Melting and Crystallization Behavior of Metallic Alloy in the Composites with Polyacrylate

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ABSTRACT: Composites of poly(n-buthyl acrylate) (PnBA) and eutectic metallic alloy composed of Bi, In, and Sn were prepared by mechanically mixing them above the melting point of the metallic alloy, and glass transition temperature of PnBA. The heating curves of differential scanning calorimetry (DSC) of the composite of PnBA and the metallic alloy showed an endothermic peak below the melting point of the metallic alloy without polymers, which indicated the formation of the interfacial phases of the metallic alloy with a lower melting point. The exothermic peaks of the cooling curves were broadened and shifted to the temperature lower than the melting point of the metallic alloy without polymers, which suggests that the crystallization of the metallic alloy was suppressed by the interaction. The mechanism of lowering the melting points and suppression of the crystallization was discussed based on the results of DSC, transmitting electron microscopy, and X-ray diffractometry. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1278–1284, 2011

Key words: alloys; composites; differential scanning calorimetry (DSC); TEM; X-ray

INTRODUCTION

The physical properties of polymer at surface or interface have attracted both scientific and industrial interests.[1–7] Whereas the physical properties of nonpolar polymers at the surface phase can differ from those of the polymers at bulk phase,[8] the interfacial interaction between polar polymer and metal dominates the physical properties of the polymer because of their strong interaction.[9] The strong interaction between polar polymer and metal arranges the polar groups, and changes the mobility of the main chains of the polymer. The change of the mobility of polymer chains induces the change of their glass transition behavior, and affects their adhesive properties.

The interaction between polymers at Al interface has been studied, and the interaction between aromatic rings in polymers and Al,[10] the formation of Al-C bonds at the interface of Al and poly(ethylene terephtalate), polypropylene, or polyethylene,[11–13] of Al-O-C complexes at the interface of Al and poly (vinyl alcohol) and trimethyl aluminum,[14,15] and of Al$^+$COO$^-$ bonds[16–18] were found by some researchers.

We carried out differential scanning calorimetry (DSC) and dielectric measurements for the thin films of poly(ethyl acrylate) (PEA), poly(n-butyl acrylate) (PnBA), poly(n-butyl methacrylate) (PnBMA) contacting with films of Ag, Al, Au, and Ni to investigate the physical properties of polyacrylates at the interface with metals.[19] The formation of the interfacial phase with lower mobility of polymer chains than that in bulk phase was observed in the films of PEA and PnBA contacting with all the metals that we used, but no such phases were detected in the films of PnBMA. This result suggests the presence of the interaction between polyacrylates and metals, which restricts the molecular mobility of polymer chains, and the absence of such interaction between polymethacrylates and metals.

Compared with the researches on the interaction from metals to polymers, there has been less number of the researches on the interaction from polymers to metals. It is convenient for the investigation of the interaction to metals to prepare mixed composites of metals. However, to make composites of metals and polymers, metallic alloys with low melting temperature are necessary, because metal and polymer need to be mixed above their melting temperature (T_m) and glass transition temperature (T_g), but below the decomposition temperature of polymer.

The composites of polymers and metals with low-melting-temperature have been prepared to observe the structure of metals, or to improve the electrical, optical, or mechanical properties of materials. Vesely et al.[20] blended polypropylene, polyethylene, or

polystyrene and some metallic alloys, and observed the structures of the composites with a optical microscope. They concluded that the phase sizes can be controlled by viscosity of the matrix. Bormashenko et al.[21,22] prepared the composites of polyethylene and metallic alloys with an extruder, and succeeded in the fabrication of the micropowders of the metals.

Zavyalov et al.[23] made the composites of poly-*para*-xylylene and Pd, Sn, or Cu, and observed their structure by scanning electron microscopy (SEM). They also measured the temperature dependence of the electric resistance of the composites, and found the semiconductor-like characteristics of their composites.

Xia et al.[24] studied the composites of polypropylene and Cu by many measurements such as SEM, X-ray diffractometry (XRD), differential scanning calorimetry (DSC) to reveal not only the structure, but also thermal properties such as thermal stability of the composites.

We focused on the melting and crystallization behavior of the metals in the composites with polymer. In our previous letter,[25] the composites of polyacrylates and metallic alloy composed of Bi, In, and Sn were prepared by mixing them with a homogenizer above the T_m of the metallic alloy and T_g of the polymers. The heating curve of DSC for the composite had an endothermic peak below the T_m of the metallic alloy without polymers, and a very broad exothermic peak was detected at the temperature lower than the T_m of the metallic alloy without polymers.

Small particles of metallic alloys with diameters of ~ 100 nm were observed in the images of transmitting electron microscopy (TEM), and the particles with diameters of ~ 100 nm seemed to be formed by aggregating smaller particles with diameters of 10–30 nm. Because the melting temperature of the nanoparticles of metal is reported to be lower than that of the same metal in bulk phases,[26–31] the formation of nanoparticles observed by TEM may cause the melting and crystallization behavior of the metals in the composites.

Because of its simple fabrication procedure, the process of mixing the polyacrylates and metallic alloy to control the melting temperature or to depress the crystallization, has the potential to be applied to produce some metallic materials, such as low-melting-temperature solider or amorphous metals.

In this full article, DSC and XRD measurements were carried out for the composites crystallized in different conditions to elucidate the melting and crystallization mechanism of the metals in the composites. Samples with different cooling process after mixing the polymer and metallic alloy were also prepared to estimate the crystallization mechanism.

TABLE I
The Physical Properties of PnBA and PMMA Used in this Study

Polymer	$M_w/10^4$	$T_g/^\circ C$	$\rho/\mathrm{g\ cm}^{-3}$
PnBA	9.90	−49	1.09
PMMA	12.0	107	1.17

EXPERIMENTAL

Materials

The metallic alloy used in this study was the low melting alloy No. 19 C of Fuji Metal Industries Co. The weight fraction of Bi, In, and Sn was reported to be 57.50%, 25.20%, and 17.30%, respectively, by the supplier. The atomic fraction can be calculated to be 42.96%, 34.28%, and 22.76%, respectively. The melting temperature was reported to be 78.8°C by the supplier. Scherpereel and Perett,[32] and Rutter et al.[33,34] studied the phase diagram of Bi-In-Sn system, and concluded that the metallic alloy with 57.2 wt % Bi, 24.8 wt % In, and 18.0 wt % Sn had an eutectic temperature at 77°C.

Pure In and Sn were purchased from Wako Pure Chemical industries. The eutectic alloy composed by 52 wt % of Sn and 48 wt % of In (51 at% of Sn and 49 at% of In) was prepared by mixing pure metals.

PnBA and poly(methyl methacrylate) (PMMA) used in this study were purchased from Aldrich, and their T_g, weight average molecular weights M_w, and density ρ were summarized in Table I. Metallic alloy and polymer were mixed in a test tube heating at the temperature higher than the T_m of the metallic alloy and T_g of the polymer. The composites mixed successfully were viscous rubbery fluid looking uniformly black, but the mixture which could not be mixed perfectly, looked spotted. Only the composites looking uniformly black were used in the following experiments.

The weight fraction of metals was fixed to be 50% in the measurements of DSC and XRD. The volume fraction of the metallic alloy was roughly calculated from the weight by assuming that no volume change was involved by preparing composites.

Measurements

DSC was carried out with TA-60WS of Shimadzu. The samples were first heated at + 10°C/min for the composites of the alloy of In and Sn, and + 20°C/min for other samples, then cooled at −10°C/min.

XRD was performed with RINT 2200 X-ray-diffractometer of Rigaku with CuKα radiation working at the range of scattering angles 2θ from 25 to 40° at 3.0°/min. A slit with a width of 0.80 mm was inserted in front of the detector. The measurements were carried out at room temperature (~ 25°C).

The metallic alloy in the composite of PnBA and the ternary metallic alloy of Bi, In, and Sn was observed by TEM. The weight fraction of metals in the composite was 63%, and the volume fraction was calculated to be 18%. The composite was sonicated in tetrahydrofuran (THF), which is a good solvent for PnBA, to obtain the suspension of metal particles. The suspension was dropped on a grid for TEM, and dried *in vacuo*. JEM 200 FX of JEOL with the acceleration voltage of 100 kV was used to take TEM images, because higher voltage decomposed the residual PnBA, and lowered the degree of vacuum.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Figure 1 shows the DSC curves for the composite of PnBA or PMMA and the eutectic metallic alloy composed of Bi, In, and Sn. The weight fraction of metals in the composites was fixed to be 50%, and the volume fraction was 11% for the composites with PnBA, and 12% for that with PMMA. The ordinate indicates the heat flow per weight of metals in samples, not weight of whole samples, because we focus on the thermal behavior of metals, and the polymers show no specific thermal changes in the temperature ranges in this study.

The DSC curves for the metallic alloy without polymers showed an endothermic peak around 80°C, and exothermic peak around 65°C, which are assigned as the melting and crystallization peaks, respectively. The discrepancy of the temperature of melting and crystallization may be caused by the slowness of the crystallization compared with the cooling rate. The heating curve for the composite of PnBA and the metallic alloy has a broad endothermic peak around 70°C in addition to the endothermic peak at 80°C. The exothermic peak is so broadened that it is difficult to appear clearly in this figure. The endothermic peak in the heating curve for the composite with PMMA was also broadened, but no peak was detected around 70°C in the cooling curve.

The endothermic peak around 70°C was also observed in the composites with poly(methyl acrylate), poly(ethyl acrylate) (PEA), and poly(*tert*-buthyl acrylate), but not detected in the composite with poly(*n*-buthyl methacrylate) (PnBMA) in our previous letter.[25] The DSC and dielectric measurements for the thin films of polyacrylates and polymethacrylate in our previous work[19] indicated that the PEA and PnBA formed interfacial phases with metals where the mobility of polymer chains was restricted, but no such phase was formed in the film of PnBMA.
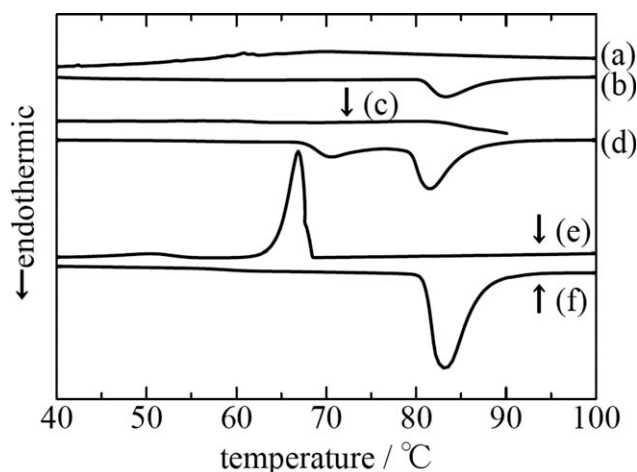

Figure 1 The DSC curves of the composite of PnBA or PMMA and the metallic alloy composed by Bi, In, and Sn: (a) cooling and (b) heating curves of the composite of PMMA and the metallic alloy (12 vol % of metals), (c) cooling and (d) heating curves of the composite of PnBA and the metallic alloy (11 vol % of metals), (e) cooling, and (f) heating curves of metallic alloy without polymers.

These results suggest that both from metal to polymer and from polymer to metal interaction exist at the interface between metals and polyacrylates, but do not exist at the interface between metals and polymethacrylates. Because the results of dielectric measurements of polyacrylates mainly reflect the mobility of carbonyl groups,[35–37] the interaction between metal and carbonyl groups may play important roles in the interaction between metals and polyacrylates, and the methyl groups bound to the main chains in polymethacrylates may interrupt the interaction of carbonyl groups.

The very broad exothermic peak of crystallization in the composite of PMMA and the metallic alloy can be caused by the high T_g of PMMA (107°C) because the diffusion of metals, which is necessary for the crystallization of metallic alloys, was highly restricted in glassy polymer.

The thermal behavior of the composites of binary metallic alloy or pure metal was investigated as shown in Figures 2 and 3, respectively. The DSC curve of the composite of PnBA and the eutectic metallic alloy of Sn and In (13 vol % of metals) had a small endothermic peak at 118°C in addition to the melting peak at the same temperature of T_m of the metallic alloy without polymers. An exothermic peak was detected in the cooling curve from 90 to 110°C, which is ~ 20°C lower than the T_m of the metallic alloy without polymers. An exothermic peak at the temperature lower than the T_m of the metallic alloy without polymers also appeared, but no split of the endothermic peak was observed in the DSC curves of the composite of PMMA (14 vol % of metals) and the metallic alloy.
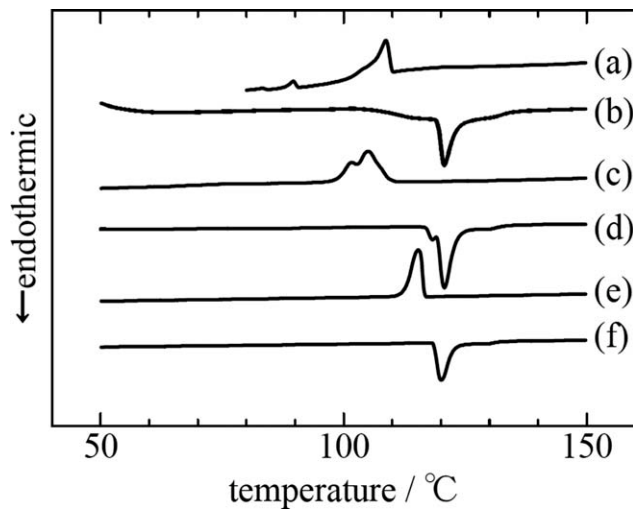
Figure 2 The DSC curves of the composite of PnBA or PMMA and the eutectic alloy composed by In and Sn: (a) cooling and (b) heating curves of the composite of PMMA and the metallic alloy (14 vol % of metals), (c) cooling and (d) heating curves of the composite of PnBA and the metallic alloy (13 vol % of metals), (e) cooling and (f) heating curves of metallic alloy without polymers.

Figure 3 indicates that no split of the endothermic peak was detected in the DSC curves of the composites of PnBA and Sn or In (13 vol % of metal), but the depression of the crystallization temperature T_c was observed in the two composites. The presence of the split of the endothermic peak in the composites of metallic alloy and PnBA and the absence of the split of the peak in the composites of pure metals and PnBA suggest that plural metals are necessary for the appearance of the endothermic peak in
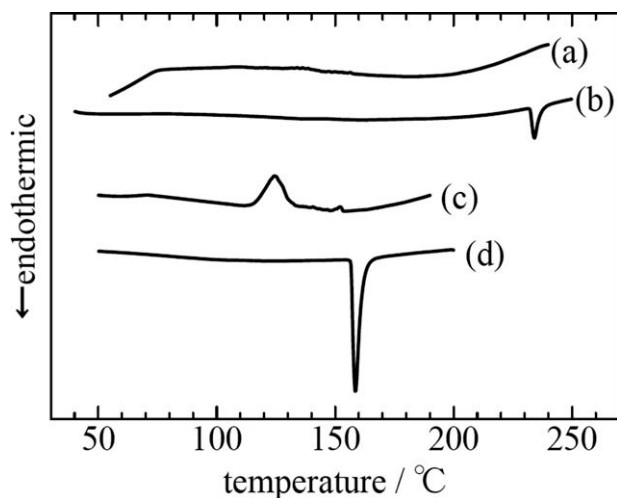
the composites below the T_m of metals without polymers.

To elucidate the mechanism of the crystallization of metallic alloy in the composites with polymers, the exothermic peak in the DSC curve for the composite of PnBA and the eutectic metallic alloy of Bi, In, Sn was analyzed in Figure 4. A very broad exothermic heat could be detected just below the temperature at which melting peak was measured, although the main exothermic peak was around 0°C. The broken lines in the figure indicate baselines, and the endothermic and exothermic heats were calculated from the area surrounded with the DSC curves and baselines. The endothermic and exothermic heat divided by the weight of metals in the composite were 40 and 41 J/g, which were approximately same as the heat of fusion of the metallic alloy without polymers (40 J/g) calculated from the data in Figure 1. These results suggest that the crystallization of the metals was depressed by the interaction with PnBA, but proceed very slowly even just below the T_m of the metallic alloy without polymers.

The existence of the broad exothermic heat was confirmed in Figure 5. The composite of PnBA and the ternary eutectic alloy was first heated from 30 to 120°C (a), then cooled from 120 to 30°C (b), and finally heated again from 30 to 100°C (c). The heats calculated from the DSC curves and baselines were 40 J/g for curve (a), 3 J/g for curve (b), and 4 J/g for curve (c), respectively. The appearance of a small endothermic peak in curve (c) indicates that the crystallization of the metals slowly proceeded in curve (b), and the broad peak in curve (b) was not a noise, but the signal of the crystallization heat. The
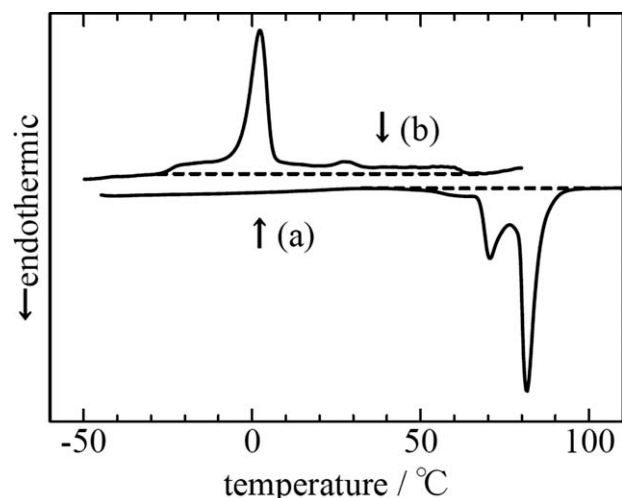

Figure 3 The DSC curves of the composite of PnBA and In or Sn: (a) cooling and (b) heating curves of the composite of PnBA and In (13 vol % of metal), (c) cooling, and (d) heating curves of the composite of PnBA and Sn (13 vol % of metal).

Figure 4 The DSC curves of the composite of PnBA and the metallic alloy composed by Bi, In, and Sn (11 vol % of metals): (a) heating and (b) cooling curves. The broken lines indicate the base lines.
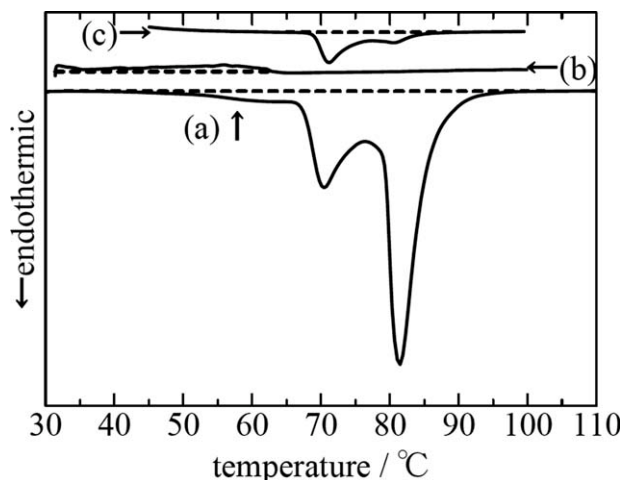
Figure 5 The DSC curves of the composite of PnBA and the metallic alloy composed by Bi, In, and Sn (11 vol % of metals). The sample was first heated from 30 to 120°C (a), then cooled to 30°C (b), and finally heated again from 30 to 100°C (c). The broken lines indicate the base lines.

slightly larger heat in curve (c) than that in curve (b) may be caused by the crystallization while the instrument changed from cooling mode to heating mode at 30°C.

X-ray diffractometry

X-ray diffraction patterns of (a) the eutectic metallic alloy of Bi, In, and Sn without polymers, (b) the composites of the metallic alloy and PnBA with the weight fraction of metals of 50% (the volume fraction of 11%) cooled to room temperature ($\sim$ 25°C), and (c) the same composited cooled in a freezer (ca. -20°C) are illustrated in Figure 6.
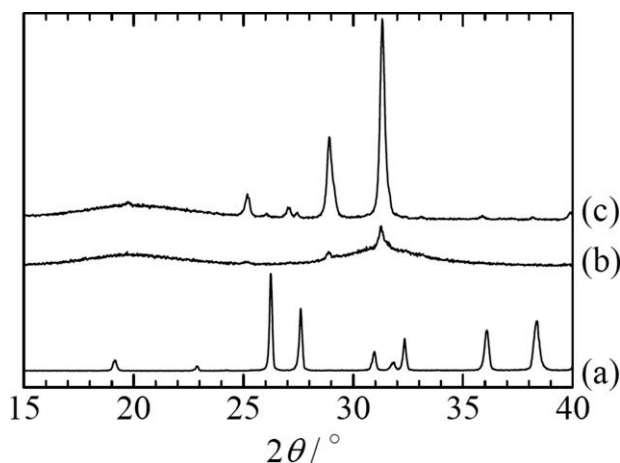

Figure 6 The XRD patterns of (a) the metallic alloy composed by Bi, In, and Sn without polymers, that of the composite of PnBA and the metallic alloy (12 vol % of metals) (b) cooled to room temperature ($\sim$ 25°C), and (c) that cooled in a freezer (ca. -20°C).

Although no clear peaks were detected in the pattern of the composites cooled to room temperature, some broad peaks appeared in the pattern of the composite cooled in a freezer. The peak angles of the composite cooled in a freezer were different from those of the metallic alloy without polymers. Very small peaks could be also detected at the same angles in the pattern of the composite cooled to room temperature. The halo around 20° in the patterns of the composites is attributed to the amorphous PnBA, not to metals.

These diffraction patterns indicate that the formation of ordinary crystalline structure was suppressed, and supercooled amorphous phase was formed in the composite cooled to room temperature, and that cooling in a freezer induced the crystalline phase of which structure was different from that of the metallic alloy without polymers. The results of XRD well agreed with that of DSC which indicated the T_c of the metals in the composite was lowered by the interaction with polymers.

Transmitting electron microscopy

A typical TEM image of metals is shown in Figure 7(a). Metallic particles with various sizes were observed, and the diameters of small particles were $\sim$ 100 nm. The particles with diameters of $\sim$ 100 nm seem to be formed by aggregation of smaller particles with diameters of 20–50 nm as shown in Figure 7(b). Because the samples were prepared by removing PnBA in the suspension of THF, the metallic particles could aggregate in the process of drying the suspension. The image in Figure 7(a) clearly indicates the existence of metallic particles with diameters of $\sim$ 100 nm in the composite, and also
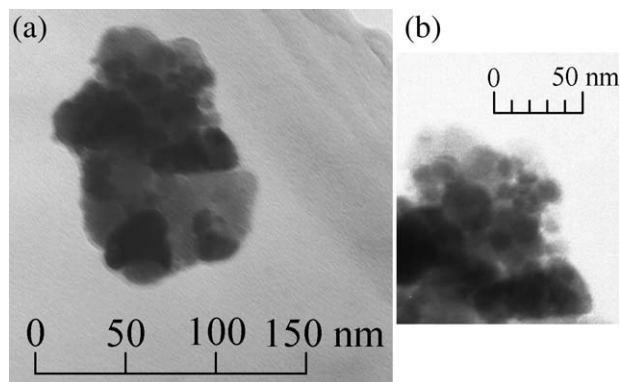

Figure 7 TEM images of metallic particles in the composite of PnBA and the metallic alloy composed by Bi, In, and Sn (63 wt % and 18 vol % of metals). The particle in Figure 7(a) seems to be formed by aggregation of smaller particles as shown in Figure 7(b). The scale bars indicate 150 nm in Figure 7(a) and 50 nm in Figure 7(b).

suggests the existence of particles with diameters of 20–50 nm.

Melting and crystallization mechanism of metals in the composites

Based on the experimental results, we propose a mechanism of melting and crystallization of metals in the composite as follows. Because the volume fraction of the metals in the composites was less than 14% in our composites, metals form isolated domains in polymer matrix above T_m of metals without polymers and T_g of polymers. As the interaction between metals and polymers was so strong, the high affinity between metals and polymers divided metallic particles into small particles with diameters of 20–50 nm as shown in the TEM images in Figure 7.

It is widely accepted that the T_m of nano-sized particles is lower than that of the same metal in bulk phase.[26–31] Lai et al.[31] prepared Sn particles with diameters of 10–100 nm, and measured their T_m. The T_m of the nanoparticles decreased significantly below 50 nm, and the T_m of Sn particles with a diameter 10 nm was 78°C lower than that of Sn in bulk phase. The endothermic peak at the temperature lower than T_m of metals without polymers was quite reasonable as the melting peak of nano-sized particles observed in Figure 7.

The depression of the crystallization of metals can be explained by the interaction between metals and polymers. Above the T_m of metals without polymers, the whole particle was liquid where Bi, In, and Sn atoms were homogeneously mixed, though the interfacial region of metals had different mobility due to the interaction with polymers. The metallic atoms need to diffuse to form micro-phases with metallic components of eutectic crystals for the crystallization. Because the mobility of the metals at the interface was restricted by the interaction with polymers, metallic atoms at the interface could not diffuse to crystallize. As a result, the crystallization just below the T_m of metals without polymers was strongly restricted and amorphous phase of metals was formed at the interface.

CONCLUSIONS

Composites of poly(n-buthyl acrylate) (PnBA) and eutectic metallic alloy composed of Bi, In, and Sn were prepared by mechanically mixing above the melting temperature T_m of the metallic alloy, and glass transition temperature T_g of the polymer. The heating curve of differential scanning calorimetry (DSC) for the composite of PnBA and the metallic alloy had an endothermic peak below the T_m of the metallic alloy without polymers, although the heating curve for the composite of poly(methyl methac-

rylate) and the metallic alloy was essentially same as that of the metallic alloy without polymers.

The peak of the crystallization in the cooling curve of the composite of PnBA and the metallic alloy was broadened, and the peak temperature was significantly lower than that of the metallic alloy without polymers. The change of the crystalline structure of the metals in the composites was investigated by X-ray diffractomery (XRD). No distinct peak was observed in the XRD pattern of the composite cooled to room temperature. Although some peaks were detected in the XRD pattern of the composite cooled to ca. −20°C, this pattern was different from that of the metallic alloy without polymers. Both results of the DSC and XRD measurements showed the very slow crystallization and the depression of crystallization at room temperature.

The images obtained by a transmitting electron microscope (TEM) showed the existence of metallic particles with diameters of ∼ 100 nm, which seemed to be formed by aggregation of smaller particles with diameters of 20–50 nm. For it has been reported that the T_m of nano-sized metallic particles is lower than that of the same metal in bulk phase,[26–31] the nano-sized particles can explain the endothermic peak below the T_m of the metal in bulk phase.

The experimental results shown above indicated that the interaction with polymers forms the phase of the metals with lower melting temperature, and suppressed the crystallization of the metals in the composites of polyacrylates and the metallic alloy.

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