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IMAGING POLYMER SURFACES AND INTERFACES USING ATOMIC FORCE MICROSCOPY

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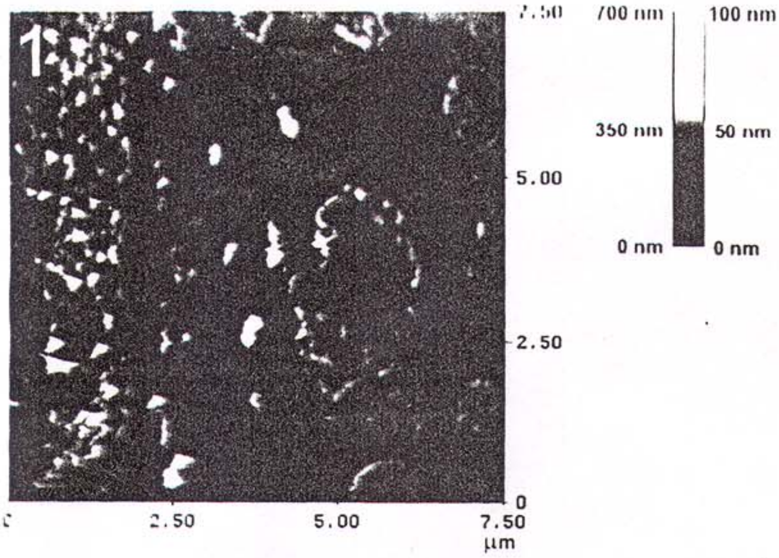
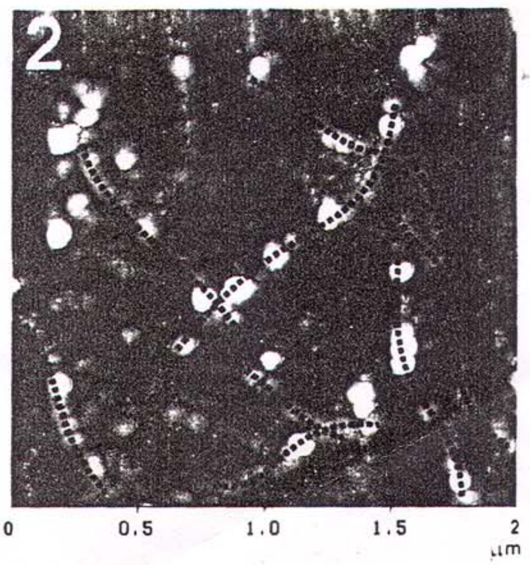
Since the pioneering work by Binning *et al.*[1], Atomic Force Microscopy (AFM) has proven to be a very useful technique to investigate surfaces and interfaces of non-conductive materials. Unlike Electronic and Tunnelling microscopies (SEM, STM), there is no need of a conductive sample to perform an AFM analysis of the material. The images are generated by a highly localised interaction between the sample surface and the AFM tip, which, in contact mode, is simply a measurement of the attraction/repulsion forces between them. Topographic images of the sample surface are then obtained by simply monitoring the deflection of a cantilever which holds the tip. Therefore, AFM is an ideal technique to investigate polymer surfaces in a sub-micrometric scale. Imaging polymer surfaces and interfaces with nanoscopic resolution can produce scientific and technological important information because many of the polymer properties and applications depend on its structure and morphology.[2] In this work, we demonstrate the feasibility and simplicity of studying polymer surfaces using AFM. In Figure 1, it is shown the cross-section of a polymeric blend interface - poly(vinylidene fluoride) / polyethylene, or simply PVDF / PE. Such blend has potential applications since it groups the pyro- and piezo-electric properties of PVDF with the low cost and mechanical properties of PE[2]. Thus, it is important to access the interface structure, looking for defects and/or other features such as material segregation. In order to obtain an interface cross-section, a cryogenic cleavage of the blend was performed at 77K which was then imaged using standard AFM techniques. The PVDF-side of the blend is shown on the left-hand side of Fig. 1 (up to ~ 2.5 µm on the scale) and the PE-side is on the right-hand side of the image. The oval features at the PE-side are segregated PVDF during the solidification process due to their different melting temperatures. Figure 2 shows a P(VDF-TrFE) - poly(vinylidene fluoride - trifluoroethylene) - surface topographic image. This material is technologically very important due to its high piezoelectric coefficient. Some of its properties vary with its phase which is reflected on the morphological structure. One can see large polymeric branches (~ 1 µm) on the surface (some of them are marked by dotted lines to serve as guides for the eye). These dendrite-like filaments are better seen on the right-hand side of Fig. 3. On the left-hand side of this figure it is shown the topographic image of a P(VDF-TrFE) surface, where few dendrite-like filaments can be observed. However, on the right-hand side, a somewhat complex ramification pattern of the filaments is observed in a much detailed image. This image was made using a new and helpful AFM mode, Phase Contrast Imaging, which enhances boundaries and contours. The known morphological structures for the P(VDF-TrFE) family are spherulites (which produces sphere-like grains up to ~ 200µm) and lamellas[2]. A dendrite-like structure has never been reported. This structure can be possibly explained either as an initial stage of lamella formation or as real dendrites which appeared in this polymer due to a large and anisotropic temperature gradient during the solidification process. Further work is currently being carried out to clear this matter up.

References:

1) G. Binning, C.F. Quate and Ch. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).
2) *Developments in crystalline polymers*, D.C. Basset ed., Applied Science Publ., Essex, 1982.





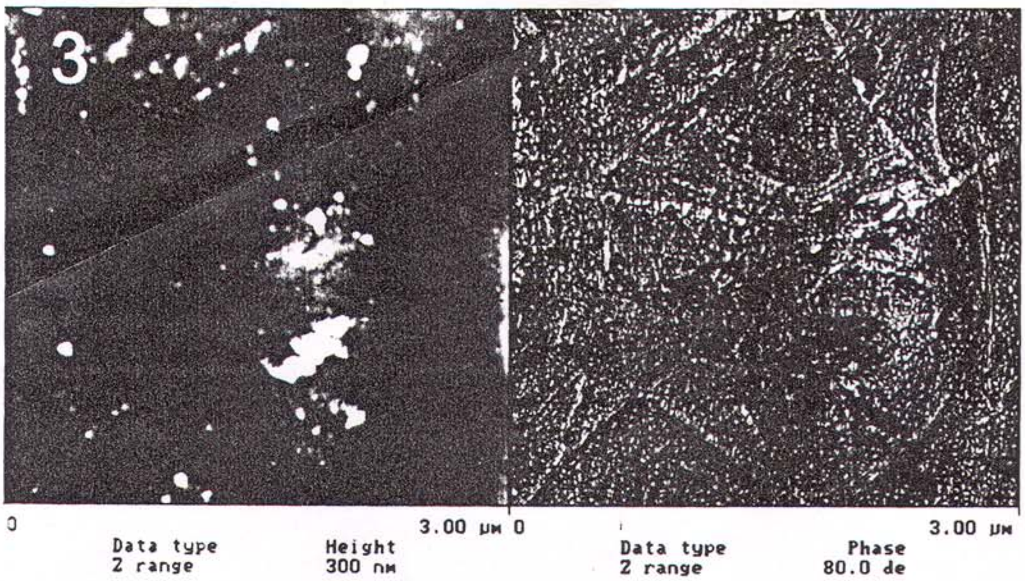


FIG. 1 - AFM image of a PVDF/PE interface. The grayscale represents the topography (0 nm : black; 700nm : white). Magnification: 9,000 x

FIG. 2 - AFM topographic image of a P(VDF-TrFE) surface. Magnification: 35,000 x

FIG. 3 - *Left:* Topographic image of a P(VDF-TrFE) surface. *Right:* Phase contrast image of the same area. Magnification: 20,000 x

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