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Relationships between lateral force and viscoelastic properties for amorphous polymer films based on lateral force microscopy

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Summary

The relationships between lateral force and viscoelastic properties of amorphous polymer surfaces with Tg's lower and higher than room temperature (295 K, RT) and their blend systems have been studied on the basis of lateral force microscopic (LFM) measurement. Under the conditions of scanning rate of 10^2 - 10^5 nm sec^{-1}, normal load of 5 nN and RT, the lateral forces of poly(methyl methacrylate) (PMMA) and polyisoprene (PI) homopolymers with Tg's fairly higher and lower than RT, respectively, did not depend on the scanning rate. Whereas, the lateral force of poly(methyl acrylate) (PMA) with Tg≤RT decreased with an increase in the scanning rate. Also, poly(vinyl acetate) (PVAc) with Tg≥RT showed slight dependence on the scanning rate. The scanning rate dependence of lateral force was similar to the frequency dependence of mechanical loss modulus. The results indicate that the magnitude of lateral force strongly depends on the state of thermal molecular motion. The lateral force-viscoelastic properties of miscible polymer blends was also investigated by LFM.

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 has been placed on understanding the surface structure of homopolymers and multiphase polymer blends (1~3), little has been known about their surface mechanical properties. 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 associated with the inherent properties of polymers such as the glass transition temperature, Tg.

The frictional force (lateral force) is expected to be dependent on the thermal molecular motion at the surface as well as the bulk. Recently, the frictional properties of solid (4) and surfactant monolayer surfaces (5) have been investigated with lateral force microscope (LFM). Also, the dependence on lateral force of scanning direction against {110} growth face of the polyethylene single crystal was reported by LFM observation (6).

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Table 1 Materials used in this study.

Polymer	Mw	Mw/Mn	Tg / K	γ_{sv} / mN·m^{-1}	Source
PMMA	120 k	2.0	390	42.6	Aldrich
PS	338 k	2.4	374	40.2	Idemitsu
PVAc	79 k	1.2	304	37.2	Junsei
PMA	274 k	1.9	287	44.7	Synthesized
PVME	77 k	2.0	249	36.0	Polymer Science
PI	52 k	1.6	210	35.0	Synthesized

However, studies on surface viscoelastic properties have been very few for amorphous homopolymers and polymer blends.

In this study, the relationships between lateral force characteristics and bulk viscoelastic properties for amorphous polymers with Tg's above or below room temperature (RT) and miscible binary blend systems have been investigated on the basis of LFM measurement under different scanning rates.

Experimental

Materials and film preparations

Poly(methyl acrylate) (PMA) and polyisoprene (PI) were synthesized by radical and anionic living polymerization. All other homopolymers were commercially available. Characteristics of homopolymers used in this study are listed in Table 1. The molecular weights were determined by gel permeation chromatography with a polystyrene standard. The surface free energy, γ_{SV}, was estimated by the contact angle using an Owens' method (7). In order to compare the effects of Tg's on the lateral force, the polymer pairs with Tg's above and below RT, for instance, the [PMA/poly(vinyl acetate)] [(PMA/PVAc)] and the [polystyrene/poly(vinyl methyl ether)] [(PS/PVME)] blend systems were used to prepare the polymer blends. The blend films were prepared by spin-coating on silicon wafer substrate and by casting on glass one for measurements of surface property and bulk one, respectively.

Bulk characterization

The Tg's of the homopolymers and the blends were measured by differential scanning calorimetry (DSC 3200, Mac Science Co.) calibrated with pure indium as a standard. The DSC thermograms were obtained at a heating rate of 20 K min^{-1}. All Tg's were evaluated from the half-height of the heat capacity jump. The dynamic mechanical properties of the homopolymers were investigated by Rheovibron DDV-01 FP (A & D Orientec Co., Ltd.) under the conditions of a heating rate of 2 K min^{-1}, a testing frequency of 3.5 Hz, and dried nitrogen purge.

Surface characterization

The surface chemical composition of the (PS/PVME) blend films was evaluated on the basis of X-ray photoelectron spectroscopic (XPS) measurement. The XPS spectra were obtained with an ESCA 850 (Shimadzu Co.Ltd.) using MgKα with an emission angle of 90

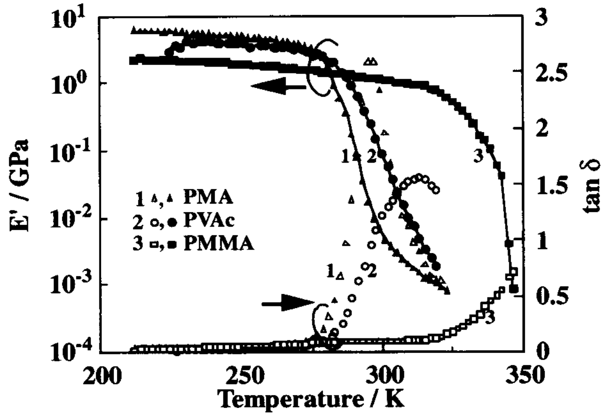


Figure 1 E' (filled symbols) and tan δ (open symbols) for PMA, PVAc and PMMA polymers at 3.5 Hz.

deg. Then, the analytical depth of XPS was ca.10.5 nm (8). Also, the attenuated total reflection Fourier transform infrared spectra (ATR FT-IR) and transmission IR spectra were obtained with FT-IR spectrophotometer (FT-IR 500, JASCO Ltd.). A Ge prism was used for ATR measurement. The analytical depth of ATR FT-IR ranged from 0.5 to 3 μm (9).

Lateral force measurement

Lateral forces of the homopolymers and their blends surfaces were investigated on the basis of LFM measurement with various scanning rates. LFM measurements were carried out by using a scanning probe microscope, SPA 300 instrument with SPI 3700 controller (Seiko Instrument Co.) at RT. The cantilever used in this study was the rectangular one with a Si_3N_4 pyramidal microtip (Olympus Co.). The bending spring constant of the cantilever was 0.09 Nm^{-1}. The scanning rate dependence of lateral force was investigated under the condition of the scanning rate from 10^2 to 10^5 nm sec^{-1} and the repulsive force of 5 nN at RT, unless otherwise specified.

Results and discussion

Dynamic mechanical analysis

The scanning rate dependence of lateral force for amorphous polymers has not been systematically studied. The relationships between frictional force and viscoelastic properties for rubber materials was reported by Grosch (10). He obtained a single master curve from temperature and scanning rate dependence on the basis of WLF equation (11). This indicates that the scanning rate dependence of frictional behavior corresponds closely to that of viscoelastic one. McLaren and Tabor (12) concluded that the frictional force characteristics were strongly related to the viscoelastic energy dissipation process.

In order to investigate the relationships between lateral force and viscoelastic behaviors of amorphous polymers at RT, the temperature dependencies of dynamic storage

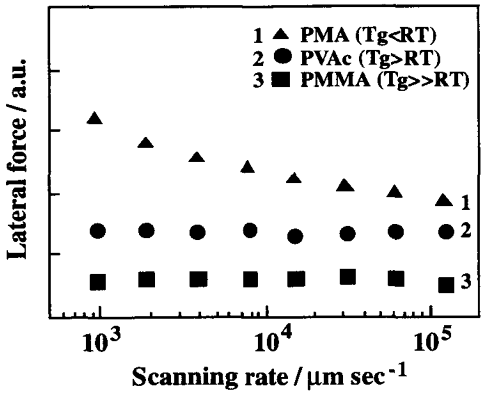


Figure 2 Scanning rate dependence of lateral force for various amorphous polymers at 293K under 5 nN as load.

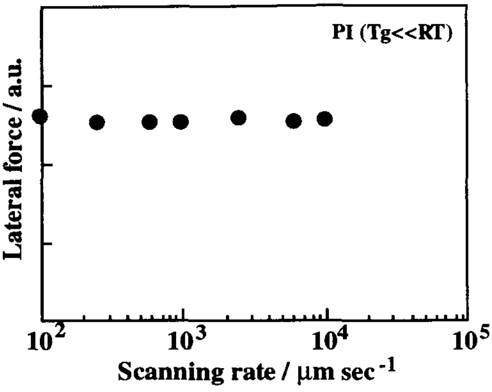


Figure 3 Scanning rate dependence of lateral force for PI at 293K under 10 nN as load.

modulus, E' and dynamic loss tangent, tan δ for various amorphous homopolymers were measured by Rheovibron as shown in Figure 1. The peak temperature of the α_a-absorption appeared in the order of poly(methyl methacrylate) (PMMA)>PVAc>PMA. Since the lateral force measurement was carried out at 293 K, the viscoelastic properties at 293 K become decisively important to understand the lateral force characteristics for these amorphous polymers. The temperature at which the tan δ curve deviates from the almost constant baseline, can be defined as Tg. Therefore, Tgs of PMA and PVAc are lower than RT, and Tg of PMMA is higher than RT. This result agreed well with DSC result as shown in Table 1. Since the tan δ maximum appeared at a temperature much lower than RT in the cases of PI and PVME, Tgs of PI and PVME are much lower than RT, which well correspond to Tgs measured by DSC of 210 K and 249 K.

Lateral force of homopolymers

Figure 2 shows the variation of lateral force with the scanning rate for the various amorphous homopolymers. The PMA in a glass-rubber transition state at RT showed the most distinct scanning rate dependence of lateral force among the three homopolymers investigated. The lateral force of PVAc slightly depended on the scanning rate, because thermal molecular motion of PVAc was more active than that of PMMA at RT due to their much different Tg even though Tg's of both polymers are higher than RT. In the case of PMMA with Tg much higher than RT, the magnitude of lateral force did not show any scanning rate dependence. Figure 3 shows the scanning rate dependence of lateral force for PI at RT. Since PI was in a rubbery state at RT, it is quite difficult to evaluate lateral force under the same condition as PMA, PVAc and PMMA. Thus, the lateral force measurement of PI was carried out at the scanning rate region from 10^2 - 10^4 nm s^{-1}. Figure 3 clearly indicates the magnitude of lateral force is independent of the scanning rate. Thus, the result suggests that the lateral force behavior on the scanning rate for various amorphous homopolymer is strongly dependent on the Tg in comparison with RT, because the lateral force measurement was carried out at RT.

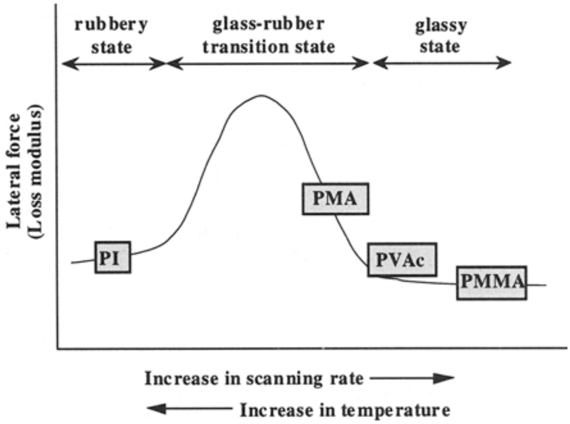
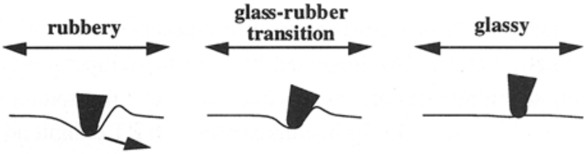


Figure 4 **Schematic lateral force versus scanning rate phase diagram observed in the lateral force behaviors of the four different polymers.**



rim size	*large*	*large*	*small*
molecular motion	*active*	*limited*	*no*
lateral force	*low*	*high*	*low*

Figure 5 **Schematic representation of surface-layer deformation due to viscoelastic energy dissipation.**

Figure 4 shows the schematic force diagram with respect to the scanning rate and temperature for the four different homopolymers with different Tg's. When the tip slides over the polymeric solid surface, a deformation (rim) is formed at the forehead of the cantilever tip, as shown in Figure 5. Therefore, the measured lateral force is strongly related to both the energy to form the rim and the deformation relaxation characteristics due to its viscoelastic properties (13). Since, in the case of a glassy state, the deformed surface behind the tip is immediately recovered, the stored elastic energy moves into the sliding tip due to the very short relaxation time. Thus, the total energy loss is small. Also, in the case of a rubbery state, it is difficult to recover the elastic energy in a short time due to the long relaxation time, but the energy to form the rim is much smaller than these for a glassy state, or a glass-rubber transition one due to very low modulus. Therefore, the resultant lateral force is low. Since, in the case of a glass-rubber transition state, the formation of the rim requires high energy due to the limited molecular mobility and the relaxation time is not short enough to recover the deformed surface, the dissipation of energy is higher in comparison with those for a glassy state and a rubbery one and then, the lateral force against the scanning rate shows the maximum as shown in Figure 4. Thus, the lateral force, in other

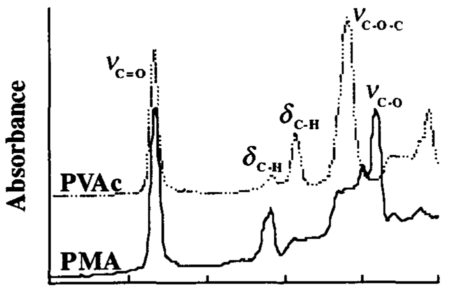


Figure 6 ATR FT-IR spectra of PMA and PVAc homopolymers.

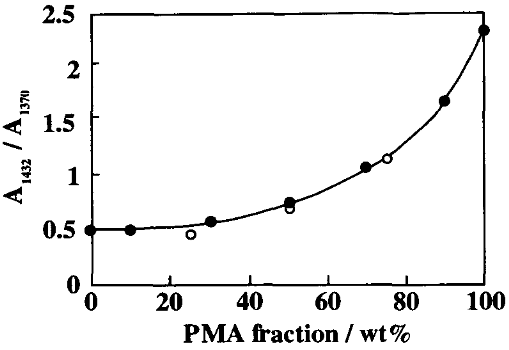


Figure 7 Relative absorbance ratio of the peak at 1370 cm^{-1} and 1432 cm^{-1} for the (PMA/PVAc) blends obtained from ATR (open circles) and transmission (filled ones) FT-IR.

words, the frictional force might be proportional to the magnitude of E". The results in Figures 2 and 3 might be, therefore, explained in consideration of the relative magnitude of Tg to RT on the basis of the scanning rate dependence of lateral force as shown in Figure 4 which corresponds to the time-temperature superposition of the viscoelastic characteristics for polymeric solids. As indicated by the time-temperature superposition principle, an increasing scanning rate corresponds to decreasing temperature. That is, the homopolymers with much higher or lower Tg in comparison with RT exhibit no dependence of lateral force on the scanning rate or temperature, while the homopolymers with Tg comparable to RT exhibit the significant dependence of lateral force on the scanning rate or temperature.

Lateral force of miscible (PMA/PVAc) blend

In order to evaluate the miscibility of the (PMA/PVAc) blends, DSC measurement was carried out. Since the DSC curves show a single baseline shift for the (PMA/PVAc) blends with all blend compositions, it can be concluded that (PMA/PVAc) blend are in a miscible state at measuring temperature employed here.

Even though the blend system is in a miscible state, its surface layer is generally enriched by the lower surface free energy component (14). Then, it is important to evaluate surface composition of the blend film. In the case of the (PMA/PVAc) blend, it is difficult to measure the surface chemical composition by XPS because the molecular structure of each component is very similar. Then, the surface chemical composition was evaluated by ATR FT-IR. Figure 6 shows the typical ATR FT-IR spectra of the PMA and PVAc homopolymers around a 1000 ~ 2000 cm^{-1} region. Careful inspection of the spectra indicates that the peaks at around 1370 cm^{-1} and 1432 cm^{-1} are assigned to the symmetric deformation and the antisymmetric one of -CH_3 ($\delta_{C\text{-}H}$) in PVAc and PMA, respectively (15). Thus, these peaks can be used to evaluate the relative surface composition for the (PMA/PVAc) blend system. Figure 7 shows the relative intensity ratio of the peaks at 1370 cm^{-1} (A_{1370}) and 1432 cm^{-1} (A_{1432}) for the (PMA/PVAc) blends. The magnitudes of A_{1432}/A_{1370} evaluated from ATR FT-IR measurements are almost same as shown in Figure 7. In consideration of the measuring sensitivity for ATR FT-IR, the result suggests that

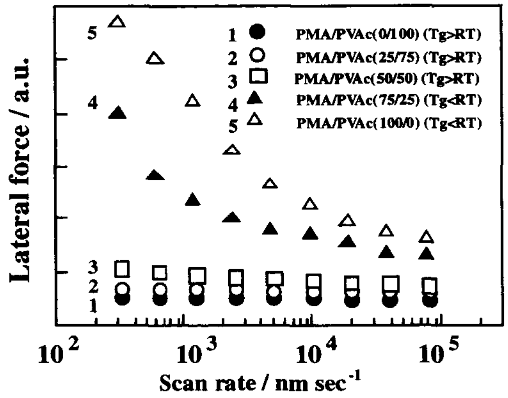


Figure 8 **Lateral force versus scanning rate for (PMA/PVAc) blends at 293K under 5 nN as load.**

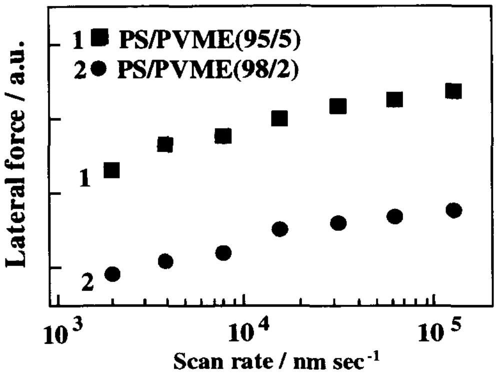


Figure 9 **Lateral force versus scanning rate for (PS/PVME) blends at 295K under 5nN as load.**

there is no enrichment of PVAc, which is lower surface free energy component, within the surface region of ca 1 μm. Therefore, the surface Tg of (PMA/PVAc) blend within analytical depth range can be assumed to be nearly equal to the bulk one.

The scanning rate dependence of lateral force for the (PMA/PVAc) blend systems with various composition ratios is shown in Figure 8. The magnitude of lateral force for all blends decreased with an increase in the scanning rate, in spite of their Tgs below and above RT. That is, the lateral force decreased remarkably with an increase in the scanning rate, in a similar fashion to that of the PMA homopolymers.

Lateral force of miscible (PS/PVME) blend

Another miscible blend system which is composed of a polymer pair with Tg's much lower and higher than RT, (PS/PVME), was investigated on the basis of the LFM measurement. XPS measurement revealed that PVME was preferentially segregated at the surface due to minimization of the interfacial free energy even though bulk PVME fraction was extremely low. Figure 9 shows the relationship between the scanning rate and lateral force for the (PS/PVME) blend film. In this blend film, the magnitude of lateral force increased with an increase in the scanning rate. Since the surface is almost covered with rubbery PVME, the surface molecular motion might be activated in comparison with its interior region in a glassy state. Thus, it seems reasonable to conclude that the surface is in a glass-rubber transition state as shown by the middle part in Figure 4 and then, the magnitude of lateral force increases with the scanning rate.

Conclusions

The relationships between lateral force and viscoelastic properties of amorphous polymers and their blend systems were investigated on the basis of LFM measurement at RT. In the case of homopolymers, two district patterns in lateral force are observed: the dependence on scanning rate for polymers with Tg's comparable to RT such as PMA and PVAc, increasing or decreasing with increasing scanning rate, respectively, whereas, independence on scanning rate for PI and PMMA with Tg much lower and higher than RT. The results from the viscoelastic characteristics are in agreement with that on the basis of time-temperature superposition. In the case of the scanning rate dependence of lateral force for miscible blend systems which are composed with polymer pairs with Tgs above and below RT, it was revealed that the dependence of lateral force on the scanning rate was strongly affected by the component being present at surface.

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