Nanometer Scale Mechanical Study on Well Defined Nanostructured Chain Aggregation of Polyethylene

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Summary: Two kinds of polyethylene chain aggregation with chain axis perpendicular and parallel to the supported substrate were designed and successfully obtained from melt under an electric field and by melt-drawn method, respectively. Their nanostructures were investigated by using transmission electron microscopy and atomic force microscopy. The chain modulus of the aggregations along and perpendicular to the chain axis were quantitatively measured to be 267 GPa and 13.8 GPa, respectively, by performing atomic force microscopy combining nanoindentation technique. This work provides new method to study polymer properties on the nanometer or molecular scale and insight into structure-property relationship on the nanometer scale for polymers, which was usually established based on micro-scale structure and macro-scale property.

Keywords: atomic force microscopy; modulus; nanoindentation; polyethylene; soft matter

Introduction

More and more efforts are focused on designing and preparing new functional polymer thin films with well chain alignment because the transfers of physical signal, such as loading, optical, electrical and thermal signals, etc., along the chain axis are more better and quicker than that along other directions, such as vertical to the chain axis. Thus, it is increasingly important to obtain the polymer thin films with high-order chain aggregation and then establish new methods for investigating the physical properties along and vertical to the polymer chain axis.

It is well know that polymer is a typical soft-matter showing the character of strong response to the weak external stimulus, i.e. the aggregation of molecular chains is strongly dependent on the physical environments and chemical compositions of the polymers. [1] Due to its simple

 CCC 1022-1360/00/$ 17,50+.50/0

chemical structure, with almost all physical parameters available, [2] polyethylene is thus selected as model sample in our works to design and fabricate the polymer thin films with well-defined chain aggregation under the external fields. In order to investigate the nanometer scale properties of polyethylene along and vertical to the chain axis, we designed two kinds of chain aggregation with chain axis vertical and parallel to the supported substrate, respectively, shown as in Figure 1. Although polyethylene is not a functional polymer, the nanometer scale mechanical response to external deformation along and vertical to the chain axis is studied by using atomic force microscopy combining nanoindentation technique. Based on the study it provides new insight into nanometer scale mechanical property of polymers and establish structure-property relationship on nanometer scale.

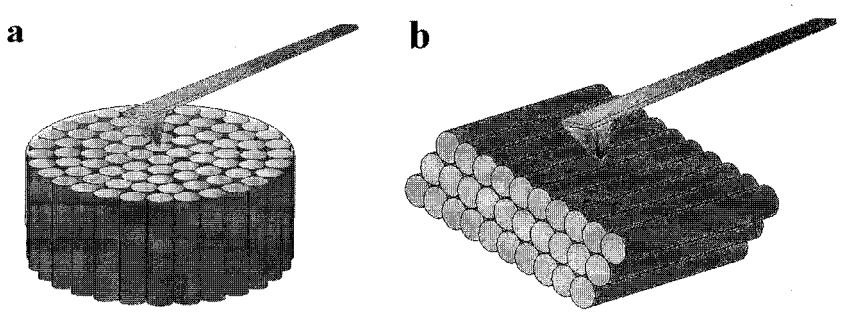

Figure 1. Schematics of nanoindentation on polyethylene chain aggregation with chain axis perpendicular to the substrate (a) and parallel to the substrate (b).

Nanostructures of Two Kinds of Polyethylene Chain Aggregation

Based on the soft ordering behavior of polymer, i. e. ordered structure is easily modulated by external fields, polyethylene chain aggregation with chain axis perpendicular to the substrate is indeed obtained from melt under an electric field. Figure 2a shows the high resolution AFM image of polyethylene chain aggregation with chain axis perpendicular to the substrate. The bright point presents the chain end of one extended polyethylene chain in the chain aggregation, similar to the schematic of Figure 1a. The AFM image shows that the chain packing is quasi-hexagonal with a = 0.822nm and b = 0.494nm, which agrees well with the results obtained by electron diffraction.[3,4] The thickness of polyethylene chain aggregation is about 50 nm by AFM, corresponding to the length of extended chain of the sample used with M_w = 5910Da and MWD of 1.1.

The polyethylene chain aggregation with chain axis parallel to the substrate is obtained by melt-drawn method. The melt-drawn polyethylene thin films with 50 nm to 100 nm thick are consisted of highly oriented lamellar crystals with growth direction perpendicular to the film drawing direction. The electron diffraction pattern shows that the structure of the highly oriented lamellae is orthorhombic with unit cell parameters of a = 0.742 nm, b = 0.496 nm and c = 0.253 nm. The lamellae display a (200) surface plane texture with the c axis, i.e. the chain axis, parallel to the drawing direction and substrate and a axis perpendicular to the plane of the film. [5] The high resolution AFM image of the lamellae (Figure 2b) clearly shows the surface chain arrangement in the lamellae with the spectral periodicity along and perpendicular to the drawing direction of about 0.26 nm and 0.50 nm, respectively. The spectral periodicity of 0.26 nm corresponds to the identify periodicity of the zigzag molecular chain (-CH2- units) of polyethylene, i.e. 0.253 nm, and the spectral periodicity of 0.50 nm corresponds to the distance between two neighboring chains in a (200) surface plane texture, i.e. 0.495 nm.

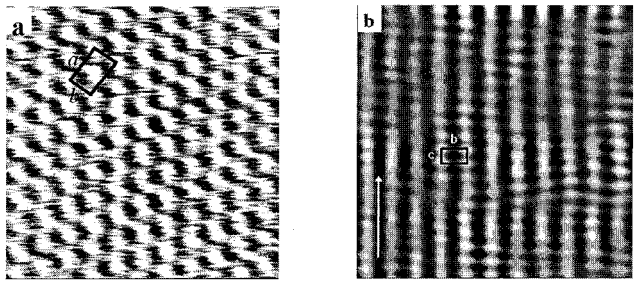

Figure 2.(a) High-resolution AFM image (5 nm × 5 nm) of the polyethylene chain aggregation with chain axis perpendicular to the substrate obtained from melt under electric field. The insert indicates an quasi-hexagonal cell. (b) High-resolution AFM image (5.27 nm × 5.27 nm) of polyethylene thin film with chain axis parallel to the substrate obtained by melt-drawn method. The insert indicates an orthorhombic cell. The arrow indicates the drawing direction.

Nanomechanics of Two Kinds of Polyethylene Chain Aggregation

The nanometer scale mechanical behavior of the polyethylene chain aggregation is quantitatively studied by using AFM combining nanoindentation technique. In brief, AFM nanoindentation curves (Figure 3a) acquired from a sample can be analyzed to give the samples' elastic modulus E_s according to the method of Oliver and Pharr corrected for the round pyramidal AFM diamond tip (Figure 3b) used in this works: [5-7]

$$E_s = \frac{(1-\nu_s^2)S}{1.065(h_0 + \Delta h_T) - 0.001S} \quad \text{(GPa)} \qquad (1)$$

where the correction factor of $\Delta h_T = (R/8)Cot^2\alpha$; h_0 is the depth of the depression that would be formed in the sample if the nanoindentation tip was a flat punch; the unloading stiffness, S = dP/dh at h = h_{max}, i.e. the initial slope of the unloading curve; R and α of ~21.6°are the tip radius and the half-included angle of the AFM diamond nanoindentation tip, respectively.

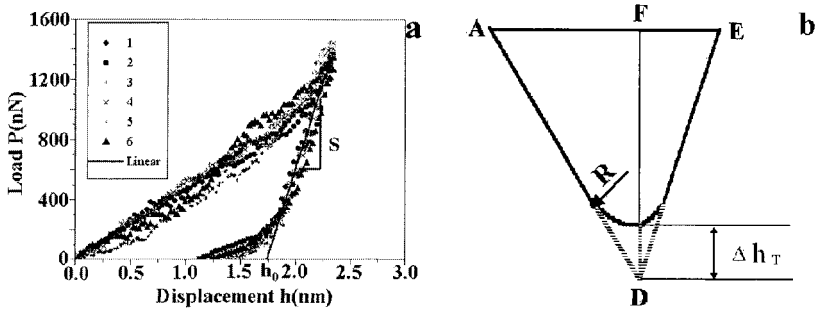

Figure 3. (a) Six typical AFM nanoindentation curves on polyethylene thin films with chain axis perpendicular to the substrate with the same indentation force. (b) The sectional profile of round pyramidal AFM diamond tip used in our works.

As shown in Figure 1 chain modulus of polyethylene perpendicular to and along the chain axis can be quantitatively obtained by performing AFM nanoindentation on the two polyethylene chain aggregations in Figure 2. Figure 4 (a) and (b) show the AFM images of post-nanoindentations on polyethylene chain aggregations with chain axis perpendicular to and along the substrate, respectively. As shown in Figure 3 every data point is collected by averaging at least six nanoindentation curves on different regions of the samples with the same indentation force. Because plastic deformation or yielding, resulting in deformation in all directions with regards to the chain axis of polyethylene, may occur during nanoindentation, it is foreseeable that the chain modulus obtained will be an averaged one on all directions. From the values of the longitudinal and transverse elastic modulus of polyethylene chain determined by wide-angle X-ray diffraction in literature [8] , namely 240 GPa and 4.3 GPa respectively, the elastic anisotropy of polyethylene chains is shown as 56. Such large elastic anisotropy may lead to a large deviation between the individual indentation measurements. [3] In order to eliminate the effect of elastic anisotropy on the nanoindentation measurements, nanoindentation with various indentation forces or depths (indentation strains) is carried out in

this work and then extrapolated, as shown in Figure 5, to the zero indentation strain or zero indentation force to get the corresponding chain modulus. From the sample with chain axis perpendicular to the substrate, the extrapolated value of the longitudinal chain modulus (along the polyethylene chain axis) is obtained as about 267 GPa (Figure 5a). While for the sample with chain axis parallel to the substrate, the extrapolated value of the transverse chain modulus (perpendicular to the polyethylene chain axis) is shown as about 13.8 GPa (Figure 5b).

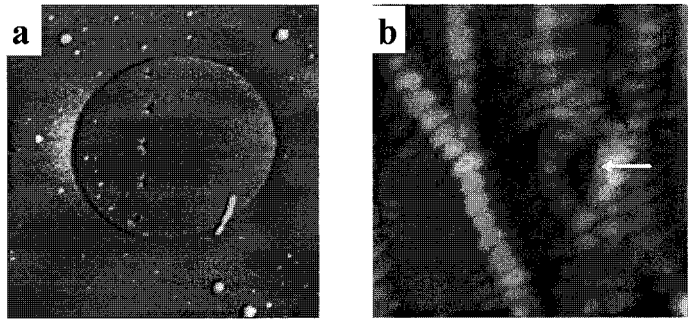

Figure 4. The AFM images of post-nanoindentations on polyethylene chain aggregations with chain axis perpendicular to substrate under various indentation forces (a); and with chain axis along the substrate under indentation force of ca. 4.5 μN (b).

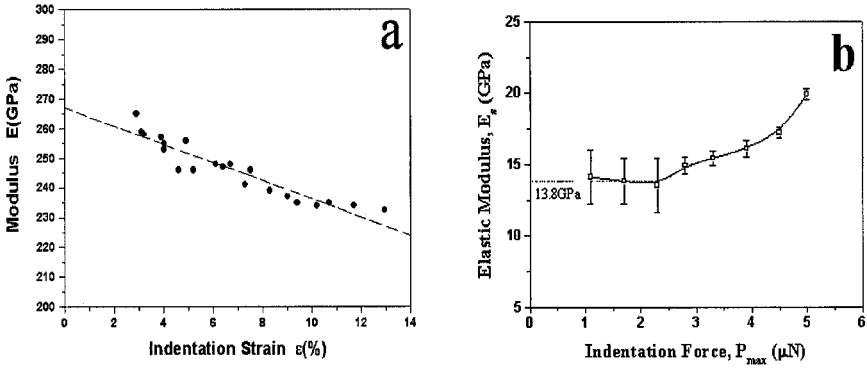

Figure 5. (a) The relationship between elastic modulus and indentation strain ε, ratio of the permanent indentation depth to the film thickness, measured from the sample in Figure 4a; (b) the relationship between elastic modulus and indentation force measured from the sample in Figure 4b.

Conclusions

The polyethylene chain aggregations with chain axis vertical and parallel to the substrate are obtained under external electric and mechanic field, respectively. The polyethylene chain modulus along and perpendicular to the chain axis are measured to be 267 GPa and 13.8 GPa, respectively, by performing AFM nanoindentation on those chain aggregations. This work provides new method to study polymer properties on the nanometer or molecular scale and insight into structure-property relationship on the nanometer scale for polymers, which was usually established based on micro-scale structure and macro-scale property.

Acknowledgements

This work was supported by the National Science Foundation of China and subsidized by the Special Funds for the Major State Basic Research Projects of the Ministry of Science and Technology of China.

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