

Soft Matter, Polymers, Composites

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Low temperature thermotropical dynamical processes in multiphase polymer systems by cryo AFM.

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The effect of thermotropical dynamical processes (e.g. processes, which are determined or changed by temperature) in soft materials is a subject of considerable interest and controversy not only in condensed matter physics, but also in the experimental electron microscopy. For example, the interpretation of TEM micrographs of thin sections based on the *a priori* assumption that since the specimen is of constant thickness (after ultramicrotomy) the image shows mass contrast only [1].

However, the detailed study of (bio-)polymer block face as well as of the section surfaces by AFM, represents numerous evidence that sample topography after ultramicrotomy varies from few to hundreds nanometers and strongly depends on the type of the sample material (Figure 1). Difference in the section thickness cause an additional input in the TEM amplitude image contrast and therefore has to be taken into account for the adequate TEM image interpretation. Appearance of the pronounced topographical contrast in the section surface results from thermotropical dynamic in soft materials and can be mainly attributed to the volumetric and enthalpy relaxation in amorphous polymers near or after the glass transition, which took place during material production and/or sample preparation for microscopical analysis. The glass transition is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard “glassy” and relatively brittle state into a molten or rubber-like state. If a glass-forming material is cooled below the glass transition temperature (T_g), its structure begins to depart from the equilibrium as a result of the decreasing molecular mobility, since the molecules are not able to reach their equilibrium conformations in the time scale of the cooling [2]. This may change the crystal structure, the degree of crystallinity, the perfection of the crystals, the orientation of both crystalline and amorphous phase, their contiguous structural morphology, the number of tie chains between the crystallites and as a consequence the entire phase volume.

In order to get an insight into the thermotropical dynamical processes, the analysis of the structural relaxation in specimens that are either in the amorphous or in the liquid crystalline state (or in a mixture of them) has been carried out (Figure 2). Cryo AFM (SNOTRA) [3] provides an opportunity to observe an evolution of the sample ultrastructure as a function of temperature *in situ*. The unique ability of the instrument to visualize structural changes over a wide range of temperatures (-120°C to $+50^\circ\text{C}$) with subsequent serial-section 3D reconstruction yields detailed information about polymer packing density, morphology and orientation of chains without contrast enhancing procedures, which is usually required for conventional EM studies. The results indicate that the different phases behave independently, exhibiting self-governing (and well different) glass transitions and with their own structural relaxations. Moreover, it seems that the changes in local order associated with a densification of the liquid-like packing lead to the development of some kind or local alignment, which favors the subsequent liquid-crystallization. Thermotropic effects investigated in this field can be caused by a phase separation process, by a phase transition between an isotropic and an anisotropic (liquid-crystalline) state and by strongly differing temperature dependencies of domains and matrix.

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4. We are very grateful to Ferdinand Hofer for fruitful discussions.

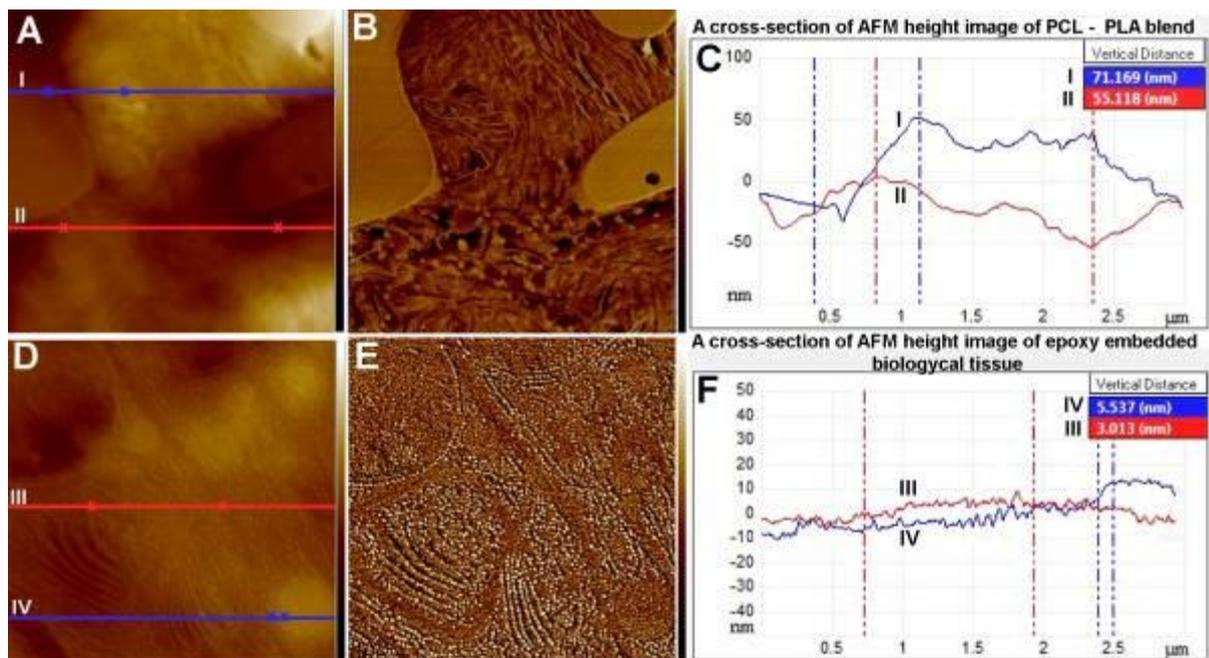


Figure 1. AFM height and phase images of the Poly[oxy(1-oxohexane-1,6-diyl)-Polylactid] polymer blend (A, B), and epoxy embedded biological tissue (D, E). (C, F) Corresponding line profiles of the block face surfaces. Phase variations: 0-100° in (B) and 0-10° in (E).

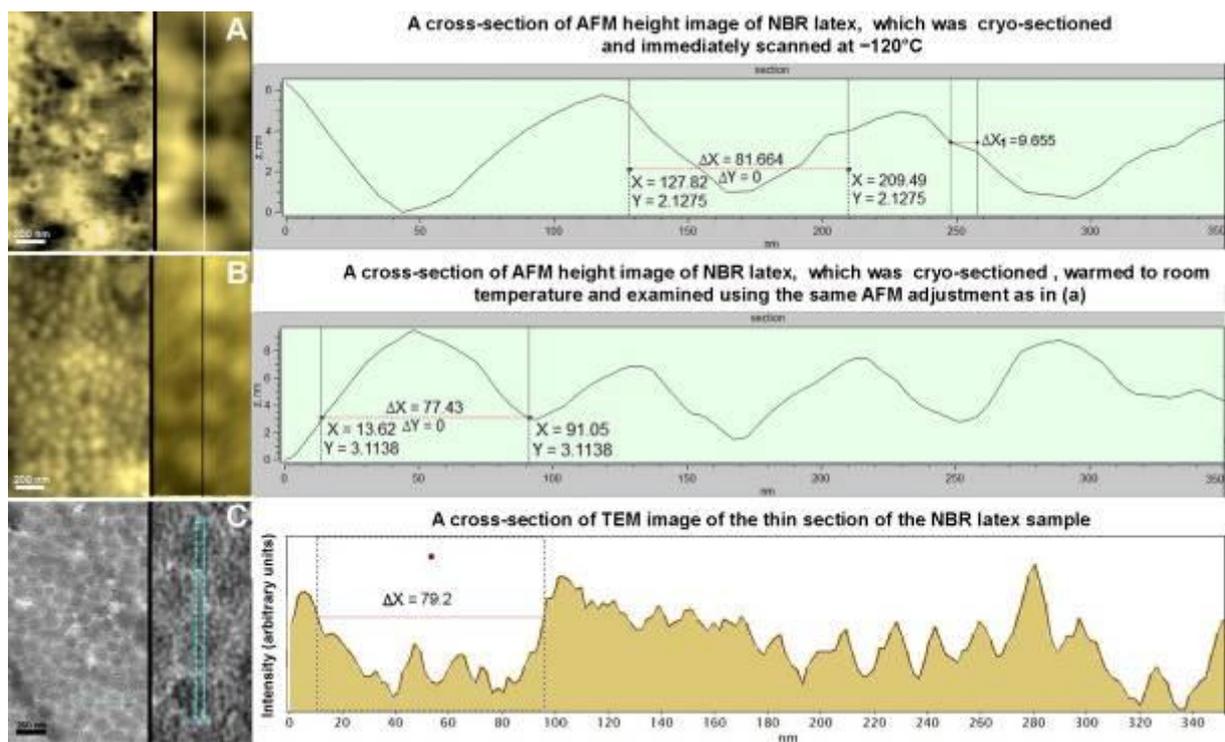


Figure 2. The morphology of a line profiles of a nitrile butadiene-rubber (NBR) latex sample characterized by cryo-AFM and TEM. (A) A topographical AFM image of an epoxy embedded latex stripe that was mounted in the cryo-chamber of SNOTRA, cryo-sectioned and immediately scanned at -120°C . (B) Immediately afterwards, the same sample was warmed to room temperature and then examined using the same AFM adjustment parameters and the same tuning fork sensor. (C) A TEM bright field image of the thin section of the NBR latex sample, which was examined without contrast enhancing procedures.