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Nanoscale morphology of melt crystallized polyethylene/graphite (HOPG) interphase

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Summary: High density polyethylene (PE) was crystallised from the melt on freshly cleaved surface of highly oriented pyrolitic graphite (HOPG) or mica. Atomic force microscopy (AFM) studies of structure of the polymer surface adjacent to the graphite or mica were performed after peeling of from the substrate. Significant differences of crystalline structure on the interface were found between PE crystallised on graphite and mica. The surface of polyethylene crystallised on graphite shows large areas with regularly arranged rectangular structures. These objects (ca 20-80 nm big) probably represent the nucleation centres of the lamellar growth. The surface of polyethylene crystallised at mica surface shows some dot-like structures showing no particular arrangement.

Introduction

The properties of the polymer layer adjacent to a filler grain can be very important from the point of view of the properties of the composite. Especially in the case of semicrystalline polymers its structure can significantly differ from the bulk if the filler has an influence on the polymer crystallisation process. Both chemical nature of the filler surface and its geometry are of importance and in some cases even epitaxial crystallisation was observed [1)]. An influence of some materials on the morphology of crystalline phase formed at the surface has been demonstrated for several polymers using optical and electron microscopy. High nucleation density on the surface of e.g. aluminium leads to transcrystallization of PE[2)]. The influence of other materials was also studied using atomic force microscopy (AFM). The oriented growth of lamellae was deduced from AFM observation of the free surface of very thin films crystallised on different substrates (e.g.[3)]) The morphology of polymer layer adjacent to the fiber was also studied by AFM on samples obtained by microtoming [4)]. Numerous papers were devoted also to epitaxial growth of polymers on different organic and inorganic crystals (mostly alkali halides), studied using electron microscopy and electron or X-ray diffraction

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(e.g. [5] and references therein). There are many controversies in this field but a common feature is that polymer chains lay flat on the host crystal surface and lamellae are perpendicular to this surface i.e. they lay edge-on. A close match of lattice spacing of the substrate crystal and polymer is important and has a definite influence on nucleation density and on the crystal structure growing at the interface.

AFM makes possible observations of fine details without etching or metallization of the surface as it is in the case of electron microscopy (EM) however only the surface of the material can be studied. An important advantage of AFM is very good resolution in the direction normal to the investigated surface, not available in EM.

In most of morphological studies on epitaxial growth of PE using electron microscopy very thin layers of PE had to be used. Such layers were deposited on substrates from vapour phase or from diluted solutions [1,5]. The crystallisation conditions were therefore different from crystallisation from the melt, which takes place in usual technological processing.

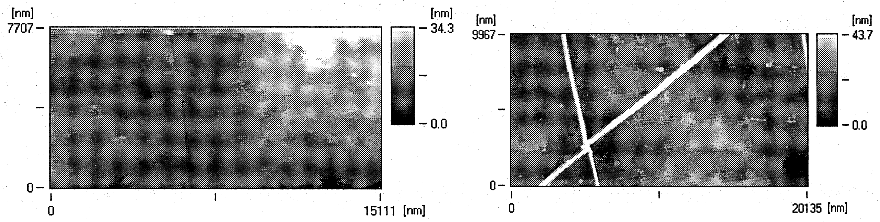
Good quality AFM images can be obtained if the surface studied is flat. Well known materials that have atomically flat surfaces on relatively big areas are graphite and mica. In this communication we present a study of the morphology of the surface of polyethylene crystallised from the melt in contact with these two materials.

Experimental

Stabiliser-free HD polyethylene (Mw=490000, Mn=34000) provided by BP Chemicals Ltd. by courtesy of Dr. G. Capaccio was used in most of experiments although commercial HDPE or LDPE give similar results. Highly oriented pyrolitic graphite (HOPG) was provided by Union Carbide. The polymer sample (0.5 mm thick) was molten at 170^0C on the freshly cleaved HOPG or mica surface. It was kept for 10 min at this temperature after slightly pressing to achieve good contact. The sample was then cooled down to room temperature (cooling rate 5^0/min). The polymer surface obtained by detaching the polymer from mica or graphite (and eventually removing gently some remaining flakes of graphite) was investigated. Both materials can be separated from the polymer without visible damaging of the PE surface and flat samples with lustrous surface are obtained. AFM observations were made using the apparatus made in University of Łódź in or Nanoscope III (Digital Instruments). Studies were performed using contact mode (V-shaped Si_3N_4 tip with radius of curvature R around 50 nm) or tapping mode (silicon rectangular tip R~ 15 nm from Nanosensors Germany) recording height and deflection or amplitude images simultaneously[6]. All scans were performed in air with a scan frequency of 2 Hz.

Results and Discussion

Large scale AFM images of the surface of PE samples detached from mica or graphite show few tenths nanometer high hills (few microns in diameter) which can be attributed to spherulitic growth in the bulk of the samples. Similar islands but more pronounced are observed in this scale on the free surface of the sample. This large scale roughness is also observed on very thin flakes of graphite which are left still adhering to the surface (Fig.1).



(a) (b)

Fig. 1 : AFM picture of PE surface (a) and of a very thin graphite flake remaining on PE after HOPG detachment (b), showing the ‘hills’ related to spherulitic growth inside the PE film. White lines are folds of the graphite flake.

Higher magnifications reveal smaller details of the polymer morphology. Fig.2 shows the surface of PE crystallised in contact with HOPG. One can clearly see „rectangular” objects more or less regularly arranged on the surface. (Fig. 2a). Their size is of the order of 20x80 nm^2 and it is surprisingly uniform on big areas (up to over 10 μm^2) some misalignments and irregularities can also be seen (Fig.2c). These objects probably represent the nucleation centres of the lamellar growth. As one can see the “long axis“ of rectangles tend to follow the same direction within domains (Fig. 2b) and to form angles close to 60^0 with neighbouring domains (Fig. 2c).

This rectangular pattern is unusual although the surface morphology of PE different than typical spherulites was also reported. Epitaxial crystallisation of PE as a thin layers on alkali halides yields rod-like structures about 20 nm thick and 100 nm long[5]. Dot-like morphology (dot size ca. 40-60 nm) was observed using AFM on the surface of highly oriented thin PE films e.g. in[8] and attributed to shish-kebab morphology. The surface of thin PE films crystallised on oriented isotactic-polypropylene (i-PP) shows cross-hatched structures with characteristic angle about 110°[9].

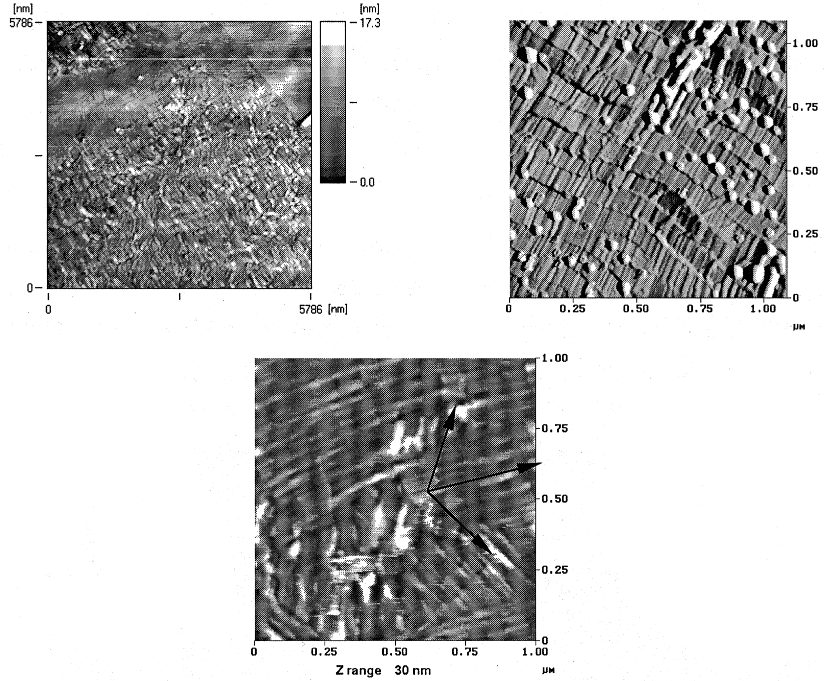


Fig. 2: AFM images of the surface of HDPE crystallised on graphite: (a) an overview showing PE surface and a remaining flake of graphite in the right-hand corner. Higher magnification of different areas showing: (b) more regular and (c) less regular arrangement of rectangular structures. (a) and (c) are height images recorded in contact mode. (b) is an amplitude image recorded in tapping mode.

The angle 60^0 between the direction of the long axes of the rectangular objects in neighbouring domains (Fig. 2c) strongly suggests that the growth of these forms is due predominantly to polymer chain arrangement on HOPG which follows the threefold symmetry of graphite planes. An ordering influence of adsorption of PE chains onto graphite surface should be taken into account since such regular arrangement is practically not observed neither on mica (Fig. 3) nor on free polymer surface.

Alkane adsorption at graphite/solution interface was well documented using mostly STM [7]. It was shown that alkanes form rectangular, extended chain 2D lamellae with chains lying, along the rows of carbon atoms of graphite. The distance between the second from the next row of carbon atoms on graphite basal plane is 0.426 nm. It is very similar to the unit cell distance in the triclinic PE phase (a=0.428 nm) and is significantly different from typical orthorhombic (a=0.740 nm, b=0.493 nm) or monoclinic (a=0.405 nm, b=0.485 nm) phase[10)]. The formation of the thermodynamically less stable PE phases (i.e. other than orthorhombic) in an initial stage (2-D nucleation) of crystallisation at the interface is not unusual. During 2-D nucleation e.g. at the NaCl /PE interface the monoclinic phase was found to be formed (in contrast to usual orthorhombic phase found in thicker films). The crystallisation of PE in monoclinic phase was observed in cases when the disregistry [11)] between the lattice parameters of the substrate and of PE was e.g. -1.5% in case of NaCl or -6% in case of p-Br benzoic acid. The dominance of the monoclinic form was observed however only in a very thin layer (few nm thick) in direct contact with the substrate [5)].

The smallest disregistry 0.47% between the lattice parameters of graphite and of PE crystal is expected for triclinic phase of PE. The disregistry between the periodicity of second from the next row of carbon atoms on graphite basal plane and of monoclinic cell of PE along a-axis is -4.93 %. In the case of orthorhombic phase also orientation of {110} plane parallel to graphite should be considered. In such case disregistry is 3.3%.

Because of small disregistries the epitaxial growth of different phases can be expected at the PE melt/HOPG interface. At present however it is not clear which phase is formed and what is the orientation of chain axis in rectangular objects. It is also not known what is the “thickness” of the contact layer. Is it only few nm thick or the rows of rectangular structures are the “apexes” of lamellae forming transcrystalline layer which can extend for several tenths of micrometers as shown in case of epitaxial growth of PE on ultrahigh molecular weight PE fibers [12,13)].

Morphology of PE crystallised on mica is not uniform. The coexistence of the lamellae 30 nm wide with dot like structures of similar size like those on PE surface crystallised in contact with HOPG but randomly arranged was observed (Fig. 3). Beside such areas often lamellae typical for less regular spherulitic structure similar to these on free surface are formed.It is not clear if there was a good contact between PE and mica in these places.

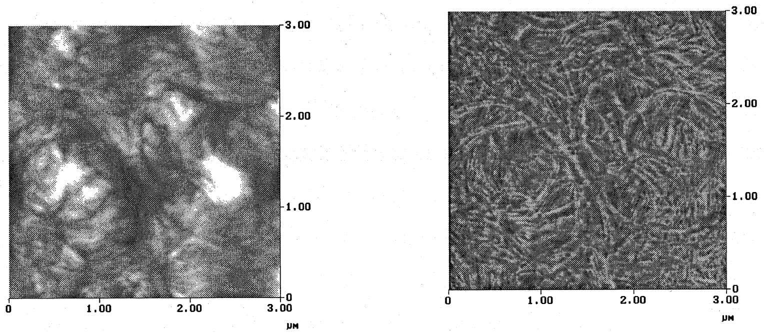


Fig. 3: Height (a) and friction (b) AFM images of HDPE crystallised on mica surface.

It is also possible that because of relatively low adhesion the PE melt is detached from the mica surface as a result of PE shrinkage during crystallisation. These observations show that mica surface has much weaker influence on the PE crystallisation than graphite.

Conclusions

AFM provides new information on polymer morphology even in relatively large scale, because of its very good z-axis resolution, which is lacking in similar scale EM pictures. AFM investigations reveal significant differences in morphology between PE crystallised in contact with graphite and mica or free surface. On graphite unusual morphology of the PE contact layer is observed: rectangular structures 20x80 nm (i.e. much bigger than typical lamellae thickness) are regularly arranged on large areas. Uniform size and orientation of these structures is indicative of an ordering of polymer melt on HOPG which is in agreement with model experiments on adsorbed paraffines. It is possible that the triclinic contact layer is the initial step of crystallisation. In the case of mica its influence on PE crystallization is not so evident.

Acknowledgements

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