bubble implosion and collapse to produce instantaneously extremely high pressure and temperature, which impacts on and fragmentizes the liquid metal Ga in the vicinity of the bubbles and further makes small Ga droplets form and well disperse in the PMMA matrix.

As we know, there is an approximate expression for spherical particle sedimentation in liquid:

$$m \cdot \frac{d^2x}{dt^2} = F_g - F_f - F_r \tag{1}$$

where m is the mass of the spherical particle, x the sedimentation distance of the spherical particles in liquid, t time, F_g the gravity of particle, F_f the buoyancy of particle, and F_r the resistance. F_g can be expressed as

$$F_g = \frac{4\pi}{3} \cdot \left(\frac{d}{2}\right)^3 \cdot \rho_p \cdot g \tag{2}$$

where ρ_p is the density of particle, d the diameter of particle, g acceleration due to gravity. F_f can be expressed as

$$F_f = \frac{4\pi}{3} \cdot \left(\frac{d}{2}\right)^3 \cdot \rho_l \cdot g \tag{3}$$

where ρ_l is the density of liquid. F_r can be expressed as

$$F_r = 3\pi \cdot \eta \cdot d \cdot \frac{dx}{dt} \tag{4}$$

where η is the liquid viscosity. From Eq. (1), we can obtain:

$$x = \frac{(\rho_p - \rho_l) \cdot d^2}{18\eta} \cdot t - C \cdot \left(\frac{d^2 \cdot \rho_p}{18\eta}\right)^2 \cdot e^{-\frac{18\eta}{d^2 \cdot \rho_p} \cdot t} + D \tag{5}$$

where C and D are constant. In our case the diameter d is very small, so Eq. (5) can be changed to

$$x = \frac{(\rho_p - \rho_l) \cdot d^2}{18\eta} \cdot t + D. \tag{6}$$

As the difference in the specific gravities ρ of Ga and that of MMA is great, from Eq. (6) we can see that the sedimentation distance x of the spherical particles in liquid is directly proportional to the square of particle diameter, which means that the droplets with bigger diameter sedimentate more quickly. During the preparation of samples, the Ga droplets continue to sedimentate to the bottom of the model, meanwhile the droplets having arrived at bottom may have a high collision possibility to coalesce and become bigger ones in order to reduce the surface energy. At the same time the viscosity η of PMMA continues to increase, thus the sedimentation rate of Ga droplets will become slower gradually. At a certain time the PMMA becomes a solid and the Ga droplets cannot move anymore, so the Ga particles are distributed in PMMA matrix with a size gradient.

The typical TEM images of Ga droplets are shown in Fig. 2, which shows that the spherical Ga droplets with different sizes are separated very well. Fig. 3 shows the distribution histograms of the Ga particle diameters. It can be seen that the diameter of Ga particles decreases with increasing D. For the samples gotten at the position $D = 0$, 9, 10, 11 mm, the average size of the particles was about $0.8 \sim 1$, 0.6, 0.3 and 0.2 μm, respectively.

Fig. 4 shows the DMA results for the pure PMMA sample. It is found that there exist broad peaks, which are the stable glass transition peak of pure PMMA. Fig. 5 shows the internal friction-temperature ($\tan\delta$–T) curves for the Ga/PMMA samples and four peaks, P_1, P_2, P_3 and P_4, appear on each $\tan\delta$–T

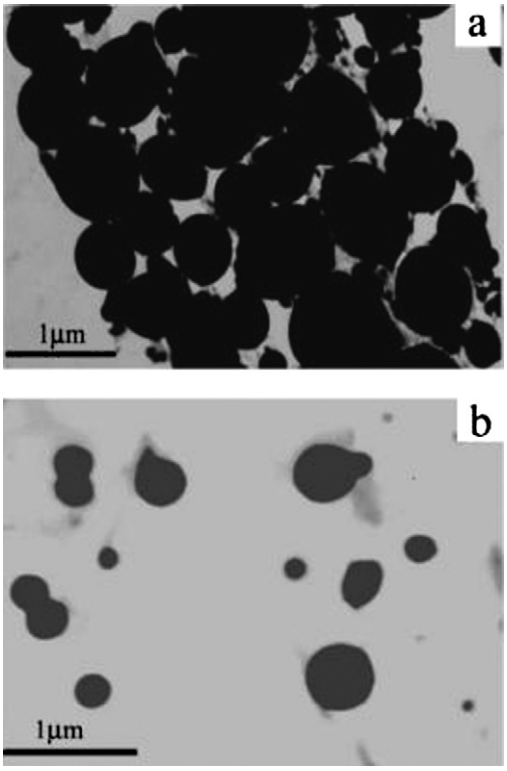

Fig. 2. TEM images of Ga particles at position $D = 0$ mm (a) and 11 mm (b). The distance from the bottom of Ga/PMMA composites samples was defined as D.

curve. Comparing with the DMA results of pure PMMA, it can be seen that these peaks are associated with Ga particles. The peaks P_1, P_2, P_3 and P_4 are located at about the melting point of α-Ga (29.9 °C), β-Ga (−16.2 °C), γ-Ga (−35.6 °C) and δ-Ga (−19.4 °C), respectively. In Fig. 6, the heating measurement DSC trace of Ga/PMMA sample with a scanning rate of 20 °C/min was shown, and there are four endothermal peaks, which are attributed to the melting of α-, β-, δ-, and γ-phases of Ga particles, as has been reported before [16]. By comparing Figs. 5 and 6, it can be concluded that the P_1, P_2, P_3 and P_4 peaks are related to the melting process of α-, β-, δ-, and γ-phases of Ga, respectively.

It is suggested that the internal friction peaks are caused by the surface melting [13]. As is well known, melting transition will first occur on the surface of materials and it has also been observed that the embedded Ga particles melt first at the boundary between the particles and matrix [1]. That is to say, a layer of liquid will surround the solid core of the Ga particles in DMA heating measurement. In other hand, in the process of DMA measurement a periodic sinusoidal stress is applied to the sample and the Ga particles will feel this stress, which may change the melting temperature of Ga particles cyclically. That is to say, the molten fraction of a particle will depend on the stress. So, the surface molten fraction of particles will be changed cyclically and the melting/solidification process at the surface molten layer of a particle may cause the vibration energy dissipation and induces the internal friction peaks.

It can be found from Fig. 5 that the four internal friction peaks show the growth and decline (or fluctuation) character

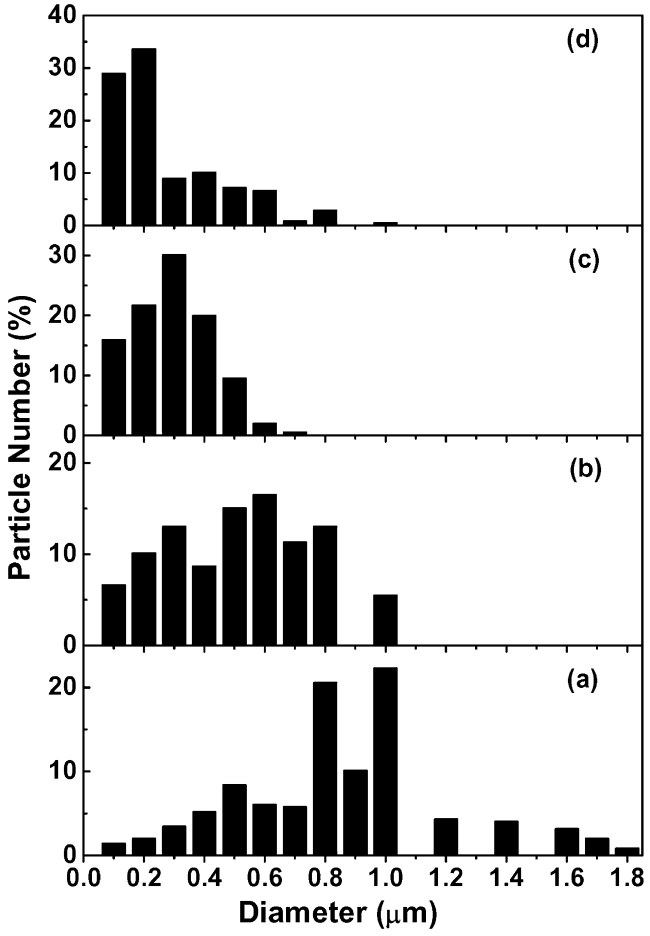

Fig. 3. Distribution histograms of the Ga particles diameters as determined from the TEM image of different samples, which were corresponding to $D = 0$ (a), 9 (b), 10 (c) and 11 mm (d), respectively. The horizontal axes are diameter of particles, and the vertical axes are the relative percentage of the number of different size particles.

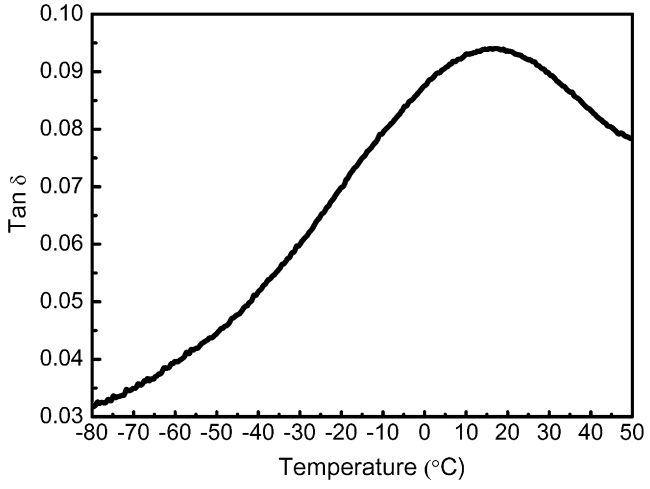

Fig. 4. Tan δ of pure PMMA during DMA heating measurement at the frequency of 0.5 Hz with a heating rate of 0.5 °C/min.

among them. In the Ga/PMMA samples obtained from the different distance D, the size of Ga particles is different (Fig. 3).

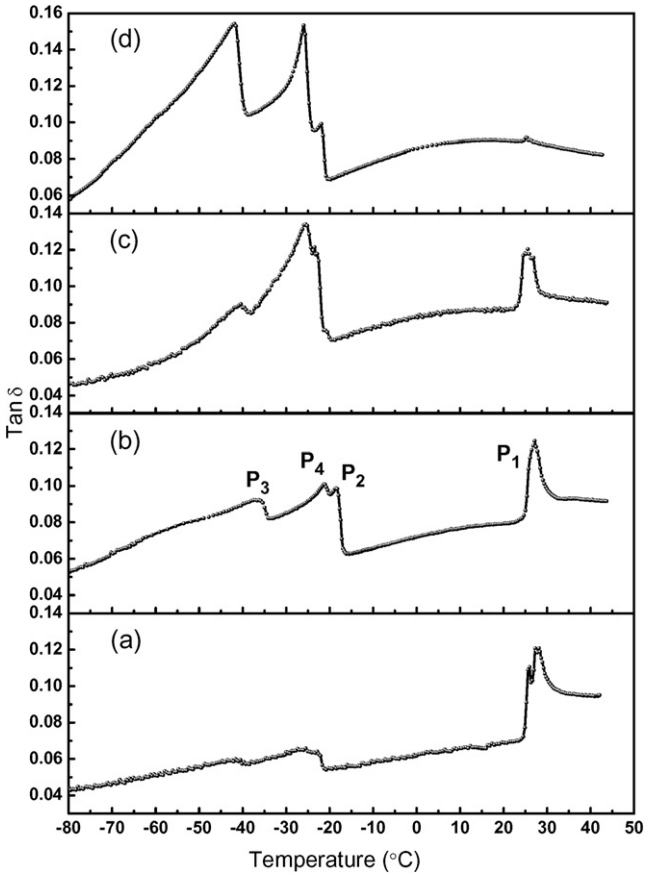

Fig. 5. Tan δ of Ga/PMMA during DMA heating measurement at the frequency of 0.5 Hz with a heating rate of 0.5 °C/min. The distance from the bottom is: $D = 0$–2 (a), 5–6 (b), 9–10 (c), 23–24 mm (d). The peaks 1–4 are related to the melting transition of α-Ga, β-Ga, γ-Ga and δ-Ga, respectively.

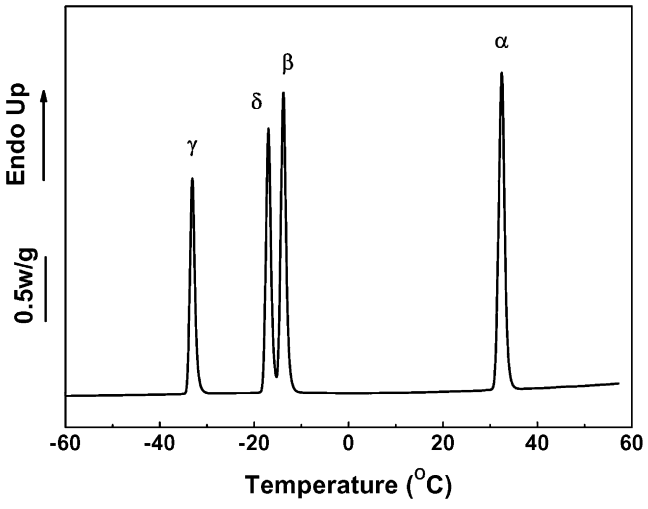

Fig. 6. Heating measurement DSC trace of Ga/PMMA with a scanning rate of 20 °C/min. The peaks are related to the melting of α-Ga, β-Ga, γ-Ga and δ-Ga ($D = 10$ mm).

It has been proved that the phase structures are closely related with sizes of Ga particles [16]. The stable phase α-Ga, is dominantly formed when the average size of Ga particles is no less than 0.8 micron, and the metastable phases β-, γ- and δ-Ga are mainly formed when the average particle size is below 0.8 micron. For the sample obtained at the $D = 0.2$ mm, the most of Ga particles is the largest and the α-Ga is mainly formed. So, the internal friction peak corresponding to the melting of α-Ga is the highest and the other peaks corresponding to the melting of β-, γ- and δ-Ga are the lowest (Fig. 5(a)). For the samples obtained at the larger D, the most of Ga particles is smaller and the metastable phases β-, γ- and δ-Ga are mainly formed. Thus, the internal friction peaks corresponding to the melting of β-, γ- and δ-Ga are higher and the peak caused by the melting of α-Ga is lower (Figs. 5(b)–(d)). The DMA results show that the internal friction peaks corresponding to the melting of solid α-, β-, γ- and δ-Ga phases are varied with the size of Ga particles.

4. Conclusions

In summary, Ga particles dispersed in PMMA were prepared by ultrasonic vibration and sedimentation method. The melting behavior of small Ga particles confined in PMMA was studied by DMA. Four internal friction peaks are observed and the peaks are associated with the melting process of solid α-, β-, γ- and δ-Ga phases. It is proved that internal friction method is suitable to study solid-liquid transitions.

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