Transactions of the Materials Research Society of Japan 26 [3] 957-960 (2001)

Surface Molecular Motion of Atactic Polypropylene Films

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Abstract: Atactic polypropylene (aPP) films were spun-coated from a toluene solution onto silicon wafer at 323 K under an inert or ambient atmosphere. Based on traditional dynamic viscoelastic measurement of the bulk aPP, glass transition temperature, T_g, at which the α_a-relaxation starts to occur, was 262 K. On the contrary, T_g at the aPP surface was evaluated to be 251 K by lateral force microscopy. Hence, it was concluded that thermal molecular motion at the aPP surface was more activated than that in the interior bulk region. Also, the degree of activation of surface molecular motion became more remarkable after the surface oxidation.

Key words: Surface glass transition temperature, Atactic polypropylene, Lateral force microscope

Introduction

Recently, surface physical properties of polymeric materials have been received a great deal of attention because they play important and crucial roles in functional applications such as adhesion, wetting, lubrication, etc.[1] The progress of this new trend in fundamental polymer science has been accelerated in last 10 years by the advent of the modern technique of scanning force microscope.[2-3]

Authors have systematically studied thermal molecular motion at the surface of monodisperse polystyrene (PS) and elucidated that glass transition temperature at the surface, T_g^s, was lower than bulk glass transition temperature, T_g^b.[3-8] The activation of surface molecular motion has been explained in terms of two factors; (1) chain end and (2) free surface effects. In the case of the monodisperse PS with hydrophobic chain ends, the chain ends are preferentially segregated at the surface to minimize the free energy at the (air/polymer) interface. Since the chain ends have larger freedom than the main chain part, an excess free volume is induced at the surface, resulting in a decrease in T_g^s. Also, at the polymer film surface, the number of nearest neighbor segments, which must move cooperatively, would be smaller than that in the interior region due to an existence of the air phase on the polymer surface. Hence, the energy barrier and/or segment size for a relatively large scale molecular motion, e.g. micro-Brownian motion, decrease/s in comparison with those/that in the bulk. Consequently, the surface is thermally more active than the bulk. Other factors, which might influence on molecular motion at the surface, have been currently studying in detail.[9]

Considering a mass consumption of polymers in the industrial field, polyolefin can be regarded as a class of the most consumed polymers on account of its reasonable cost.[10] Thus, in order to function surface of polyolefin, it is of importance to understand surface properties. The objective of this research is to elucidate thermal molecular motion of polypropylene (PP). In general, crystalline isotactic PP has been used due to the superior mechanical properties to atactic PP (aPP). However, aPP is used in this study to simplify the system as the first benchmark of our series of surface molecular motion for polyolefin because the effect of crystallinity on surface molecular motion might be trivial due to its lower crystallinity.

Experimental

The polymer used in this study was atactic polypropylene (aPP) which was purchased from Ardlich, and then reprecipitated twice from a boiling hexane solution to methanol so as to remove any additives such as anti-oxidants. Table 1 shows characterizations of the purified aPP. The M_n and molecular weight distribution, M_w/M_n, were determined by gel permeation chromatography using *o*-dichlorobenzene as an eluent at 413 K. Also, T_g^b, crystallinity and tacticity were determined by differential scanning calorimetry, wide angle X-ray diffraction (WAXD) measurement and ^{13}C-

Table 1 Characterizations of aPP after purification.

M_n	M_w/M_n	T_g^b / K	Crystallinity	Tacticity		
				atactic	*isotactic*	*syndiotactic*
9.2k	2.7	261	0.10	0.681	0.228	0.091

NMR measurement, respectively. A toluene solution of aPP was prepared with the concentration of 5 wt% at 363 K. aPP film was spun-coated from the toluene solution onto heated silicon wafer with native oxide layer to be 323 K under nitrogen or ambient atmosphere. Then the film was annealed at 393 K for 24 h under vacuum. The film thickness evaluated by ellipsometric measurement was approximately 540 nm, which was sufficient to avoid any ultrathinning effects on surface molecular motion.

Surface molecular motion was analyzed by lateral force microscope (LFM, SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. LFM measurement was carried out at the heating rate of 0.4 K min^{-1} in vacuo so as to avoid the surface oxidation and a capillary force effect induced by surface-adsorbed water. A cantilever with a bending spring constant of 0.09 N m^{-1}, of which both sides were coated by gold, was used. The normal force to the cantilever tip was set to be 10 nN in a repulsive force region. It was confirmed that the sample surface was not damaged by scanning the tip under the current experimental conditions. Molecular motion of bulk aPP was also examined by Rheovibron (DDV01-FP, Orientec Co., Ltd.) based on the dynamic spring analysis (DSA) method at the heating rate of 1 K min^{-1} under nitrogen purge. Surface oxidation was monitored on the basis of the atomic concentration of oxygen by X-ray photoelectron spectroscopy (XPS, Phi ESCA 5800, Physical Electronics, Co.). The X-ray source was monochromatic Al K_α operated at 14 kV and 25 mA. The emission angle of photoelectron was 90 deg.

Results and Discussion

First, thermal molecular motion at the surface of aPP film prepared under nitrogen atmosphere was examined by LFM. Since the origin of lateral force is closely related to its loss modulus, it has been widely accepted that a lateral force-temperature curve corresponds well to a loss modulus, E'',-temperature relation.[5,11] Figure 1 shows the temperature dependence of lateral force for the aPP film at the scanning rate of 10^3 nm s^{-1}. The lateral force was invariant with respect to temperature up to approximately 250 K, and then started to increase with the increasing temperature. The LFM measurement was truncated at a temperature higher than 265 K because the given normal

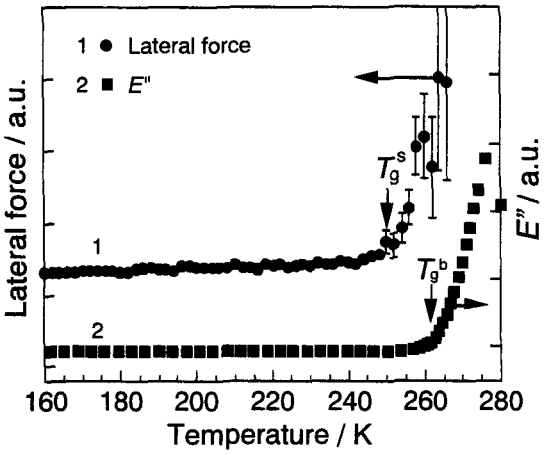

Figure 1 Temperature dependence of lateral force for the aPP film prepared in N_2. T_g^s and T_g^b were defined as intersections of the best-fitted base line and tangent to data increment, as shown by the vertical arrows.

force onto the cantilever tip could not be remained a constant due to the surface stickiness. For a comparison, molecular motion of the bulk sample was also measured at the frequency of 70 Hz, as shown in Figure 1. This measuring frequency is almost equivalent to the scanning rate of a probe tip for the LFM measurement employed. The clear peak observed on the E''-temperature curve has been well understood thus far and can be assigned to α_a-relaxation process corresponding to the micro-Brownian motion.[12] A temperature, at which E'' starts to increase in α_a-relaxation region, can be empirically defined as T_g.[13] Hence, T_g^b of the aPP is evaluated to be 262 K from Figure 1. This value is in excellent accordance with T_g^b by DSC. Even at the surface, T_g can be evaluated as the same notion. That is, a temperature, at which lateral force starts to increase in α_a-relaxation region, can be defined as T_g^s.[8] Thus, it seems reasonable to claim from Figure 1 that T_g^s is 251 K, which is lower than the corresponding T_g^b of 262 K. This clearly indicates that thermal molecular motion at the aPP surface is more active than that in the interior region, and is qualitatively in accordance with simulation results by Mansfield and Theodorou.[14]

As briefly stated in *Introduction*, the authors have rationalized the activation of surface molecular motion for monodisperse PS mainly based on two factors; chain

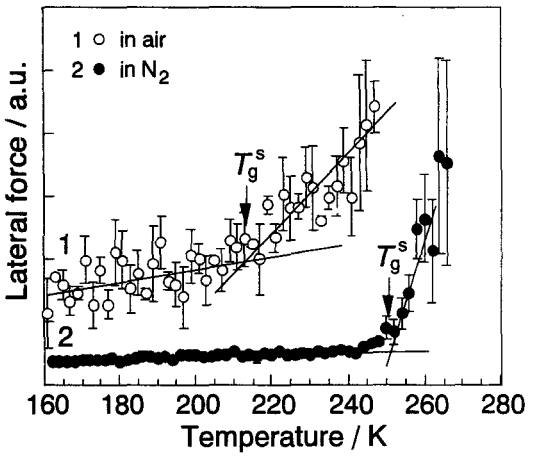

Figure 2 Temperature dependence of lateral force for the aPP films prepared in air and N_2. Both films would have oxidized and unoxidized surfaces, respectively.

end and free space effects.[8] In the case of the aPP used, it is hard to know for the moment what the chemical structure of chain ends is. Thus, it can be hardly predicted how crucial the chain end effect on surface molecular motion is for the aPP. Since the free space is always existed on the polymer surface, however, the energy barrier and/or segment size of the α_a-relaxation should be reduced at the surface even for the aPP. This leads to the activation of thermal molecular motion at the surface. In addition, the aPP has the broad polydispersity index such as 2.7, and thus it seems most likely that smaller M_n components, being lower T_g components, are preferentially segregated at the surface.[15,16] The surface enrichment of shorter chains would be also one of reasons why T_g^s was lower than T_g^b for the aPP.

Gracias et al. have not observed any peculiarities of T_g^s for aPP, from the same source as ours, based on modulus measurement using SFM.[17] The discrepancy of T_g^s between theirs and this report might be arisen from the difference of the analytical depth between both measurements. In their measurement, the surface modulus was evaluated from the slope of a force-distance curve, meaning that a tip was deeply indented and then pulled off. Hence, it can be envisaged that a result obtained did not necessarily reflect characteristics only at the surface and thus their magnitude of T_g^s was the same as T_g^b value. In contrast, the tip indentation depth upon our LFM measurement is calculated to be less than 1 nm by JKR theory.[18]

In the case of the aPP used, anti-oxidation agents were extracted to study surface molecular motion without any influence from anti-oxidation agents. Since in general, polyolefin surface is easily oxidized without

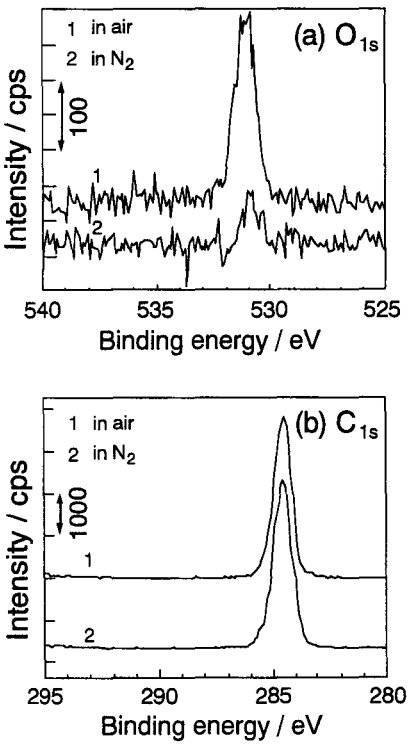

Figure 3 XPS spectra of the aPP films prepared in air and N_2: (a) O_{1s}, (b) C_{1s}.

anti-oxidation agents, it is inferred that thermal molecular motion at the surface is remarkably affected by oxidation. Figure 2 shows the lateral force variation with temperature for the aPP films prepared under the ambient and nitrogen atmospheres, which correspond to oxidized and unoxidized samples, respectively. Deferring to what extent both samples were oxidized, surface molecular motions at both surfaces are first compared. In the case of the aPP film prepared in air, a temperature at which lateral force started to increase was much lower than that of the aPP film prepared in N_2. That is, the surface of the aPP film prepared in air is thermally more active than that of the aPP film prepared in N_2. Based on the threshold temperature on the lateral force-temperature curve, T_g^ss of the aPP films prepared in air and N_2 were determined to be 215 and 251 K, respectively, as shown in Figure 2.

In order to address to what extent the surface was oxidized, XPS measurements were carried out for the samples used in Figure 2. Parts (a) and (b) of Figure 3 show O_{1s} and C_{1s} spectra of the aPP films prepared in air and N_2, respectively. A clear O_{1s} peak was observed at the binding energy of 531 eV for the aPP film prepared in air, as shown in (a) of Figure 3. In contrast, a slight peak can be somehow discerned at the same binding energy for the aPP film prepared in N_2. Also, C_{1s} peak at the binding energy of 285 eV, corresponding to neutral

carbon, seems to be the same for both films, as shown in (b) of Figure 3. Hence, it is conceivable that the aPP surface was oxidized during the film preparation process in the air. For a quantitative comparison, the atomic ratio of oxygen and carbon, (O/C) was calculated from peak areas of oxygen and carbon. The (O/C) values of the aPP films prepared in air and N_2 were 3.4 x 10^{-2} and 6.5 x 10^{-3}, respectively. Thus, it can be envisaged that the surface of the aPP film prepared in air was more oxidized than that prepared in N_2 by a factor of 5.

Finally, it must be discussed why thermal molecular motion at the surface is supposed to be more vigorous after oxidation. In general, the oxidation process contains the chain scission reaction as an elemental step.[10] This means that the fraction of smaller M_n components at the surface increases with the progress of oxidation. Since such smaller M_n components exhibit lower T_g, surface molecular motion becomes more active after oxidation.

Conclusions

Surface relaxation behavior of aPP films was examined by lateral force microscopy. It was revealed that T_g^s was lower than the corresponding T_g^b even for the aPP films. Also, when the surface was oxidized, a decrement of T_g^s from the corresponding T_g^b became remarkable due to increased fraction of smaller M_n components at the surface.

Acknowledgement

The authors thank Mr. Etsushi Akashige, CACs, Inc. for his help of GPC measurement. This was in part supported by a Grant-in-Aid for COE Research (#08CE2005) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1) F. Garbassi, M. Morra, E. Occhiello, "Polymer Surfaces from Physics to Technology", John Wiley & Sons, Chichester (1994).

2) P. Mailvald, H. J. Butt, S. A. C. Gould, C. B. Prater, B. Drake, J. A. Gurley, V. B. Elins, and P. K. Hansma, *Nanotechnology*, **2**, 103-106 (1991).

3) T. Kajiyama, K. Tanaka, I. Ohki, S.-R. Ge, J.-S. Yoon, and A. Takahara, *Macromolecules*, **27**, 7932-7934 (1994).

4) K. Tanaka, A. Taura, S.-R. Ge, A. Takahara, and T. Kajiyama, *Macromolecules*, **29**, 3040-3042 (1996).

5) T. Kajiyama, K. Tanaka, and A. Takahara, *Macromolecules*, **30**, 280-285 (1997).

6) T. Kajiyama, K. Tanaka, N. Satomi, and A. Takahara, *Macromolecules*, **31**, 5150-5151 (1998).

7) N. Satomi, A. Takahara, and T. Kajiyama, *Macromolecules*, **32**, 4474-4476 (1999).

8) K. Tanaka, A. Takahara, and T. Kajiyama, *Macromolecules*, **33**, 7588-7593 (2000).

9) K. Akabori, K. Tanaka, A. Takahara, and T. Kajiyama, in preparation.

10) "Polypropylene Handbook" Ed. by E. P. Moore, Jr., Carl Hanser Verlag, Munich (1996).

11) J. A. Hammerschmidt, W. L. Gladfelter, and G. Haugstad, *Macromolecules*, **32**, 3360-3367 (1999).

12) M. Takayanagi and K. Hayashi, *Rept. Prog. Polym. Phys. Japan*, **5**, 127-130 (1962).

13) See Fig. 4 in ref. 7.

14) K. S. Mansfield and D. N. Theodorou, *Macromolecules*, **24**, 6283-6294 (1991).

15) K. Tanaka, A. Takahara, and T. Kajiyama, *Macromolecules*, **30**, 6626-6632 (1997).

16) K. Tanaka, A. Takahara, and T. Kajiyama, *Macromolecules*, **31**, 863-869 (1998).

17) D. H. Gracias, D. Zhang, L. Lianos, W. Ibach, Y. R. Shen, and G. A. Somorjai, *Chem. Phys.*, **245**, 277-284 (1999).

18) K. L. Johnson, K. Kendall, and A. D. Roberts, *Proc. R. Soc. London A*, **324**, 301-313 (1971).

(Received March 26, 2000; Accepted April 18, 2001)