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Atomic force microscopy study of polypropylene surfaces treated by UV and ozone exposure: modification of morphology and adhesion force

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Abstract

Exposing polypropylene (PP) to ozone in the presence of UV light is a simple and effective way of modifying its surface to improve its wettability and adhesion. Atomic force microscopy (AFM) showed a dramatic change in the morphology and a clear increase in the adhesion force resulting from the modification of a PP film by UV/ozone exposure. A relationship has been demonstrated between a change in surface energy (measured by wetting contact angle) and the adhesion force (measured by AFM). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

For many applications in the plastics industry, the surface of polypropylene (PP) needs to be modified in order to improve its wettability and adhesion properties. One of the techniques used to modify the surface is the exposure of the polymer to ozone in the presence of UV light [1,2]. This exposure results in an increase in the surface energy of the polymer through the breaking of molecular bonds on the surface and the addition of polar oxygen atoms. Changes in the surface composition and wettability have been extensively investigated with XPS and contact angle goniometry [1–3].

Understanding local changes in the structure and surface energy of the modified PP film is important in controlling the modification. In this paper we report on the changes in the surface morphology and adhesion force of PP film surfaces after modification measured using atomic force microscopy (AFM) [4]. AFM is capable of imaging surface features on a nanometer-scale and of measuring the adhesion force between the probe tip and sample surface [5–8]. The morphology changes from a fibre-like network structure to one of mounded reaction products as a first step in the modification. We also found that the adhesion force measured on the surface shows a remarkable increase after the modification. The adhesion force measurement is consistent with previous contact angle observations [1,3] and can be related to the surface energy increase upon modification.

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2. Experimental

Both non-contact and contact modes of a commercial AFM (Explorer, TopoMetrix) were employed in this study. In non-contact AFM, a stiff silicon cantilever with a spring constant of about 28 N/m was used which was 130 μm long, 29 μm wide and 3.7 μm thick with a cantilever resonance of approximately 280 kHz. The tip apex radius was ~20 nm. Non-contact AFM functions by monitoring the reduction of the oscillation amplitude of the cantilever when the tip is close to the surface. Images were obtained at a set point where the oscillation amplitude became half of that in free space.

A soft silicon nitride cantilever with a nominal spring constant of 0.03 N/m was used in contact mode AFM. The cantilever was 200 μm long, 18 μm wide and 0.6 μm thick with an attached tip whose apex radius was ~20 nm. Contact mode AFM was used to obtain lateral force images [9] from the torsional movement of the cantilever [10] and to measure adhesion forces from force–distance curves.

Thermally extruded, biaxially oriented PP [1] film produced from a homopolymer resin (molecular weight $M_w = 1.9 \times 10^5$, polydispersity = 6.0) was used in this study. Surface modification was performed by exposing the PP film to ozone in a chamber with a mercury vapour lamp generating UV light [1]. Dry air at a flow rate of 1000 sccm (standard cubic centimetres per minute) was provided through a generator which produced ozone at a concentration of 2×10^{17} molecule/cm^3 as detected by UV absorption. All AFM measurements were performed in ambient atmosphere with a typical relative humidity of 50%. The images consist of 500 lines with 500 points per line collected at a scan rate of 10 μm/s.

3. Results and discussion

Fig. 1 shows non-contact AFM topographic images for (a) the untreated, (b) 3 min and (c) 15 min UV/ozone treated PP film surfaces. The untreated PP film surface is characterized by a fibre-like network structure which results from the biaxial orientation process. The resulting strand diameters are approximately 40 nm. After UV/ozone treatment for 3 min, the PP film surface shows a remarkable change in morphology from the original surface, as small mounds form on the strands. During the modification, atomic oxygen formed from the photo-decomposition of ozone is believed to react with PP chains [1]. Extended oxidation of PP results in the formation of low molecular weight oxidized material (LMWOM) which is believed to be a component of the surface structure.

When the treatment time was increased to 15 min, the morphology of the modified surface shows a mixture of small mounds and large droplets. These droplets are thought to be formed by the aggregation of the mounds during the UV/ozone exposure. The shape of the droplets may be determined by the surface tension of the liquid-like materials formed during the modification process. Because both mounds and droplets coexist on the longer-term treated PP film surface, it is also possible that the droplet consists of different materials from the surrounding mounds. With increased surface oxidation, it is not hard to imagine that the polymer chain scission continues, the molecular weight of the newly formed material decreases, which increases the liquidity of the material and results in aggregation of the mounds on the surface to form the droplets.

Because the UV/ozone modification is used to improve the wettability and adhesion force on the surface, we measured force–distance curves to probe adhesion force variations on modified PP film surfaces for which the AFM images showed that the surface morphology had changed. Shown in Fig. 1d are three typical force-distance curves measured on untreated, 3 and 15 min treated PP films, respectively. Force–distance curves are measured by bringing the tip from a distance (e.g., 500 nm) to make contact between the tip and the surface (i.e., origin point) followed by retraction of the tip from the surface. The arrow lines in Fig. 1d show the adhesion forces between the tip and three different surfaces, which are measured at the point where the tip is eventually pulled from the surface in the retracting process [5–8]. It is clear that the adhesion force increased with increasing treatment time.

The reproducibility for the change in the adhesion forces observed in Fig. 1d was determined by measuring a number of force–distance curves on various

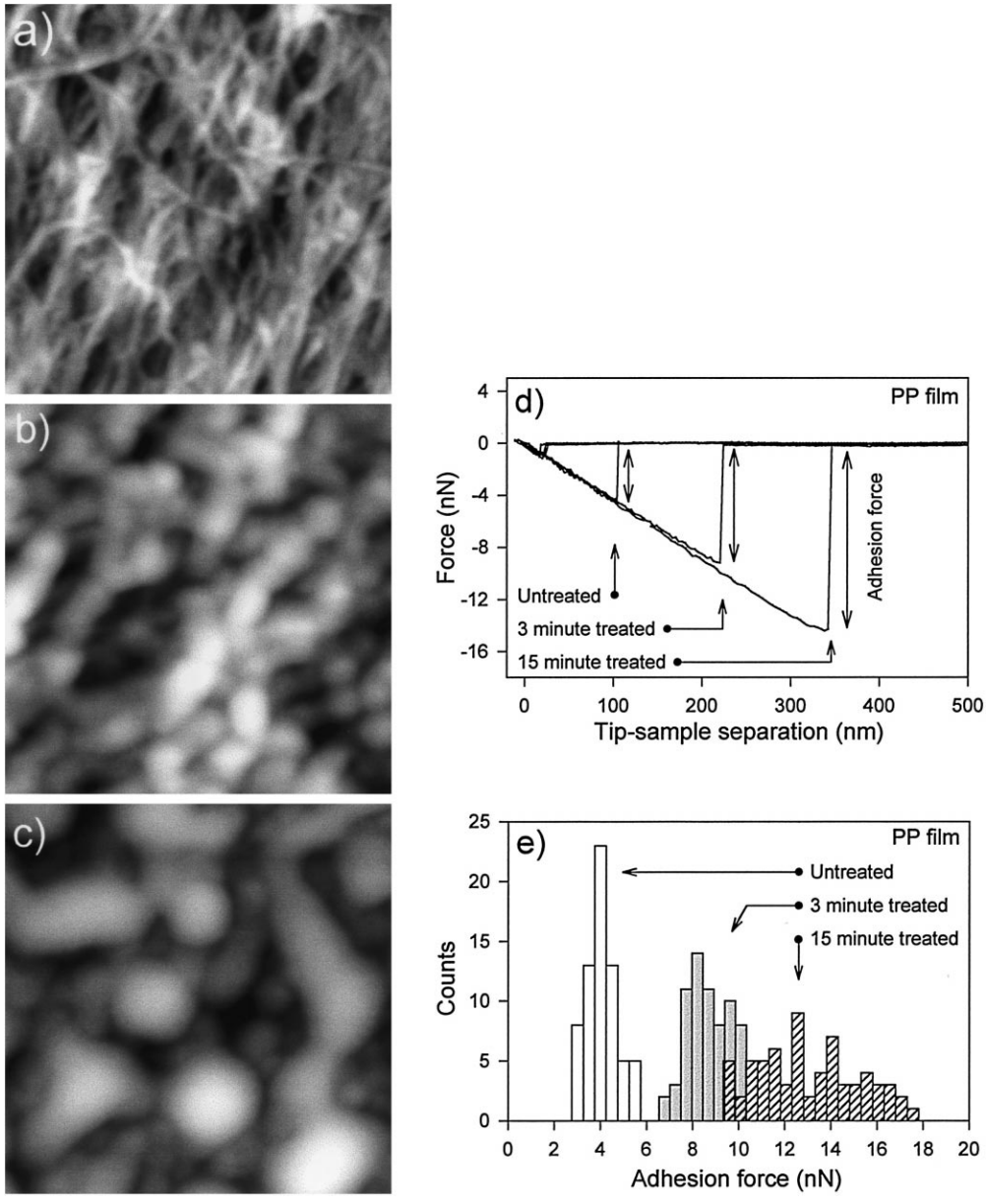

Fig. 1. Non-contact AFM topographic images for (a) untreated, (b) 3 min, and (c) 15 min UV/ozone treated PP films in a 1000 nm square area. Gray-scale ranges for the three images are 21, 16, and 26 nm, respectively. Three typical force–distance curves obtained on the three different films are shown in (d), in which the insert arrow lines indicate the adhesion forces. Shown in (e) are histograms of the adhesion forces for the untreated (open bar), 3 min (close bar) and 15 min (striped bar) treated PP films, respectively. The speed of the tip movement during force–distance curve measurement was 1000 nm/s.

locations for the three different films. The histograms for the distribution of the adhesion force measured from the untreated, 3 and 15 min treated PP films are shown in Fig. 1e. The average adhesion forces are 4.3, 8.9 and 13.3 nN for the untreated, 3 and 15 min treated PP films, respectively. The standard deviations of those adhesion forces are 0.7, 0.9 and 2.2 nN, respectively. It is clear that there exists a

remarkable difference in adhesion force among the three different films. We noted from Fig. 1e that for the 15 min treated PP film, the adhesion force has a broad distribution and its lower part overlaps with the higher part of that of the 3 min treated PP film. It is likely that the droplets and surrounding mounds observed in Fig. 1c are responsible for this broad distribution. The overlap indicates that the mounds and surrounding mounds, respectively, on the 3 and 15 min treated PP films may have similar adhesion force.

In the case of contact between a sphere and flat surface, the Johnson–Kendal–Roberts theory indicates that the adhesion force F is related to the work of adhesion w (or interaction energy) as $F = -(3/2)\pi Rw$ [11], where R is the radius of the sphere. The work of adhesion can be related to surface energies of the sample γ_1 and tip γ_2 and their interfacial energy γ_{12} as $w = \gamma_1 + \gamma_2 - \gamma_{12}$ [11]. In our experiment the surface energy of the tip, γ_2, is considered to be constant; therefore, the change in adhesion force is a measure of the combination of the surface energy of the sample surface and the interfacial energy between the tip and sample surface.

Moreover, the properties of the tip itself contribute to the measurable adhesion force in the force–distance curve. In order to eliminate possible changes that could affect the interaction between the tip and surface, we took the precautions of using the same tip and completing the experiment in a short time. In practice, several tips were used in the experiment and additional scatter in the adhesion force measurements was introduced. However, the trend of an increase in the adhesion force with increasing UV/ozone treatment was always observed. The adhesion force measured by AFM indicates an increase in the surface energy, which is consistent with the data from contact angle measurements [1]. The force–distance measurement thus appears to be a promising method to evaluate the change in surface energy, which is the main parameter governing the wettability and adhesion properties on polymer surfaces.

Fig. 2 shows the non-contact AFM topographic images of the PP surface treated for 3 min (a) and 15 min (b) after being washed with water. For the 3 min treated PP film, as shown in Fig. 2a, the surface shows some recovery so that it resembles the untreated surface, possibly because the modification is less extensive than that of PP film surface treated for longer time. The diameter of the strands in the net-like structure in Fig. 2a is roughly twice of that of the untreated strands, as can be seen in Fig. 1a. This thickening may result from a cross-linking interaction in the strands or by the selective destruction of the finest strands in the network.

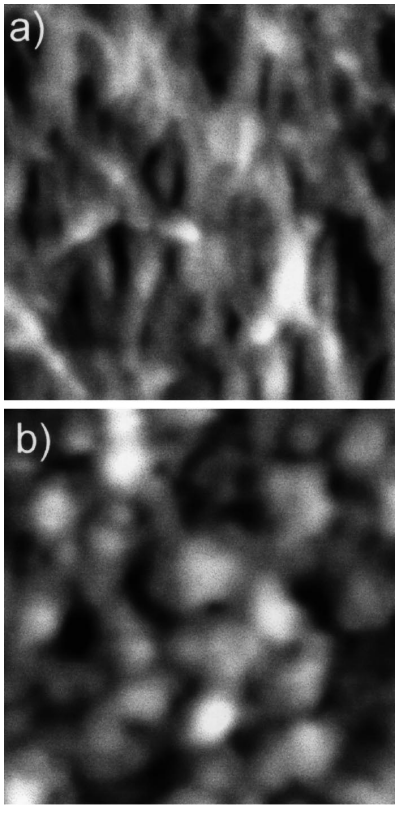

Fig. 2. Non-contact AFM topographic images of PP films treated with UV/ozone for (a) 3 min and (b) 15 min, after water washing, in a 1000 nm square area. Gray-scale ranges for the two images are 25 and 12 nm, respectively.

For the 15 min treated PP film, it is clear from Fig. 1c and Fig. 2b that the droplet structures disappeared and the surface is dominated by mounds. However, complete recovery of this long-time-treated PP film surface to the original fibre-like structures was not observed. This observation is consistent with XPS data and contact angle data [3], which indicated that the oxygen to carbon ratio and contact angle on

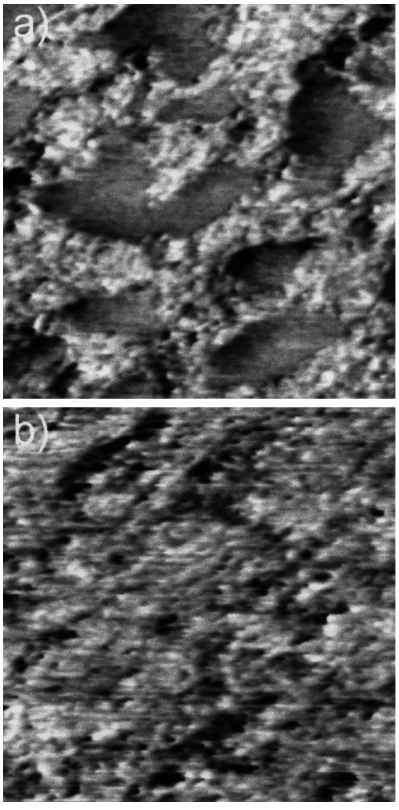

Fig. 3. Lateral force images for (a) 15 min UV/ozone treated PP film surface and (b) its water-washed surface in a 1000 nm square area. Gray-scale ranges for the two images are 1.5 nA, which is the direct output of the photodetector corresponding to the torsional movement of the cantilever.

the water-washed UV/ozone treated PP film did not return to the values for the original PP film. In fact, both XPS and IR measurements of the UV/ozone treated PP film indicated that the treatment extends deeply into the treated PP film [2].

By comparing Fig. 1c and Fig. 2b, it is apparent that water-washing resulted in the disappearance of the droplet structure. In order to probe differences between the droplet structure and surrounding mounds, we performed lateral force imaging on the 15 min treated sample before and after water-washing. The lateral force images are shown in Fig. 3, while the concurrently collected contact AFM topographic images (not shown here) are comparable to those seen in Fig. 1c and Fig. 2b, respectively. We can clearly see in Fig. 3a that the image shows two different areas on the modified PP film surface. The droplet structures show a smooth lateral force distribution, while the surrounding surface shows much smaller features. As shown in Fig. 3b, on the other hand, lateral force imaging shows that only the smaller features remain after water-washing.

The lateral force data in Fig. 3 are derived from the torsional movement of the cantilever when scanning the tip across the surface, and can be a measure of the interaction between the tip and surface features. The different lateral force distributions on the droplet surface and surrounding surface indicate different surface structures. Therefore, the lateral force image in Fig. 3a shows that there may be two phases on the modified PP film surface. On the other hand, as shown in Fig. 3b, the modified PP film surface after washing shows only one structure, indicating the LMWOM had been washed away and the underlying surface without local differences remains. Judging from only the topographic images, it might be hard to recognize that there are two different phases on the long-time modified PP film surface.

4. Conclusion

Exposing a polypropylene film to UV light and ozone resulted in the formation of mounds which arise from the formation of low-molecular-weight-oxidized-materials. Also, an increase in surface energy, which is the reason for the improvement of wettability and adhesion performance of polymer, was deduced from the force–distance curve measurement which allowed us to measure the adhesion force between the surface and tip. Increasing the treatment time showed an increase of the surface energy and the formation of droplets which are considered to be the aggregation of short oxidized polymer chains formed during the oxidation process. The materials formed during the modification were soluble in water; however, complete recovery to the original state was not observed.

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