

Depression of Melting Point of Eutectic Metal Alloy by the Interaction with Polyacrylates in
Metal-Polymer Composites

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Abstract

The composites of polyacrylates and eutectic metal alloy composed by Bi, In, and Sn were prepared by mixing the metal and polymer above the melting point of the metal alloy (80 °C) with a homogenizer. Two melting peaks, which were assigned as the melting peak of the original metal alloy and that of the interfacial phase of the metal alloy interacting with polyacrylates (70 °C) by differential scanning calorimetry. Metal particles with the diameter of about 100 nm which were stabilized by the interfacial interaction with polyacrylates were observed by transmission electron microscopy. The melting peak at 70 °C was assigned as the melting peak of these small particles.

Keywords: metal alloy; polyacrylate; composite; interfacial interaction

1. Introduction

There have been many researches [1-5] on the physical properties of polymer at interface, because they dominate important characteristics of polymer materials such as durability, biocompatibility, and adhesion. The molecular mobility of some polymers bearing polar groups is strongly affected by the interaction at metal interface. We prepared thin films of polyacrylates on metal-coated glass plates and reported that metal induced polyacrylates to form the interfacial phase where the molecular mobility was restricted by the interaction between the carbonyl groups and metal interface [6].

On the other hand, high melting temperature of metals and low decomposition temperature of polymers make it difficult to prepare composites to investigate the physical characteristics of metal at the interface with polymers. There are some papers on the composites of low-melting-point metal alloys and polyethylene [7-10], polypropylene [8], or polystyrene [8], but they focused on the morphology of the composite and the fabrication of microstructure.

In this communication, we prepared the composites of polyacrylates and eutectic low-melting-point metal alloy composed by Bi (57.50 wt%), In (25.20 wt%), and Sn (17.30 wt%) to measure the melting point and crystallization temperature by differential scanning calorimetry (DSC). The morphology of the composite was observed by transmission electron microscopy (TEM).

2. Experimental

The low-melting-point metal alloy No. 19C purchased from Fuji Metal Industries was used in this study. Four polyacrylates: poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(*tert*-butyl

acrylate) (PtBA), and poly(*n*-butyl acrylate) (PnBA) and one polymethacrylate: poly(*n*-butyl methacrylate) (PnBMA) were mixed with the metal alloy. PMA, PEA, PnBA, and PnBMA were purchased from Aldrich, and PtBA was the product of Polymr Source. The weight average molecular weight M_w , glass transition temperature T_g , and density ρ of the polymers were summarized in Table 1. The metal alloy and polyacrylates were mixed with a homogenizer at 3,000 rpm at ca. 130 °C. Tetrahydrofuran (THF) was added to mix the metal alloy and PnBMA to reduce the viscosity, and evaporated in vacuo. The measurements described below were carried out only for successfully mixed composites looking uniformly black.

DSC was carried out with TA-60WS of Shimadzu. The heating rate and cooling rate was +20 °C/min, and -10 °C/min, respectively. The composite of the metal alloy (63 wt%) and PnBA was poured into THF, and sonicated to wash out the PnBA. DSC was also conducted for the precipitate collected by centrifugation.

TEM images were obtained with JEM 200 FX of JEOL. The suspension of the composite of the metal alloy (63 wt%) and PnBA in THF was prepared by sonication. It was dropped onto a TEM grid, and dried in vacuo. The acceleration voltage was lowered to 100 kV because the higher voltage decomposed the residual PnBA, and worsened the vacuum.

3. Results and discussion

Figure 1 shows the DSC curves of the composites of PnBA and the metal alloy with different content.

Whereas only one melting peak was observed in the curves for 100 % metal alloy at 80 °C, a broad endothermic peak appeared at 70 °C in the curves of the composites. The intensity of the former peak decreased, and that of the latter peak increased by decreasing the metal content in the composites. These curves suggest the coexistence of the phase affected by some interaction between polymer and metal, and the same phase as 100 % metal alloy.

The bottom curve in Figure 1 is the result for the composite with 63 wt% of the metal alloy after washing out PnBA. There are two possible reasons for the endothermic peak induced by mixing polymers. One is the structural change of the metal alloy, and the other is its chemical change. However, as the DSC curve of the composite after removing PnBA was essentially identical to that of pure metal alloy, some structural change of the metal alloy induced the endothermic peak at 70 °C.

Figure 2 shows the bright field images of TEM of metal particles in the composite of the metal alloy (63 wt%) and PnBA. Various sizes of particles were observed in the composite. The diameter of the particle shown in Figure 2(a) was ca. 100 nm, and it was composed with smaller particles with the diameter of ca. 10 nm. We are now trying to obtain the dark field images and electron diffraction patterns by taking clearer TEM images of the smaller particles with less residual polymer.

There have been so many researches on nano-sized metal particles for their distinct electric, magnetic, chemical, and catalytic characteristics [11-15], and it was proved that the melting temperature of nanoparticles is significantly lower than that of corresponding bulk metal. The endothermic peaks at 70 and 80 °C can be explained as the melting peaks of the particles with size of 100 nm shown in Figure 2

(a) and that of larger particles in Figure 2 (b).

In order to estimate the origin of the interaction stabilizing the small particles of metal alloy, DSC curves for the composites of the metal alloy and other polyacrylates and polymethacrylate were obtained as shown in Figure 3. The weight fraction of the metal alloy was fixed to be 50 % except for the composite of the metal alloy and PnBMA (20 %), because PnBMA was too viscous to be mixed at high metal content.

The DSC curves in Figure 3 (a) were obtained by heating samples. While there were two endothermic peaks in the DSC curves of the composites of the metal alloy and polyacrylates as shown in Figure 1, the curve of the composite of PnMBA and the metal alloy was essentially identical to that of the metal alloy without polymers.

We carried out DSC and dielectric measurements for thin films of PEA PnBA, and PnBMA on glass plates coated with various metals [6]. The contact with metal induced PEA and PnBA to form the interfacial phase where the segmental motion of polymer chains was restricted by the interaction between metal and the carbonyl groups in polymers, but no such interfacial phase was detected for PnBMA. The presence of the interfacial interaction between polyacrylates and metal, and the absence of the interaction between polymethacrylates and metal, well agreed with the results in Figure 3(a).

The DSC curves in Figure 3 (b) were obtained by cooling samples. The exothermic peaks of crystallization in the composites were broadened and the peak temperature was ca. 70 °C lower than that of the metal alloy without polymers.

From the results of DSC and TEM, we expect the formation of the interfacial phase of the metal alloy as follows. Melt metal began to be crystallized at 80 °C, but the mobility of metal at the interfacial region was restricted by interacting with polyacrylates. The broad peak of crystallization and the depression of the crystallization temperature were caused by this restriction. The interaction with polyacrylates also prevented the formation of large crystals of metal, and induced the formation of small particles observed in Figure 2(a). The lower melting point in Figure 1 and 3(a) was the melting point of the small particles.

4. Conclusion

Two endothermic peaks were observed in the DSC curves for the composites of low-melting-point metal and polyacrylates, and assigned as the melting point of the original metal (80 °C) and that of metal interacting with polyacrylates (70 °C). TEM images indicated the formation of metal particles with the diameter of 100 nm. The endothermic peak at 70 °C was inferred to be the melting peak of the small metal particles stabilized by the interfacial interaction with polyacrylates which prevented the formation of larger particles by restricting the mobility of metal at the interfacial region.

5. References

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Figure captions

Figure 1 The DSC curves of the composite of PnBA and the metal alloy. The numbers right to the curves indicate the weight fraction of the metal alloy in the composites. The bottom curve is the result

of the composite with 63 wt% of the metal alloy after washed with THF.

Figure 2 TEM images of metal particles in the composite of the metal alloy (63 wt%) and PnBA. The

scale bars indicate 150 nm in Figure 2(a), and 3 μm in Figure 2(b), respectively.

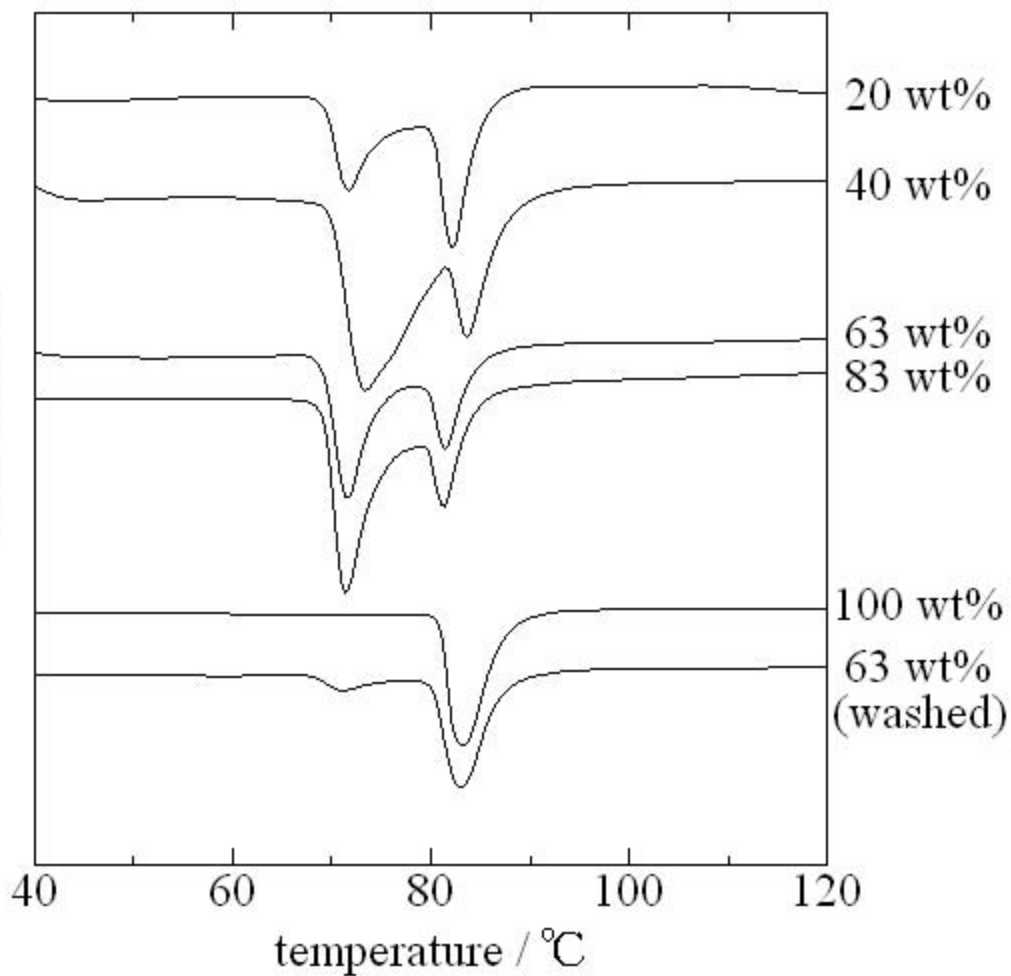
Figure 3 The DSC curves of the composite of the metal alloy and polyacrylates and polymethacrylate.

The curves in Figure 3 (a) and (b) were obtained by heating and cooling, respectively.

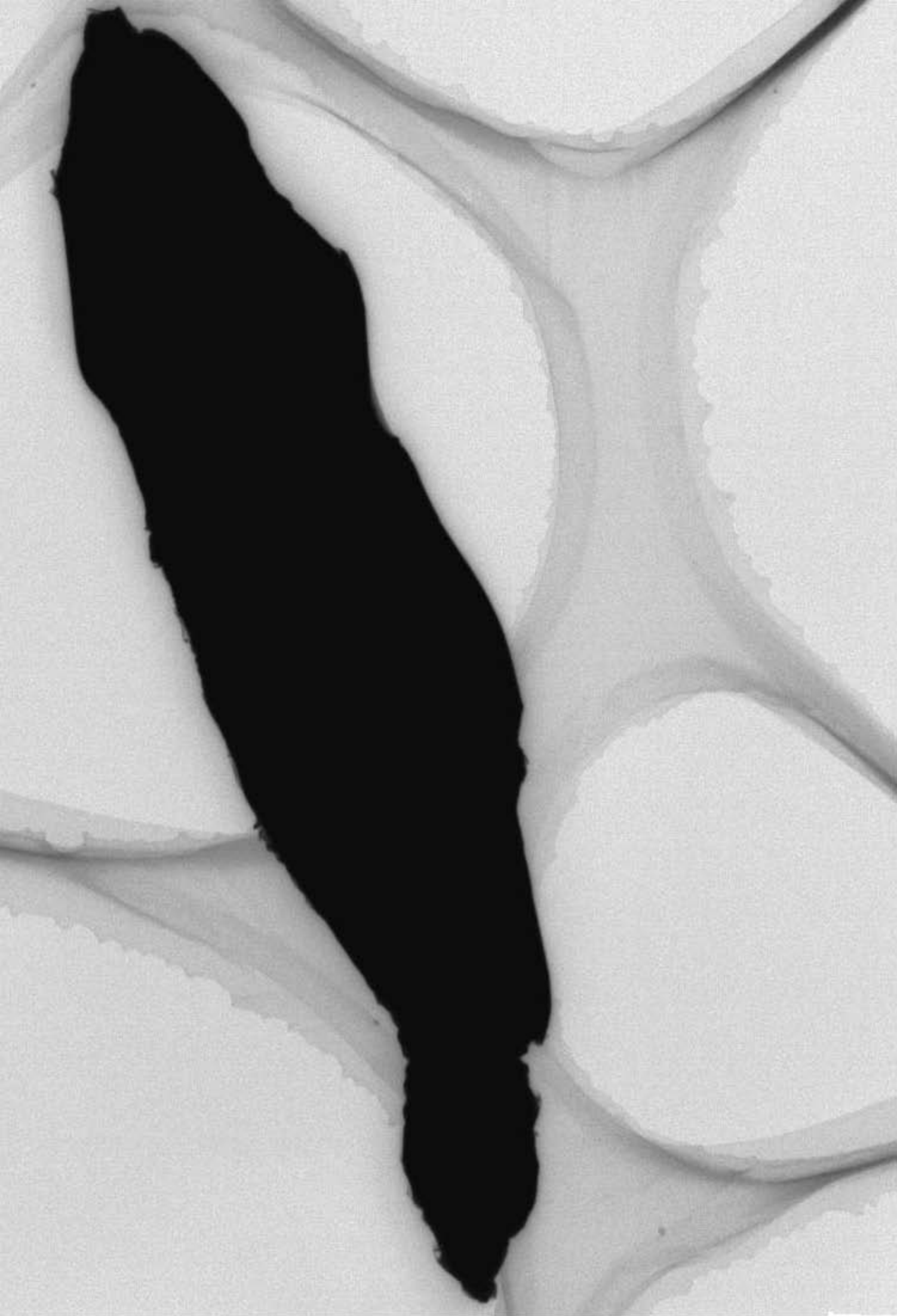
Table 1 Physical properties of polymers used in this study.

Polymer	$M_w / 10^4$	$T_g / ^\circ\text{C}$	$\rho / \text{g cm}^{-3}$
PMA	3.07	-27	1.22
PEA	9.50	-39	1.21
PtBA	2.65	40	1.12
PnBA	9.90	-54	1.09
PnBMA	33.7	15	1.07

← endothermic







0 μm

1 μm

2 μm

3 μm

