Study on surface structure of amorphous polymer blends on the basis of lateral force microscopy

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Abstract

The relationship between glass transition temperature (T_g) and lateral force of amorphous polymer blends composed of components having T_g's lower and higher than room temperature (295 K) was studied on the basis of lateral force microscopy (LFM). Although the lateral force for the homopolymer is deeply related to its surface viscoelastic property or T_g, the LFM results revealed that the lateral force dependence on the scan rate of the miscible polymer blends, [poly(methylacrylate)/poly(vinylacetate)] and [polystyrene/poly(vinylmethylether)], was similar with that of the component whose lateral force behavior shows the dependence on the scan rate, regardless of their T_g. This result suggests that the lateral force of miscible polymer blend reflects the sum of each component contribution, depending on the surface structure of the blend. Therefore, it was concluded that the information about surface structure can be obtained from the measured lateral force behavior of a miscible polymer blend. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Lateral force; Thermal molecular motion; Surface structure

1. Introduction

Surface structure of polymeric solid films is one of the emerging research fields since there are several differences in the aggregation state and the thermal molecular motion between surface and bulk. Although much emphasis was placed on understanding the surface structure of homopolymers and multiphase polymer blends [1–3], little was known about their surface mechanical properties on the molecular level such as adhesion, lubrication, wear and friction. Surface mechanical properties of polymeric solids might be closely related to the thermal molecular motion and the aggregation state at the surface, which are thought to be directly linked to the inherent properties of polymers such as the glass transition temperature (T_g).

The surface frictional force is expected to be dependent on the thermal molecular motion at the surface as well as in the bulk. The equation relating the frictional force (F) to damping was proposed by Tabor and co-workers [4]. And it is given by Eq. (1).

$$F = K(G)^{\frac{1}{3}} \tan \delta \qquad (1)$$

where G, $\tan \delta$ and K are the dynamic shear modulus, dynamic damping and a constant, respectively. As a result

of the relationship between the dynamic mechanical properties and the friction force behaviors, the temperature and scan rate dependence of friction should follow a time-temperature superposition principle. Therefore, the frictional force of multiphase polymer blends is deeply related to their molecular motions. Recently, the frictional properties of surfactant monolayer surfaces [5,6] and homopolymers [7–10] were investigated by scanning force microscopy. However, few of them dealt with the relationship between their lateral force behaviors and viscoelastic properties of the multiphase polymer blends in terms of surface composition or property.

In this study, the relationships between lateral force behavior and T_g of amorphous polymer blend pairs having T_g's above or below room temperature (*RT*), such as [poly(methylacrylate)/poly(vinylacetate)] (PMA/PVAc) and [polystyrene/poly(vinylmethylether)] (PS/PVME) blends, were investigated on the basis of lateral force microscopy (LFM) observation under different scan rates and then the results were compared with their viscoelastic properties.

2. Experimental

2.1. Materials and film preparations

PMA was synthesized by radical polymerization using

Table 1
Materials used in this study

Polymer	M_w	M_w/M_n	T_g(K)	γ_{SV} (mN M^{-1})	Purification (solvent/nonsolvent)	Source
PS	338 k	2.38	374	40.2	Benzene/Methanol	Ube Co.
PVME	77 k	1.98	249	36.0	Toluene/n-Hexane	Polym. Sci
PMA	274 k	1.93	287	44.7	Benzene/Methanol	Synthesized
PVAc	79 k	1.23	304	37.2	Acetone/n-Hexane	Junsei
PMMA	120 k	2.00	390	42.6	Benzene/Methanol	Aldrich

2-azobisisobutyronitrile at 433 K for 40 min in benzene. Purification of the PMA was accomplished by reprecipitation in methanol from benzene solution followed by drying in a vacuum oven until kept at a constant weight. All other homopolymers were commercially available and purified by the similar method described as PMA using different solvent/nonsolvent pairs listed in Table 1. Characteristics of homopolymers used in this study are listed in Table 1. The molecular weights were determined by gel permeation chromatography with polystyrene standard. The surface free energy, γ_{sv}, was estimated by the contact angle using Owens' method [11]. In order to compare the effects of T_g's of homopolymers and those of polymer blends on the lateral force at the surface, the polymer blend systems were prepared by polymer pairs with T_g's above and below the RT (i.e. 295 K), for example, (PMA/PVAc) and (PS/PVME) blend systems. Blend films were obtained by spincoating on Si wafer and casting on glass for measurements of surface property and bulk, respectively. Acetone was used as a solvent for (PMA/PVAc) system, while toluene was used as a solvent for (PMA/PMMA) and (PS/PVME) systems.

2.2. Bulk characterization

The T_g's of homopolymers and blends were measured by differential scanning calorimetry (DSC 3200, Mac Science Co.) calibrated with pure indium as a standard. In order to avoid the effect of residual stress from the samples packed in the aluminum pan and to remove any small traces of solvent, samples were heated to a temperature 30 K above its T_g and then cooled to 253 K. Thermograms were

Fig. 1. Lateral force versus scan rate for various polymers under 5 nN, as load.

obtained at a heating rate of 10 K min^{-1}. All T_g's were evaluated from the halfheight of the heat capacity jump.

2.3. Surface characterization

The surface chemical composition of the (PS/PVME) blend film was evaluated on the basis of X-ray photoelectron spectroscopic (XPS) measurement. The XPS spectra were obtained with an ESCA 750 (Shimadzu Co. Ltd.) using MgKα with emission angle, 90°. Then, the analytical depth of XPS was ca.10.5 nm [12]. The surface composition, the average PVME weight fraction, was evaluated on the basis of the ratio of the XPS peak intensities for the neutral carbon (at 285 eV) and the ether carbon (at 286.5 eV). The C_{1s} spectra for the (PS/PVME) blend films were deconvoluted into the three peaks corresponding to the neutral carbon, the ether carbon, and the shake-up of π-π^* of the benzene ring by a standard nonlinear curve fitting. Then, the PVME weight fraction, w was calculated by Eq. (2).

$$\frac{I_{c-o}}{I_{total}} = \frac{2w/M_{VME}}{8(1-w)/M_S + 3w/M_{VME}} \qquad (2)$$

where I_i is the intensity of each core-electron photoemission spectrum. M_S and M_{VME} are the molecular weights of the styrene and vinyl methyl ether repeat units, respectively.

2.4. Lateral force measurement

Lateral forces of homopolymer and their blend surfaces with various scan rates and loads were investigated on the basis of LFM observation. The AFM and LFM images were obtained by a scanning force microscope, SPA 300 instrument with SPI 3700 controller (Seiko Instrument Co.) at RT. The cantilever used in this study is rectangular one with a Si_3N_4 quadrangular pyramid microtip (Olympus Co.). The bending spring constant of the cantilever is 0.09 N m^{-1}. In order to avoid the lateral force caused from cantilever bending, the scanning direction was perpendicular to the long axis of the cantilever. Details for the LFM measurement were reported elsewhere [13]. The measured lateral force might reflect the tribological properties, mainly, related to the frictional phenomenon between sample surface and cantilever tip. The dependence of the lateral force on the scan rate was investigated under the scan rate on the range of 0.3 to 100 μm sec^{-1}, and under the repulsive force of 5 nN at RT unless otherwise specified.

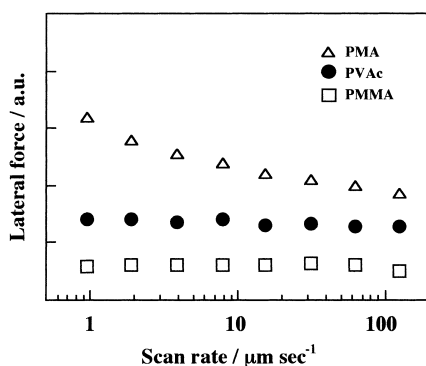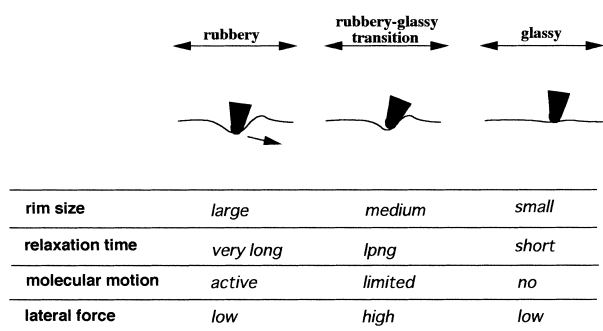Fig. 2. Schematic representation of the surface deformation in the three phase states during sliding.

3. Results and discussion

Fig. 1 shows the variation of the lateral force for the various homopolymers with the scan rate. The PMA, which is in a rubbery-like state at *RT*, showed the highest lateral force and the largest scan rate dependence among the three homopolymers investigated, regardless of the scan rate. The lateral force of PVAc depended slightly on the scan rate and was higher than that of PMMA, because thermal molecular motion of PVAc is more active than that of PMMA at *RT* owing to their much different T_g, even though the T_g's of both polymers are higher than *RT*. In the case of PMMA with T_g higher than *RT*, the magnitude of the lateral

Fig. 3. 2D-LFM image (A) and 3D-LFM image with two different scan rates (B) under 5 nN for (PMA/PMMA 95/5 w/w) blend film.

force did not show any dependence of the scan rate. Thus, the result suggests that the lateral force dependence on the scan rate of a homopolymer is strongly related to the magnitude of the difference between its T_g and reference temperature (here *RT*).

The measured lateral force is strongly related to the energy required to deform the polymer by the cantilever tip and its surface viscoelastic property [14]. In the glassy state, the deformed surface is immediately recovered and the stored elastic energy moves into the sliding tip as a result of very short relaxation time. Thus, the total energy loss is small. In the rubbery state, it is difficult to recover the elastic energy owing to a long relaxation time, but the energy to build up the rim is much smaller than that of glassrubber transition state. Therefore, the lateral force is low. In the glassrubber transition state, however, the dissipation of energy is high and then the lateral force shows a maximum, since the formation of the rim needs high energy owing to the limited molecular mobility and the relaxation time is not enough to recover the deformed surface. Thus, it may be said that the lateral force might be proportional to the tan δ as observed in the case of the rolling friction [15–17]. Fig. 2 shows the schematic representation of a rim formed at the forehead of cantilever tip as the tip slides over polymeric solids.

To study the contribution of T_g for a lateral force behavior of the binary blend, the lateral force dependence on the scan rate of the blend pair having T_g's lower and higher than *RT*, was investigated on the basis of the LFM measurement. Fig. 3 shows line scans and LFM image obtained simultaneously with two different scan rates of the (PMA/PMMA 95/5 w/w) blend film, where the blend film was in a phase-separated state. It is expected that the PMMA domain and the PMA matrix can be apparently distinguished on the basis of the result of lateral force behaviors shown in Fig. 1; the lateral force of PMA decreased with increasing the scan rate and was higher than that of PMMA whereas the lateral force of PMMA did not show any dependence on the scan rate. Therefore, it seems reasonable to conclude that the bright and the dark are composed of PMA-rich and PMMA-rich phases, respectively.

However, in the case of the miscible polymer blend, the measured lateral force behavior should reflect the thermal molecular motion of blend because surface mechanical property of polymeric solids is closely related to the thermal molecular motion and the aggregation state at the surface. Fig. 4 shows the line scans on (PS/PVME 99/1 w/w) blend film surface with various scan rates. The surface-layer T_g of the (PS/PVME 99/1 w/w) blend film, was estimated from the bulk T_g and surface chemical composition calculated by XPS result, was ca. 325 K as shown in Table 2. Although the surface T_g of this blend is higher than *RT*, the lateral forces for this blend increased with the scan rate. In the case of (PS/PVME) blend films with 80/20 and 70/30 compositions whose T_g's are lower than *RT*, however, similar lateral force dependence on the scan rate was observed. These
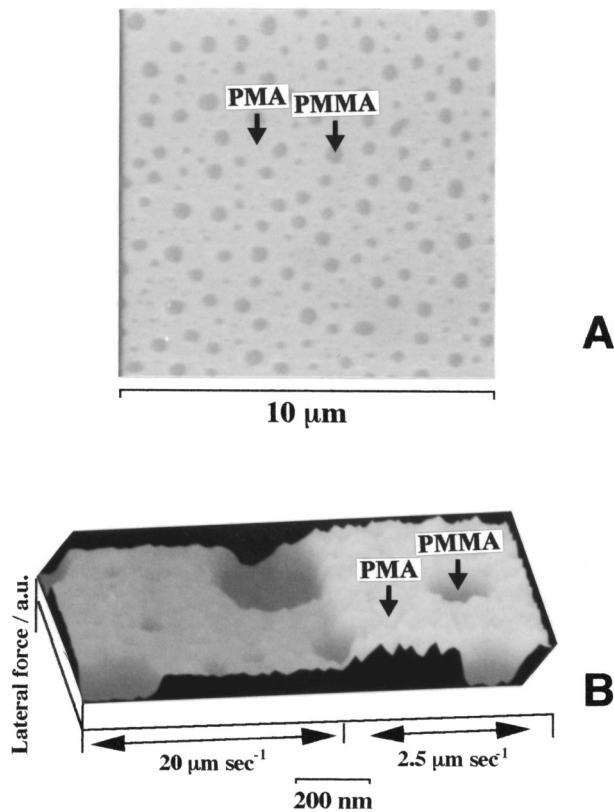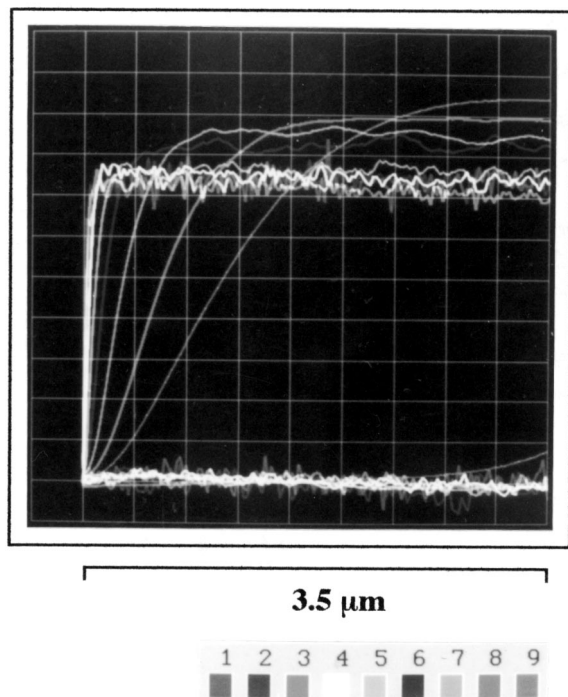
Fig. 4. Loop scans of (PS/PVME 99/1 w/w) blend film with various scan rates under 5 nN, as load. (1: 0.3, 2: 0.7, 3: 1.3, 4: 2.6, 5: 5.2, 6: 10.4, 7: 20.9, 8: 41.8, 9: 83.5 μm·sec^{-1}).

Fig. 5. T_g's of (PMA/PVAc) blends measured by DSC.

results are not in accord with those of the homopolymer with T_g higher than *RT*. This indicates that the lateral force dependency on the scan rate of a miscible blend is clearly different to that of the homopolymer related with its T_g or tan δ behavior at the measured temperature. Take it into consideration that the lateral force of PMMA having T_g higher than *RT* was independent on the scan rate, this result indicates that the lateral force dependence on the scan rate of the miscible blend is governed by the component whose lateral force is changed with the scan rate (here PVME), regardless of blend T_g. Although the measurement of lateral force of PVME is difficult owing to strongly stick property, therefore, it might be expected that the lateral force of PVME increases with increasing the scan rate. This assumption is well supported by the relation between viscoelastic property and lateral force behavior of homopolymer.

To obtain more information from the lateral force behavior of the miscible blend, the lateral force behavior of miscible (PMA/PVAc) blend film was also investigated. Since DSC curves of the (PMA/PVAc) blends show single glass transition in all blend composition, it can be concluded that PMA and PVAc are miscible, as shown in Fig. 5.

Recently, it was reported by Jones and Kramer that the total surface excess is more strongly dependent on the value of the Flory–Huggins interaction parameter between the segments of the two polymers than on the differences in surface energies between the components of the blend [3,18]. Casting solvent and film thickness also play an important role in influencing the surface composition of a blend [19]. The total surface excess of a low surface energy component, therefore, could not be estimated from the difference of surface energies and interaction parameter.

In order to study the lateral force behavior, it is important to know the surface-layer composition (a few nm thickness) of the blend film. In the case of (PMA/PVAc) blend, however, it is difficult to measure the surface chemical composition by XPS because the molecular structure of each component is very similar. Although the surface chemical composition in the top ca.1 μm of the surface, analytical depth, could be evaluated on the basis of attenuated total reflection infrared and transmission i.r. spectroscopic measurements, it is not principally an isotope effect because the lateral force measured by LFM is affected by the top few nanometers, i.e., surface property [13]. Fig. 6

Table 2
Surface composition, expected surface T_g and lateral force behavior of (PS/PVME) blend films from DSC, XPS and LFM measurements

	PVME weight fraction		T_g (K)		Lateral force[a]
	Surface	Bulk	Surface[b]	Bulk	
PS/PVME (70/30 w/w)	75	30	253	315	increasing
PS/PVME (80/20 w/w)	68	20	270	322	increasing
PS/PVME (95/5 w/w)	35	5	305	355	increasing
PS/PVME (99/1 w/w)	25	1	325	368	increasing

[a] As the scan rate is increased.

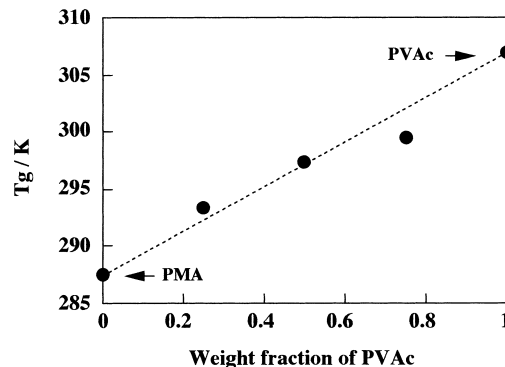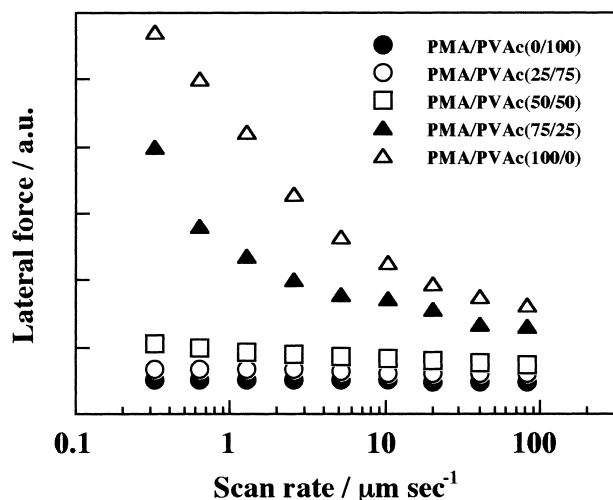[b] Evaluated from surface composition.

Fig. 6. Lateral force versus scan rate for (PMA/PVAc) blend films under 5 nN, as load.

assumption of the tip indent depth of ca.1.1 nm [13];

$$T_{g,\text{blend}} = \frac{(C_{\text{PMA}}W_{\text{B,PMA}}T_{g,\text{PMA}} + W_{\text{B,PVAC}}T_{g,\text{PVAC}})}{(C_{\text{PMA}}W_{\text{B,PMA}} + W_{\text{B,PVAC}})} \quad (3)$$

$$F_{\text{blend}} = C_{\text{PMA}}V_{\text{S,PMA}}F_{\text{PMA}} + (1 - V_{\text{S,PMA}})F_{\text{PVAc}} \quad (4)$$

$$W_{\text{S,PMA}} = \frac{V_{\text{S,PMA}}\rho_{\text{PMA}}}{(V_{\text{S,PMA}}\rho_{\text{PMA}} + V_{\text{S,PVAc}}\rho_{\text{PVAc}})} \quad (5)$$

where the subscripts S and B refer to the surface and bulk, respectively. As expected, the surface enrichment of PVAc having the lower surface free energy was observed, as shown in Fig. 7. Therefore, it can be concluded that the lateral force of a miscible polymer blend film can be strongly affected by the following two factors, that is, the surface composition and the rubbery-like component in blend regardless its T_g.

4. Conclusions

Since the LFM technique reflects the tribological properties at the surface, the lateral force measurement of the miscible polymer blend could provide the information about its surface structure owing to the close relationship between the dynamic mechanical properties and the frictional force. In this study, the relationships between surface structure and lateral force of miscible amorphous polymer blend systems, such as (PMA/PVAc) and (PS/PVME) blend films, were investigated on the basis of LFM observation under the conditions of scan rate 0.3 ~ 100 μm sec^{-1} and RT. From the results of (PMA/PVAc) and (PS/PVME) blend systems, it is concluded that the dependence of lateral force of a miscible blend on the scan rate is mainly controlled by the component showing the lateral force dependence on the scan rate, regardless of blend T_g. Also, the surface composition of miscible (PMA/PVAc) blend was determined by measuring the lateral force.

Acknowledgements

shows the effect of the scan rate on the lateral force of (PMA/PVAc) blend films. The lateral forces of all blends decreased with increasing scan rate, regardless of blend compositions and the slope was orderly changed with the blend composition. Considering the lateral force of homopolymer is related to its T_g (or dynamic mechanical property) and the magnitude of the lateral force of a miscible polymer blend reflects the sum of contribution of each component property, the information about the surface structure of a miscible blend film can be obtained from the measured lateral force values. The relative contribution constant (C) to each component in a blend might be calculated from T_g behaviors of the blend because of the close relation between the lateral force behavior and T_g of a homopolymer. (see Eq. (3)) The surface weight fraction of PMA ($W_{\text{S,PMA}}$) was estimated from Eq. (4) that the lateral force of the blend (F_{blend}) at constant scan rate is proportional to the combination with the fractional surface coverage of each component and C. The surface-layer volume (V_S) of each component in the blend can be converted to the surface-layer weight fraction (W_S) using density (ρ), under the
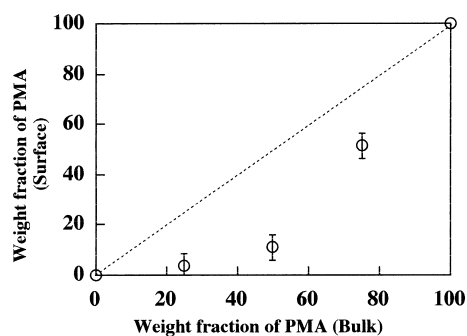
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Fig. 7. Surface weight fraction of PVAc calculated by Eq. (5).

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