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Thermal molecular motion at surface of atactic polypropylene films

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Abstract

Surface molecular motion in atactic polypropylene (aPP) films was studied by scanning force microscopy. Glass transition temperature at the surface, T_g^s, was determined to be 251 ± 1 K on the basis of temperature dependence of lateral force, whereas its bulk glass transition temperature, T_g^b, by dynamic viscoelastic and differential scanning calorimetric measurements was 262 K. In general, polyolefin is easily oxidized, and thus, many kinds of additives are mixed in it for practical use. Hence, effects of oxidation and additives on surface properties of the aPP surface were examined as well. To achieve oxidation, the aPP films were annealed at 428 K for 100 min under the ambient atmosphere. After this treatment, T_g^s decreased by approximately 15 K in comparison with the intact film due to degradation of surface chains. On the contrary, in the case of the aPP containing 10 wt% antioxidant, T_g^s was almost the same as that of the intact film before and even after the oxidation treatment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Surface molecular motion; Atactic polypropylene; Scanning force microscopy

1. Introduction

Surface structure and physical properties of polymeric materials have been received a great deal of attention recently because they play important and crucial roles in functional surface applications such as adhesion, wetting, lubrication, etc. Thus far, we have systematically studied molecular motion and mobility at the surface of various polystyrene (PS) films, and elucidated that glass transition temperature at the surface, T_g^s, was lower than the corresponding bulk glass transition temperature, T_g^b [1–3]. These enhanced molecular motion and mobility at the surface have been, for the moment, explained in terms of reduced cooperativity [2] and chain end effect [3]. To confirm whether our notion is universal for amorphous flexible polymers, it is of importance to study this issue using different polymers, although enhanced surface mobility of the PS films have been reported by other groups as well [4–6].

Considering a mass consumption of polymers in the industrial field, polyolefin can be regarded as a class of most consumed polymers on account of its excellent cost performance [7]. Of polyolefin, isotactic polypropylene (iPP), which is a typical semi-crystalline polymer, has superior mechanical properties and thermal stability [8]. Thus, it seems that understanding surface aggregation states and physical properties of iPP is quite important so as to function its surface. In a last decade, surface of the iPP has been structurally explored with the advent of modern experimental techniques, e.g. scanning force microscopic (SFM) observation [9–11] and grazing incidence X-ray diffraction measurement [12]. On the other hand, for thermal molecular motion at the iPP surface, little information has been known. Gracias et al. have studied surface mechanical properties of the iPP based on nano-indentation method using SFM, and have not seen any differences of molecular motion between surface and bulk [13,14]. This result was well advocated by their surface vibrational spectroscopic measurements. Besides, Uedono et al. [15] have examined open spaces and relaxation processes in a subsurface region, approximately 200 nm, of the iPP using monoenergetic positron beams. Although they discernibly observed an enlarged open spaces in the region compared with the bulk, T_g in the subsurface region was comparable to T_g^b. However, since molecular motion at the semi-crystalline polymer surface is strongly influenced by the fraction of crystalline phases, a surface in which the contribution of crystalline regions can be negligible should be studied at first. Then, it will turn to be possible to clarify the contribution of amorphous region to thermal and

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mechanical properties at the semi-crystalline iPP surface. Such a situation can be realized by using atactic polypropylene (aPP). To date, there are two pioneer works dealing with molecular motion and mobility at the aPP surface, and unfortunately, both results seem to be controversial. Mansfield and Theodorou [16] studied dynamics in surface layers of glassy aPP based on molecular dynamics simulation. They concluded that the mean-squared displacement of atoms in the surface regions is much enhanced in comparison with that in the interior region on account of reduced density, and that this trend became more remarkable closer to the outermost surface. In contrast, Gracias [13] using SFM, claimed a contradict result, that is, molecular motion at the surface of the aPP was the same as that in the bulk, as reported for the iPP system.

In general, the surface of polyolefin is easily oxidized under the ambient circumstance [8], resulting in that surface structure and properties are drastically changed. This is because the oxidation process would be started from the air/polymer interface due to the presence of air on surface chains. Thus, various kinds of antioxidants (AOs) have been hitherto developed, and empirically mixed into the polyolefin for the purpose of practical use. Although the addition of additives into the polyolefin is quite effective to prevent surface oxidation, its mechanism has not been clarified yet. Recently, Duwez et al. [17] successfully mapped lateral distribution of additives at the iPP surface. However, an effect of additives on thermal molecular motion at the surface is still open.

The objective of this research is to reveal thermal molecular motion at the aPP surface, as the first benchmark of our systematic study for surface mobility in semi-crystalline and crystalline polymers, and effects of oxidation and additives on it. Obtained information in this research would be useful for fundamental polymer science as well as application for practical industry.

2. Experimental section

2.1. Materials and film preparation

aPP used in this study was purchased from Ardlich (Registration No. 42818-3), and then, reprecipitated twice from a boiling hexane solution to methanol in order to remove crystalline component and any additives. The number-average molecular weight, M_n, and the molecular weight distribution, M_w/M_n, where M_w is the weight-average molecular weight, of the aPP were 9.2k and 2.7, respectively, by gel permeation chromatography (GPC) using *o*-dichlorobenzene as an eluent at 413 K. Its T_g^b and crystallinity were determined to be 260 and 0.10, respectively, by differential scanning calorimetric and wide angle X-ray diffraction measurements. Also, tacticity of the aPP based on pentad by ^{13}C nuclear magnetic resonance measurement [18] was 68.1% atactic, 22.8% isotactic and 9.1% syndiotactic. A toluene solution of the aPP with the concentration of 5 wt% was prepared at 363 K, and then, aPP films were spun-coated from it onto silicon wafers with native oxide layer kept to be 323 K under the nitrogen atmosphere. The films were annealed at 393 K for 24 h under vacuum to remove a residual strain imposed during the film preparation process. Also, aPP films containing 10 wt% AO (aPP/AO) were prepared in the same procedure. AO used here was tetrakis (methylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)) methane (ADKSTAB AO-60), which was kindly supplied by Asahi Denka Kogyo K.K. The thicknesses of the films evaluated by ellipsometric measurements were approximately 540 nm, which was sufficient to avoid any ultrathinning effects on surface molecular motion. Oxidation treatments for the aPP and (aPP/AO) films were carried out by exposing the films to ambient atmosphere at 428 K for 100 min.

2.2. Surface characterizations

Surface molecular motion was examined 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 vacuum 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 0.11 ± 0.02 N m^{-1} [19], of which both sides were coated by gold, was used. Radius of curvature of tips was estimated to be 42.8 ± 2.6 nm by using monodisperse gold colloid particle [20]. The normal force onto the cantilever tip was set to be 10 nN in a repulsive force region. Under this experimental condition, it was preconfirmed that the surface was not damaged. Hence, we invoke that the LFM measurement was carried out in an elastic regime. Molecular motion of bulk aPP sample was also measured using Rheovibron (DDV01-FP, Orientec Co., Ltd) at the heating rate of 1 K min^{-1}. It was experimentally difficult to prepare a self-supported film of the bulk aPP due to its viscous property. Hence, a method of dynamic spring analysis (DSA), which enables to measure relative dynamic viscoelastic functions even for highly viscous materials as well as fragile films, was applied [21]. In this case, however, it is quite hard to obtain an absolute value of dynamic modulus, because the cross-sectional area of the specimen can be hardly known. Surface oxidation was monitored on the basis of the surface 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 photoelectrons was 15°.

3. Results and discussion

At first, thermal molecular motion at the surface of aPP

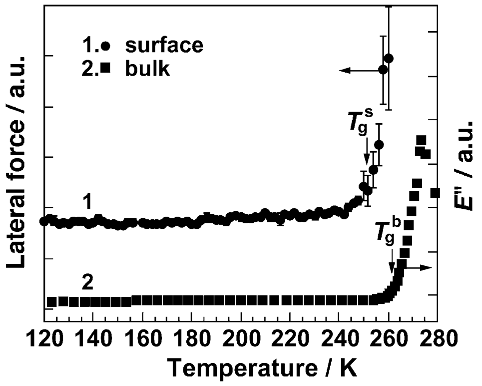

Fig. 1. Lateral force–temperature curve for the aPP film at the given scanning rate of 10^3 nm s^{-1}. For a comparison, E'' variance with temperature for the bulk aPP sample measured at the frequency of 35 Hz is shown as well.

film was examined by LFM. Since lateral force is originated from energy dissipation during a tip slides on the sample surface, the temperature dependence of lateral force corresponds well to the dynamic loss modulus, E'', variation with temperature [2,22]. Fig. 1 shows the temperature dependence of lateral force for the aPP film at the scanning rate of 10^3 nm s^{-1}. Lateral force was invariant with respect to temperature up to approximately 250 K, and then, started to increase with increasing temperature. The measurement was truncated at a temperature higher than 265 K because the given normal force onto the cantilever tip could not be remained a constant due to the surface stickiness. For a comparison, the relation between temperature and E'' for the bulk sample measured at the frequency of 35 Hz was also shown in Fig. 1. This measuring frequency is almost equivalent to the scanning rate of the probe tip for the LFM measurement employed.[1] An abrupt increase observed on the temperature–E'' has been assigned to the α_a-absorption corresponding to the micro-Brownian motion of the main chain part [24,25]. A temperature, at which E'' starts to increase in the α_a-relaxation region, can be empirically defined as T_g [2]. Hence, T_g^b of the aPP was evaluated to be 262 K from Fig. 1. This value was in excellent accordance with T_g^b measured by DSC. Even at the surface of the aPP, T_g can be evaluated as the same concept. That is, a temperature at which lateral force starts to increase in the α_a-relaxation region can be defined as T_g^s [2,22]. Thus, it seems reasonable to claim from Fig. 1 that T_g^s in the aPP film is 251 ± 1 K being discernibly 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 internal region, and is in qualitative agreement with simulation results by Mansfield and Theodorou [16]. Unfortunately, in LFM measurement, the overall profile reflecting the surface α_a-relaxation could not be observed due to surface stickiness above 265 K, as shown in Fig. 1. Therefore, detail rheological analysis of the surface α_a-relaxation to extract activation energy could not be made.

As briefly stated in Section 1, we strongly believe for the moment that the vigorous molecular motion observed at the surface of amorphous polymers is mainly attained by two factors. The first is a chain end effect [3,26]. When surface free energy of chain end groups is lower than that of the main chain part, the chain ends are preferentially partitioned to the surface. In this case, since the chain ends have larger freedom compared with the main chain part, an excess free volume is induced at the surface, resulting in activation of molecular motion at the surface. In the case of the aPP used, however, the chemical structure of chain ends is unknown at present. Thus, it can be hardly predicted how crucial the chain end effect on surface molecular motion is for the aPP used here. The second factor is that the cooperativity for the segmental motion is reduced at the surface [2,27]. That is, energy barrier and/or segmental size for the α_a-relaxation are/is reduced at the surface. This notion can be applied even for the aPP because the free space is always existed on polymer segments at the surface. Moreover, the aPP used has the relatively large 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 [28–31]. 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 [30,31].

When a probe tip vertically indents into sample surface by changing z-piezo displacement, a repulsive force between the tip and the surface is observed. Based on this force–distance curve, surface modulus can be examined on the basis of its slope. Although Gracias et al. [14] examined the temperature dependence of surface modulus following the aforementioned procedure, they have not observed any peculiarity for molecular motion at the aPP surface. Hence, we have done the same experiment as what they did. The tips used here were the same as those for our LFM measurements. In Fig. 2, the inset shows a typical

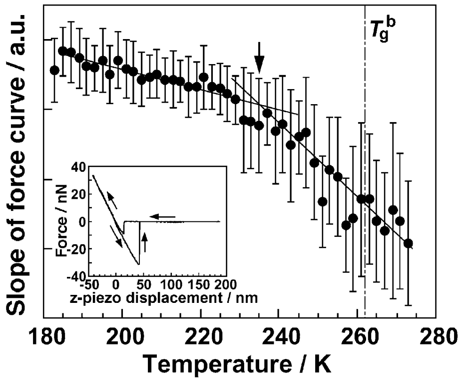

Fig. 2. Temperature dependence of the slope of the force–distance curve for the aPP film. The inset shows a typical force curve for the aPP film. The slope at the repulsive force of 10 nN was used to plot the main panel.

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[1] According to JKR theory [23], the radius of the circle, a, of contact between a tip and the sample surface was 13.1 nm. The corresponding frequency, f, to the current scanning rate, v, can be calculated by $v/2a$, and its value was 38.2 Hz.

force–distance curve for the aPP, and the main panel shows the temperature dependence of slope of the advancing force curve at the repulsive force of 10 nN. This force region was comparable to the normal force applied onto a sliding tip for LFM measurements. The temperature–slope relation slightly decreased with increasing temperature up to 230 K, and then, its decrement with temperature became remarkable. Since this is a static measurement for surface modulus unlike LFM measurement, we are not sure whether the inflection point on the main panel of Fig. 2 corresponds to T_g^s. Actually, the temperature at the inflection point was much lower than T_g^s determined by LFM measurement. However, in any event, Fig. 2 makes it clear that mechanical properties at the aPP surface starts to change at a temperature lower than T_g^b.

We now turn to an oxidation effect on surface molecular motion in the aPP film. Fig. 3 shows the temperature dependence of lateral force in the aPP films before and after oxidation treatment, which was carried out at 428 K for 100 min under the ambient atmosphere. The curve for the intact film is the same data shown in Fig. 1. Although the curve shape for the treated aPP film was similar to that for the intact film, a temperature at which lateral force started to increase was shifted to lower than that of the intact film. Also, the reproducibility and the signal to noise ratio for the measurements of the treated aPP films were somewhat poor in comparison with the intact film. Thus, T_g^s in the treated aPP film was determined on the basis of independent six runs (three runs for the intact film) and its value was 236 ± 7 K, which was lower than T_g^s in the intact film by 15 K. The discrepancy of T_g^s in the aPP films before and after the treatment should be assigned to surface oxidation, and thus, XPS measurements for both films were made in order to address to what extent the surface was oxidized after the treatment.

Fig. 4(a) and (b) shows the O_{1s} and C_{1s} spectra of the aPP films before and after the oxidation treatment. A clear O_{1s} peak was observed for the treated aPP film, while this peak for the intact film was trivial in the same intensity range, as shown in Fig. 4(a). The O_{1s} peak for the treated aPP film was solved into two peaks corresponding to carbonyl and ether oxygen atoms at 532.2 and 533.5 eV, respectively, as shown by dotted curves (Fig. 4(a)). The fractions of both were 0.89 and 0.11. Also, the C_{1s} peaks corresponding to the neutral, ether and carbonyl carbons were observed for the treated aPP film, whereas the ether and carbonyl carbons could be hardly seen for the intact film. Hence, it is apparent that the aPP surface was oxidized during the oxidation process in air, and that ether and carbonyl groups were introduced there. The (O/C) values for the aPP films before and after the oxidation treatment were calculated to be 7.1×10^{-3} and 1.3×10^{-1}, respectively. Fig. 5 shows the schematic representation of well accepted oxidation mechanism of aPP [32]. The first elemental step is a reaction to generate a radical on an α-carbon in the backbone. Then, oxygen reacts

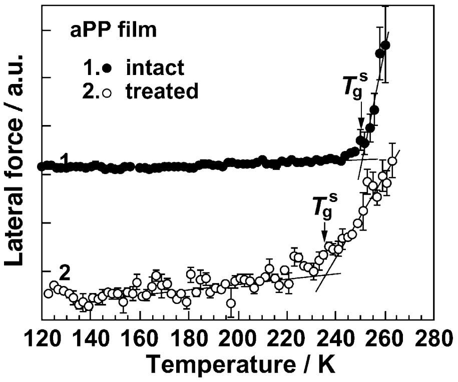

Fig. 3. Temperature dependence of lateral force for the aPP films before and after the oxidation treatment at 428 K for 100 min.

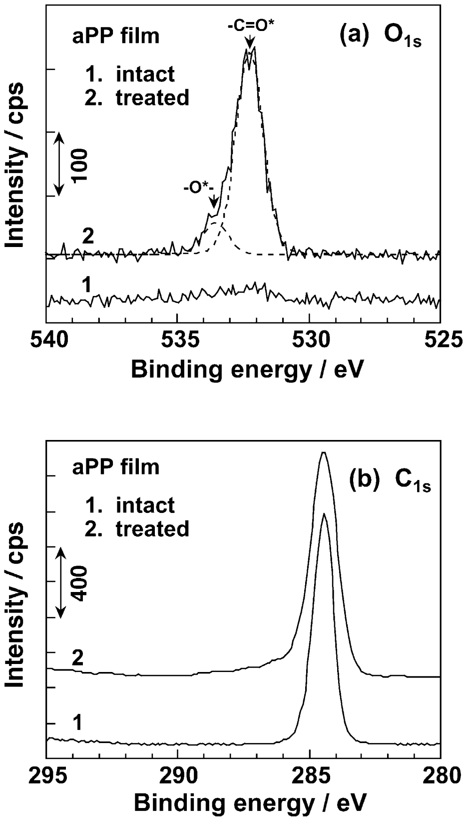

Fig. 4. Typical XPS spectra of the aPP films before and after the oxidation treatment: (a) O_{1s}, (b) C_{1s}.

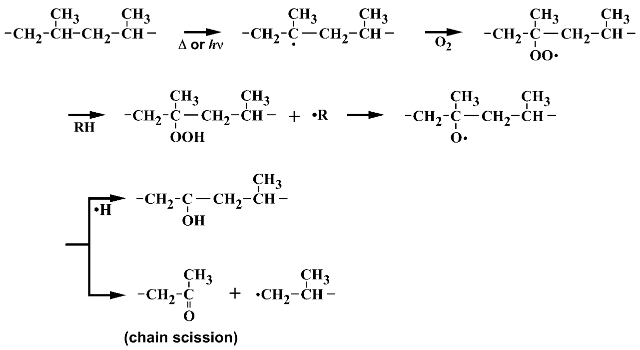

Fig. 5. Schematic representation of an oxidation mechanism for the aPP.

with that part, resulting in the formation of oxygen radical in the main chain, which mainly stabilizes by chain scission, as shown in Fig. 5. In this case, molecular weight of a chain decreases and a carbonyl group is introduced into the chain end group. Also, some content of oxygen radicals in the main chain stabilizes by pulling different hydrogen out, probably from α-portion, resulting in the incorporation of ether oxygens into the main chain. Taking into account this mechanism with our XPS results, it seems most likely that chain scission is a main reaction during the oxidation process, meaning that molecular weight of surface chains decreases. If that is the case, physical properties at the surface drastically change, and this is actually what was observed in Fig. 3. An oxidation effect on surface properties has been extensively explored by Bradley et al. [33–35] using various polymer films.

At present, it is difficult to deduce experimentally to what extent molecular weight of surface chains decreased. Instead, the whole amount of the aPP film was gathered after the oxidation treatment under the ambient atmosphere at 428 K for 100 min, and then, GPC measurement for it was made. Fig. 6 shows the molecular weight distribution for the aPP before and after the oxidation treatment. M_n of the aPP decreased from 9.2k to 1.5k, which was about one-sixth M_n of the intact aPP, and also, M_w/M_n of the film increased from 2.7 to 3.3. This is the direct evidence that the fraction of smaller M_n components increases with the progress of the oxidation. Also, XPS results revealed that oxygen atoms were introduced into the surface region with the 18.3 times $(= 1.3 \times 10^{-1}/7.1 \times 10^{-3})$ concentration after the oxidation treatment. Once a chain is degradated by one cleavage, two end groups are newly formed. Invoking that both end groups are terminated by two carbonyl groups, molecular weight of surface chains are roughly calculated to be 1.1k $[= 9.2\text{k}/(18.3 \times 0.89/2)]$, which is slightly lower than 1.5k based on the GPC measurement. This might indicate that oxidation reactions proceed more in the surface region rather than in the bulk. This simple argument seems quite reasonable because aPP chains at the outermost surface have oxygen atoms as neighbors. Hence, it seems reasonable to claim that further activation of molecular motion at the surface observed after the oxidation treatment is due to a decrease in M_n of surface chains.

Ke [36] studied T_g^b variation with M_n for aPP, and revealed that T_g^b was given by $(265 \pm 1) - 1.1 \times 10^5/M_n$. Since the concentration of chain ends being closely related to the free volume fraction is proportional to $1/M_n$, T_g^b is inversely proportional to M_n [37]. When M_n decreases from 9.2k to 1.5k or even to 1.1k, T_g is supposed to decrease by 61 or 88 K based on their equation. Nevertheless, the observed decrement of T_g^s after the oxidation treatment was only 15 K. This means that the chain end concentration at the surface does not effectively increase, even though M_n of surface chains decreases. As discussed above, chain ends would be terminated by carbonyl group, which has relatively higher surface free energy than the main chain part. If that is the case, chain ends might migrate into the interior bulk region to minimize the interfacial energy of the system [3,38,39]. Therefore, the decrement of T_g^s after the oxidation treatment was not as large as expected from the decrement of M_n for surface chains.

Polymer materials generally used contain many kinds of additives. Thus, from the point of industrial view, it is important to examine an effect of AOs on surface molecular motion of polymer materials. Fig. 7 shows the temperature dependence of lateral force for (aPP/AO) films before and after the oxidation treatment. The AO was mixed into the aPP with a high concentration such as 10 wt% to enhance its effect, if any, and the surface fraction of the AO determined by XPS was almost comparable to the bulk ratio. Also, the (aPP/AO) system was miscible under the current experimental condition. T_g^s in the (aPP/AO) film before the treatment was 250 ± 4 K, which was again equal to T_g^s in the intact aPP film within our experimental accuracy, meaning that a discernible plasticizer effect by the AO was not observed. Thus, it is conceivable that the presence of the AO used here does not alter the segmental motion in the aPP film under the current AO concentration. T_g^s in the (aPP/AO) film after the oxidation treatment was 253 ± 3 K. Since the distinct T_g^s reduction was not observed, it can be envisaged

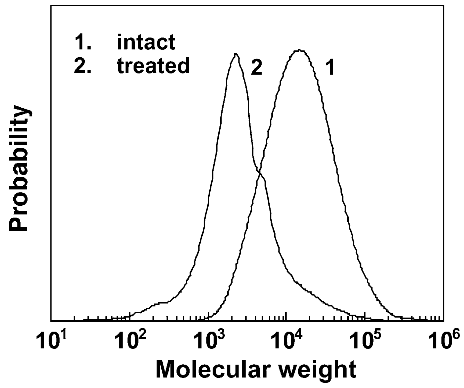

Fig. 6. Molecular weight distribution for the aPP before and after the oxidation treatment.

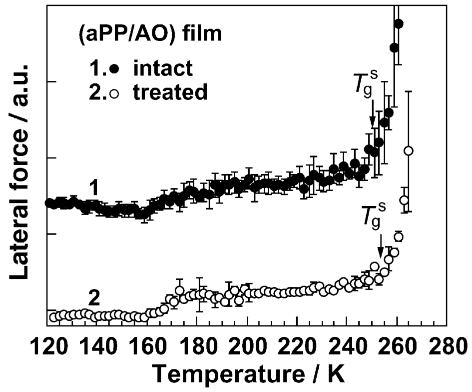

Fig. 7. Temperature dependence of lateral force for the (aPP/AO) films before and after the oxidation treatment.

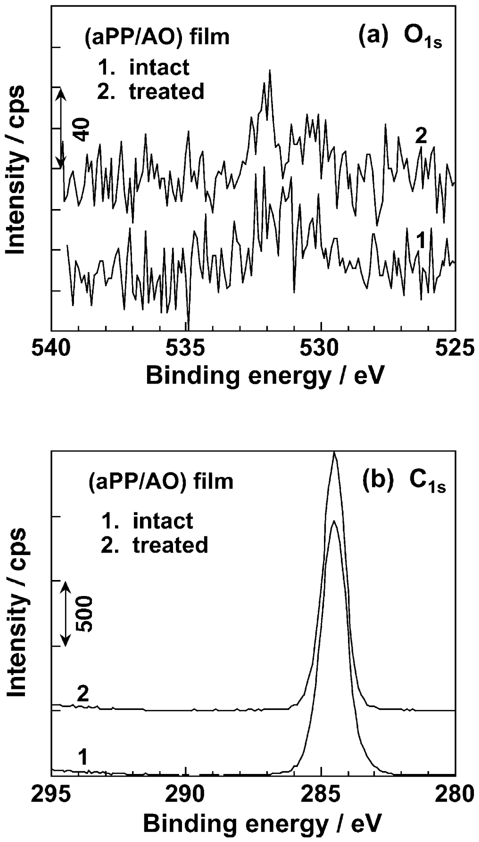

Fig. 8. Typical XPS spectra of the (aPP/AO) films before and after the oxidation treatment: (a) O_{1s}, (b) C_{1s}.

that aPP molecules at the surface were not degraded under the presence of the AO. The one point, which should be addressed, is that the noticeable alteration of lateral force was observed at around 170 K in Fig. 7, which was not observed at the aPP surface without the AO. Since a similar increase in E'' was observed at the same temperature for the bulk (aPP/AO) sample based on the dynamic viscoelastic measurement, it is plausible that the increase in lateral force at 170 K is assignable to some sort of local mode relaxation concerned with the AO.

To confirm a validity of the AO on surface oxidation, XPS measurements for the (aPP/AO) films before and after the treatment were performed. Fig. 8 shows the O_{1s} and C_{1s} spectra of the (aPP/AO) films before and after the oxidation treatment. A clear difference of the O_{1s} and C_{1s} spectra before and after the treatment was not observed at all. Thus, it seems reasonable to consider that the AO mixed into the aPP prevents the oxidation reaction at the surface and holds surface molecular motion in the aPP film unchanged.

4. Conclusions

Surface relaxation behavior of the aPP film was examined by LFM. T_g^s in the aPP film based on the temperature dependence of lateral force was 251 ± 1 K, which was lower than T_g^b of 262 K. Hence, it was claimed that molecular motion at the aPP surface was more active than that in the interior bulk region, as reported for the case of PS. After the oxidation treatment at 428 K for 100 min, T_g^s further decreased due to decreasing M_n of surface chains. Also, T_g^s in the (aPP/AO) film was also studied, and was found to be almost the same as that in the intact aPP film. Even after the oxidation treatment, T_g^s value remained the same, implying that the AO prevents the oxidation reaction at the surface.

Acknowledgments

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