Nanoscale probing a glass transition temperature of heterogeneous azo-polymers using atomic force microscopy

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Abstract. Azo-polymer materials found diverse applications in many interdisciplinary areas, including frequency conversion, surface relief grating and others. In such devices, stratified polymer systems are often used, in which each layer ranges from 5 nm to 100 nm in thickness. One of the key characteristics of the polymer is the glass transition temperature Tg, which indicates the thermal stability of polymer, depending on its thickness and environment. The method for determining Tg that used in this work is based on recording the dependence of the oscillation phase of an atomic-force microscope probe on the sample temperature. To study the possibility of determining the local Tg, a cross section of a multilayer polymer system, polyethylene/polyamide with the layer thicknesses of 50-100 nm, is used. Tg is measured by a change in the phase of oscillation of the cantilever, which is caused by the loss of energy of the cantilever due to the change in Gibbs energy of the polymer during the thermal expansion. It was possible to measure the local temperature within the glass transition points of the sample and for chemical identification methods used different areas of enhanced optical microscopy (nano - Raman and nano-IR).

1. Introduction
One of the key characteristics of the polymer is the glass transition temperature Tg, at which the polymer changes from a glassy state to a plastic. This parameter allows to judge the stability of the polymer under light, heat and mechanical influence. In addition, with a decrease in the thickness of the polymer, a size effect is observed when, with characteristic film thicknesses of <100 nm, Tg can fall very quickly. As a result, such systems become unstable, which limits their practical application [2]. To date, several methods have been proposed for determining Tg [3], however, known techniques do not allow the determination of the Tg of ultrathin films and the measurement of local (size of the region <100 nm) Tg values. In addition, for the complex characterization of polymer nanocomposites, information on their chemical composition with a spatial resolution of several nanometers is necessary. Thus, the purpose of this work was to measure the local Tg in the interfaces of two or more polymers.

2. Thermoinduced probe microscopy for determining the glass transition temperature of polymers
The method of determining the glass transition temperature used in the work is based on recording the dependence of the oscillation phase of an atomic-force microscope probe on the sample temperature [4]. Measurements are carried out in semi-contact mode, the sample is heated with a constant speed...
and as the sample is heated the phase of oscillation of the cantilever is recorded. Determining the \( T_g \) is carried out by the phase jump of the oscillation of the cantilever, which is reproduced during heating and cooling of the sample. Article 4 describes the technique of the experiment, and also shows that for polymer films with a thickness less than 100 nm \( T_g \) drops significantly and can reach room temperature.

Phase oscillation of the cantilever located near the sample surface depends on such parameters as the stiffness of the cantilever, the frequency and amplitude of its free and non-free oscillations, quality factor and energy dissipation during the oscillation period. The plot of the dependence of the phase on temperature can be explained by the loss of energy of the cantilever associated with the Gibbs energy and the entropy and enthalpy of the system changing during the transition to the glassy state, as a result of which the cantilever phase undergoes a jump. The reason for the increasing/decreasing of phase during heating/cooling is changing cantilever stiffness and shift the resonant frequency [5].

To study the possibility of determining the local \( T_g \) with a solution of the order of 10 nm, a cross section of a polyethylene/polyamide multilayer polymeric system with layer thicknesses of 50–100 nm was used in the work. Figure 2 shows the topography (Figure 2a) of the sample and the results of measuring local \( T_g \) for two points at which various polymers are supposedly located. To determine the points of research \( T_g \) the image of the phase contrast of the cantilever oscillations is used (Figure 2b), since it provides more accurate information about the difference in the viscous properties of the studied regions of the sample. For point 1, the glass transition temperature lies in the range from 39 o C to 42 o C, which is consistent with the known value of \( T_g \) for polyamide (from 40 °C to 50 °C). The glass transition temperature of polyethylene lies in the range of -80 ± 5 °C therefore, as expected, in the range under study for point 2 there is no change AFM phase. The difference obtained in point 1 of the values of \( T_g \) during heating and cooling of the sample due to the dependence of \( T_g \) of this sample from the kinetics of temperature effects [3].

**Figure 1.** AFM topography of the cross-section of alternately deposited films of polyethylene and polyamide; b) phase contrast taken for the same sample; c) the dependence of the phase of oscillation of the cantilever on the temperature of the sample at point 1; d) the same dependence at point 2.

Our studies confirm the applicability of the described method to determine the local \( T_g \) polymeric hetero-structures. However, this method cannot judge exact morphology of the test sample made from polymers with a close glass temperatures, because local chemical identification is necessary.
3. Tip–enhanced optical methods

3.1. Tip-enhanced Raman spectroscopy

Raman spectroscopy is one of the powerful methods for chemical analysis of substances. This technique yields information on molecular vibrations and, consequently, get insights into the chemical composition of the sample. However, the application of this method is limited by the diffraction limit. One of the mechanisms for enhancing Raman scattering is a combination of Raman spectroscopy and probe microscopy. It means that a metallic tip is brought into the focused laser beam and localized plasmon resonances are excited at the tip apex [6]. Applying the antenna to the surface of the sample causes an increase in the Raman scattering signal and allows only sample region, located directly under the tip of the optical antenna [7]. Figure 2 shows the Raman signal maps taken without (figure 2b) and with using an optical antenna (figure 2b), which allow, in contrast to AFM images (figure 1a, 1b), to diagnose the chemical composition of individual layers with subwave spatial resolution [8,9].

![Figure 2. a) Scheme of experiment b) Raman map of a polyethylene/polyamide sample taken without amplification by the probe; c) Raman map with amplification by the probe.](image)

3.2. Nano-IR Spectroscopy

An alternative method, which allows determining the chemical composition of a sample beyond the light diffraction limit, is nano-IR spectroscopy, which allows obtain local infrared (IR) absorption spectra. The specimen under investigation is irradiated with an IR laser with tunable wavelength. If the laser is tuned to the wavelength at which the sample is absorbed, the absorbed wave induces thermal expansion in the sample, recorded with an AFM probe in contact with the sample. Thermal expansion recorded by the AFM cantilever is directly proportional to the absorption coefficients of the material [10]. By registering this response in the selected wavelength range, the IR absorption spectrum of the sample is reconstructed. In this case, the spatial resolution of this method is determined by the size of the tip of the AFM probe.

For the studied cross section, polyamide and polyethylene films 50-100 nm thick deposited on each other were removed nano-IR spectra for two different regions (figure 3). The figure shows the resonant absorption frequencies for polyamide. Having determined the resonance frequency of absorption of one of the polymers, you can remove the sample map and obtain a contrast image of the spatial distribution of polyamide and polyethylene.
Figure 3. Local IR absorption spectra taken from two different points of the sample.

The map, taken at a frequency of 1660 cm$^{-1}$ (figure 4d) — the resonance frequency of absorption of polyamide, shows the contrast between the absorption of light by different parts of the sample with different chemistry composition. Figure 4d illustrates the fact that the sample consists of two different polymers, with different resonant absorption frequencies of IR radiation. In the course of these experiments, it was possible to achieve a spatial resolution about 10 nm.

4. Conclusion

Using the technique described above, the local glass transition temperature of a layered polymer interface was determined. In addition, the combination of thermally induced probe microscopy, and enhanced optical spectroscopy and nanoscopy (Raman and IR) makes it possible to determine the local glass transition temperature of polymer interfaces with nanometer accuracy. Thus, this study opens up the possibility of determining the local glass transition temperature of polymer heterostructures and mixtures with a nanometer spatial resolution.

References

[1] Lu L, Zheng T, Wu Q et al 2015 Chemical Reviews 115 (23) 12666–12731
[2] Keddie J L et al 1994 Faraday Discuss 98 219–230
[3] Abiad M G, Carvajal M T and Campanella O H 2009 Food Engineering Reviews 1 (2) 105–132
[4] Kharintsev S S, Chernykh E et al 2017 J. Phys. Chem. C. 121 (5) 3007–3012
[5] Meincken M et al 2003 Surf. Interface Anal. 35 1034–1040
[6] Hayazawa N, Inouye Y, Sekkat Z et al 2000 Opt. Commun. 183 333–336
[7] Kawata S, Inouye Y and Verma P 2009 Nat. Photonics 3 88–394
[8] Kharintsev S, Alekseev A and Loos J 2017 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 171 139–143
[9] Kharintsev S S, Gazizov A R, Salakhov M Kh and Kazarian S G 2018 Physical Chemistry Chemical Physics 20 (37) 24088–24098
[10] Dazzi A, Prater C B, Hu Q et al 2012 Appl. Spectros. 66 (12) 1365–1384