Polymer Bulletin

Thermal Properties of Polyacrylates at Metal Interfaces

**Kazutaka Fukui, Shinjiro Honmura, Kazuhiro Iida, Yasuhiro Matsuda (✉),
Atsushi Sugita and Shigeru Tasaka**

Department of Materials Science and Chemical Engineering, Faculty of Engineering,
Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8561, Japan
E-mail: tymatud@ipc.shizuoka.ac.jp

Summary

The thermal properties of polyacrylates films sandwiched with metal were studied by differential scanning calorimetry. There were two glass transition relaxations, and the relaxation at the lower temperature, which was almost the same as the glass transition temperature of a bulk sample, diminished with thinning the polymer film. The glass transition relaxations at the higher temperature can be explained by the segmental motion of polymer chains interacting with metal surfaces at the interface. The results for the dielectric measurements for the sandwiched films also showed the similar relaxation modes.

Introduction

The physical properties of polymer chains at the interface between polymer and a substrate or at the surface between polymer and the air dominates the adhesion, durability, and biocompatibility of polymer materials. [1] The characteristics of polymer chains at interface or surface are investigated by measuring the physical properties of thin polymer films prepared by solution casting or spincasting methods. Since Beaucage et al. [2] had determined the glass transition temperature (Tg) of thin films by ellipsometry, many researchers measured Tg of thin polymer films by ellipsometry [3], X-ray reflectivity [4], Brillouin light scattering [5], and positron spectroscopy [6]. Lin et al. [7] estimated the mobility of polymer segments by deuterium NMR to show the higher mobility of polymer segments than that in the bulk phase.

Kajiyama [8] investigated the molecular motion of polystyrene (PS) with narrow polydispersity at the surface by scanning viscoelastic microscopy and lateral force microscopy for a thin film of the PS. They concluded that the Tg of PS at the surface was lower than that of corresponding PS in the bulk phase. The thermal behaviors of polymer at the interface were also reported for poly(methyl methacrylate) (PMMA) adsorbed on silica [9]. The thermograms showed two distinct peaks which were assigned as the Tg of PMMA in bulk phase and that of PMMA forming hydrogen bonds between silanol and carbonyl groups.

There have been also many reports on the interaction between polymer chains and metal, such as that between aromatic rings and aluminum [10], Al-C bonds at the

interface of aluminum and poly(ethylene terephtalate), polypropylene or polyethylene [11-13], Al-O-C complexes at the interface of poly(vinyl alcohol) and trimethyl-aluminum [14,15], and Al^+COO^- bonds[16-18].

In this paper, we investigated the surface interaction between polyacrylates (PAs) and metal, which enables PAs to act as adhesives in the electric industry and automobile industry. The thermal properties and molecular mobility of polyacrylates sandwiched by Al or Ag were estimated by differential scanning calorimetry (DSC) and dielectric relaxation measurements.

Experimental

2.1 Samples

Three samples of polyethylacrylate (PEA) were used for this study. One sample with broad polydispersity was purchased from Aldrich, and the two samples with narrow polydispersity were the products of Polymer Source Inc. Polybutylacrylate (PBA) and polybutylmethacrylate (PBMA) with broad polydispersity were purchased from Aldrich. The weight average molecular weight M_w and the ratio of M_w and number average molecular weight M_n of these samples are summarized in Table 1. Tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries.

The sandwiched films of the polymers were prepared as follows. Aluminum (Al) or silver (Ag) was evaporated onto glass substrates with a vacuum evaporator, JEE-400 (JEOL Datum Ltd.). Thin films of the polymers were prepared on these glass substrates by casting THF solutions. The same metal was evaporated onto these films to increase the area of the interface between the polymer and the metal.

The thickness of the polymer films were determined with a polarizing microscope (Labophot-Pol, Nikon Corperation) equipped with an optical multiple-beam inter-ferometer.

Table 1 The molecular weight and polydispersity of PA samples.

polymer	$M_w / 10^3$	M_w / M_n
PEA	82.0	3.44
PEA	23.8	1.07
PEA	5.50	1.06
PBA	99.0	
PBMA	337	

2.2 Differential scanning calorimetry

The sandwiched films were scratched from the glass substrates with a scraper and packed into Al pans. The sample mass of DSC samples were more than 1 mg. We also prepared metal-coated glass substrates and scratched them to obtain metal powder for the reference samples of DSC measurements. The thermal properties were measured with DSC-60 (Shimadzu Corporation) under nitrogen atmosphere at a heating rate of 20°C/min. The samples were first heat above 100°C to remove the absorbed water and gases, then were cooled to -100°C and reheated for measurements to 100°C.

2.3 Dielectric relaxation measurement

Dielectric analyses were conducted with an LCR meter HP4284A (Yokogawa-Hewlett-Packard) for PA films sandwiched with Al. The applied voltage was 200 mV,

and the frequency was 1 kHz. The samples were heated at 3°C/min. The area of the electrode was ca. 9 mm².

2.4 Infrared spectrometry

Infrared (IR) spectra of PA thin films on Ag-coated glass substrates (not sandwiched films) were measured with FTIR-8900 (Shimadzu Corporation) equipped with a re-flection absorption spectroscopy unit. IR spectral measurements of thin films of PAs on the glass substrates without Ag-coating were also carried out for the comparison.

Results

3.1 Differential scanning calorimetry

Figures 1-3 show the DSC curves of bulk samples of polymers and polymer films sandwiched with metal. While the DSC curve for PEA ($M_w = 8.20 \times 10^4$) film with the thickness of 510 nm sandwiched with Ag was essentially identical to that for bulk sample of PEA, another Tg signals at ca. 30°C were observed for the DSC curve of thinner films of PEA, and no original Tg could be detected for the film with the thickness of 40 nm in Figure 1. These results strongly suggests that the Tg signals at ca. 30°C were caused by the glass transition of PEA chains at the interface of which mobility was restricted by the interaction between the metal interface. Although a very small endothermic signal was observed at 30°C in the DSC curve of PEA film with the thickness of 510 nm, the weight fraction of restricted PEA chains to the whole PEA was too low to show a clear signal. On the other hand, the weight fraction of bulk PEA was too small for the PEA film with the thickness of 40 nm to have bulk Tg.
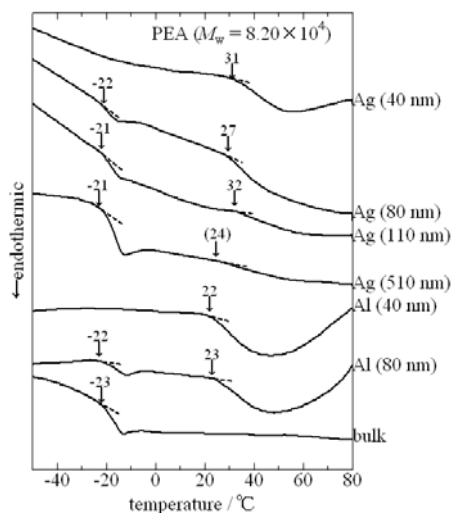

Figure 1. DSC curves for PEA ($M_w = 8.20 \times 10^4$) films with different thickness sandwiched with Al or Ag. The thicknesses of the films are shown in the numbers in parentheses. The numbers above the curves show Tg.
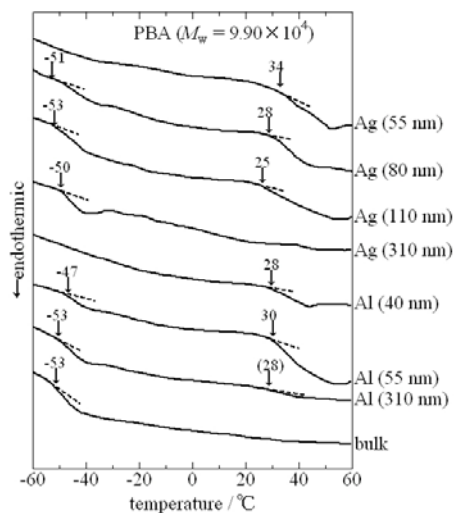
Figure 2. DSC curves for PBA ($M_w = 9.90 \times 10^4$) films with different thickness sandwiched with Al or Ag. The thicknesses of the films are shown in the numbers in parentheses. The numbers above the curves show Tg.

The similar additional Tg signals were observed for PBA films in Figure 2. The additional Tg signals appeared for PEA and PBA films sandwiched with bothe Ag and Al as shown in Figures 1 and 2. We prepared polymer films sandwiched with nickel or gold in the same procedure, and obtained essentially the same DSC curves.

PBMA films had Tg at around 30°C, but this is the Tg of PBMA in bulk phases, which has rigid main chain for the steric effect of its α-methyl group. No additional Tg signals were observed for PBMA films sandwiched with Ag or Al. Although the detailed reasons why PBMA films had no additional Tg could not be elucidate, its α-methyl group may interrupted the interaction between PBMA and metals, because PBA bearing no α-methyl group had Tg of its restricted chains.

In order to clarify whether PEA chains interact with metals at its chain ends or not, DCS measurements were carried out for the sandwiched films prepared from PEA with different molecular weights. If PEA interacts with metals at their chain ends, PEA with lower molecular weight will have the additional Tg for thicker films, and the Tg of bulk phase will disappear for thinner films. Figure 4 describes the DSC curves of PEA ($M_w = 2.38 \times 10^4$ and 5.50×10^3) films with different thickness. The DSC curves showed no molecular weight dependence, which implied that PEA did not interact with metals at their chain ends.
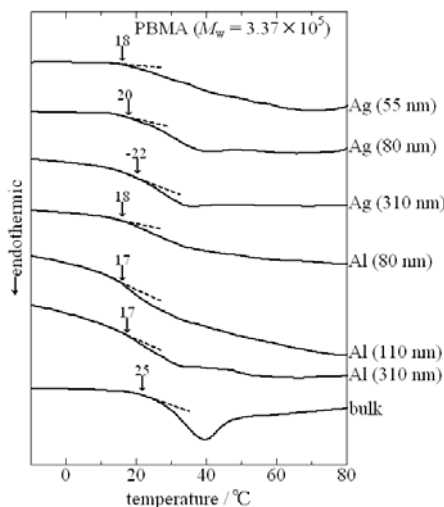

Figure 3. DSC curves for PBMA ($M_w = 3.37 \times 10^5$) films with different thickness sandwiched with Al or Ag. The thicknesses of the films are shown in the numbers in parentheses. The numbers above the curves show Tg.
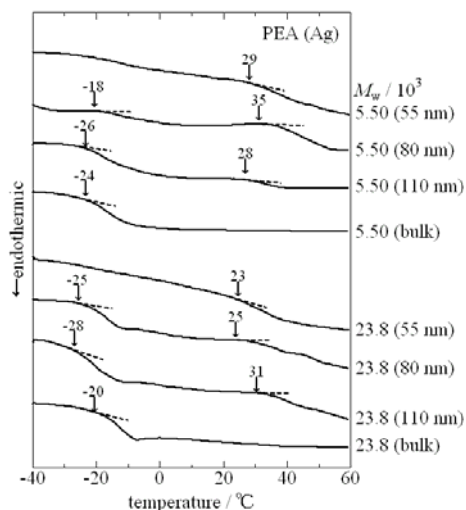
Figure 4. DSC curves for films of PEA with different molecular weight sandwiched with Al or Ag. The thicknesses of the films are shown in the numbers in parentheses. The numbers above the curves show Tg.

3.2 Dielectric relaxation measurement and Infrared spectrometry

In order to clarify the mechanism of the interaction between PAs and metals, we focused on the mobility of the carbonyl groups and made dielectric relaxation measurement and infrared spectrometry for PA films. Figures 5-7 summarize tan δ for the sandwiched films of PEA ($M_w = 8.20 \times 10^4$), PBA, and PBMA at different temperature.

The tan δ for thick (more than 80 nm) films of PEA have single relaxation peaks of glass transition of polymers in the bulk phases at the temperatures which are slightly higher than Tg observed by DSC. Double peaks were observed for thin films of PEA, as the similar way for DSC curves. While the double peaks also appeared for PBA films thinner than 17 nm, no double peaks were observed for PBMA even for the film with thickness of 17 nm.
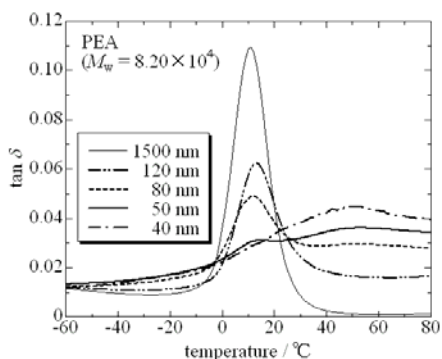

Figure 5. The temperature dependence of tanδ for PEA ($M_w = 8.20 \times 10^4$) films with different thickness on glass substrates coated with Ag.

Figure 6. The temperature dependence of tanδ for PBA ($M_w = 9.90 \times 10^4$) films with different thickness on glass substrates coated with Ag.
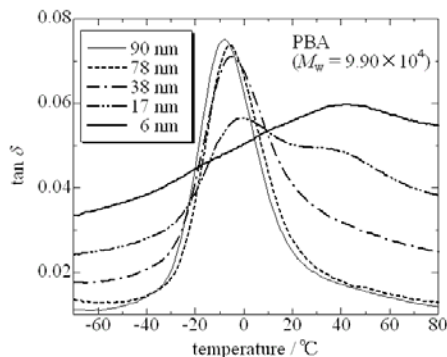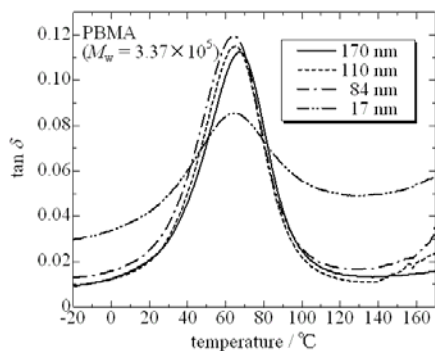

Figure 7. The temperature dependence of tanδ for PBMA ($M_w = 3.37 \times 10^5$) films with different thickness on glass substrates coated with Ag.

As the dielectric relaxation of PAs reflects mainly the mobility of carbonyl groups, the additional peak can be explained by the glass transition of polymer chains of which thermal motion was restricted by their carbonyl groups oriented normal to metal surface.[19-21]

Table 2 summarizes the wavenumber at the peaks of carbonyl stretching bands for PAs. The peak wavenumber of PA films on glass substrates coated with Ag was higher than that of PA on glass without Ag-coating. Because the wavenumber of an IR band is generally decreased by the interaction of the chemical groups with surface, this peak shift seems to be a little strange for that of carbonyl groups interacting metal

surface. However, if the interaction between carbonyl groups and metal disturbs other specific interaction of the carbonyl groups, the band of the carbonyl groups can shift to higher wavenumber. Although the detailed structural change of the polyacrylates by the interaction with metal has not been clarified in this study, the shift of the IR band shown in Table 2 supports the structural change of the carbonyl groups induced by the interaction with metal surface.

Table 2 The wavenumber at the peaks of carbonyl stretching bands for PA films.

polymer	glass substrate	wavenumber / cm^{-1}
PEA[a]	not coated	1735
PEA[a]	Ag-coated[b]	1740
PBA	not coated	1735
PBA	Ag-coated[b]	1740
PBMA	not coated	1728
PBMA	Ag-coated[b]	1731

[a] $M_w = 8.20 \times 10^4$. [b] The thickness of the polymer films were 55 nm.

Discussion

It has been reported that polymer chains adsorbed at the interface [9] or in the composite with fillers [22-24] have higher Tg than that of corresponding polymers in bulk phases. There are mainly three factors for the higher Tg; chemical bonds between the polymer chain ends and the substrates, surface segregation, and the dipole interaction between the polar polymers and metal interface. As demonstrated in Figure 4, the independence of the double Tg behavior on the molecular weight of the polymers suggests that there were no chemical bonds between the polymer chain ends and metal substrate. The results of dielectric relaxation measurements and IR spectrometry support the existence of the dipole interaction between PEA and PBA and surface metals.

The results of DSC, dielectric relaxation, and IR measurements suggest that the interaction of the carbonyl groups in PEA and PBA, and metal interface restricts the molecular motion of polymer chains causing the additional Tg observed DSC. As the bulkiness of the methyl groups interrupts the interaction between carbonyl groups and metal interface, no additional Tg and dielectric relaxation mode of restricted chains were detected for PMBA films.

Conclusions

DSC measurements were carried out for the polymer films of PEA, PBA, and PMBA sandwiched with Ag or Al films. Additional Tg were observed for PEA and PBA films at the temperature which was higher than the Tg in their bulk phases, while no additional Tg were detected for PMBA films. The additional Tg became clearer and the Tg in their bulk phases faded by thinning the polymer films.

The DSC curves for the sandwiched PEA were independent of the molecular weight of PEA, which suggests that the interaction between PEA and the metals was not the chemical bonds between the chain ends and surface metals. The results of dielectric relaxation measurements and IR spectrometry for PEA show the interaction between the carbonyl groups in PEA and the metal surface.

Considering theses results, we conclude that the most plausible cause of the additional *T*g was the glass transition of the PEA or PBA chains of which molecular motion was restricted by the alignment of their carbonyl groups. As the alignment of the carbonyl groups in PMBA was interrupted by its methyl groups, no additional *T*g was observed for PMBA.

References

1. Tretinnikov ON, Nakao K, Ohata K, Iwamoto R (1996) Macromol. Chem. Phys. 197:753
2. Beaucage G, Compost R, Stein RS (1993) J. Poly. Sci. Polym. Phys. Ed. 31: 319
3. Keddie JL, Jones RAL, Cory RA (1994) Europhys. Lett. 27:59
4. Wallace WE, van Zanten JH, Wu WL, (1995) Phys. Rev. E. 52:R3329
5. Forrest JA, Dalnoki-Veress K, Dutcher JR (1997) Phys. Rev. E. 56:5705
6. DeMaggio GB, Frieze WE, Gidley DW, Zhu M, Hristov HA, Yee AF (1997) Phys. Rev. Lett. 78:1524
7. Lin WY, Blum FD (2001) J. Am. Chem. Soc. 123:2032
8. Kajiyama T, Tanaka K, Satomi N, Takahara A, (2000) Sci. Tech. Adv. Mater. 1:31
9. Blum FD, Young EN, Smith G, Sitton OC, (2006) Langmuir 22:4741
10. Pireaux JJ, (1994) Synth. Met. 67:39
11. Bou M, Martin JM, Le Mogne T, Vovelle L (1991) Appl. Surf. Sci. 47:149
12. Marcus P, Hinnen C, Imbert D, Siffre JM, (1992) Surf. Interf. Anal. 19:127
13. DeKoven BM, Hagans PL (1986) Appl. Surf. Sci. 27:199
14. Akhter S, Zhou X-L, White JM (1989) Appl. Surf. Sci. 37:201
15. Cotton FA, Wilkinson G (1966) Advanced Inorganic Chemistry, A Comprehensive Text. 2nd ed. Interscience, New York
16. Schultz J, Lavielle L (1989) Makromol. Chem. Macromol. Symp. 23:343
17. Rancourt JD, Hollenhead JB, Taylor LT (1993) J. Adhesion 40:267
18. Gerenser LJ, ACS Symp. Ser. (1990) 440:433
19. Tasaka S, Ohta H, Inagaki N IEEE Trans. Ultrason. Ferroelect. Freq. Contr., 47,1316 (2000).
20. J. Ide, S. Tasaka and N. Inagaki, Jpn. J. Appl. Phys., 38,2042 (1999).
21. J.S. Sharp and J.A. Forest, Eur. Phys. J. E 12, s01, 023(2003)
22. Zhang W, Li Y, Wei L, Fang Y, (2003) Mater. Lett. 57:3366
23. Xie T, Yang G, Fang X, Ou Y, (2003) J. Appl. Polym. Sci. 89:2256
24. He JP, Li HM, Wang XY, Gao Y (2006) Eur. Polym. J. 42:1128