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Sample preparation and AFM analysis of heterophase polypropylene systems

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Abstract

This paper reports how atomic force microscopy (AFM) could be used to get detailed information about the morphology in heterophasic polypropylene samples. Part of the work is devoted to how the sample preparation for AFM bulk analysis could be performed to optimise the information that could be gathered from the samples. Cryomicrotomation together with routine operation modes in AFM, i.e. tapping mode and contact mode is shown to be a powerful tool to characterise the distribution of segregated phases as well as the structure in these phases. The quality of the morphology images obtained from a refined sample preparation and the amount of information that could be drawn from them is believed to be comparable to, or even better than that obtained from more elaborate scanning electron microscopy examinations on stained surfaces. The quality of the images allows for image processing which enables compositional analysis.

Keywords: Atomic force microscopy; Ethylene–propylene copolymer; Sample preparation

1. Introduction

Increase in the low temperature impact strength of polypropylene (PP), is a key to further broadening of the application areas and an improvement in the competitive strength of PP. Therefore, modified PP systems have been introduced to meet application demands. The most widely used method to improve the impact properties of PP, is through copolymerisation with another α-olefin in a multi-stage reactor system, resulting in a heterophasic system with dispersed rubber particles in a PP matrix. Post-reactor modifications by elastomer compounding or fibre reinforcement are also common.

Such modifications to improve the impact properties are often detrimental to other desired properties. The development of new systems that show an improved balance between properties represent therefore one of the major challenges to the PP industry. For instance, an improved balance between impact strength and stiffness, impact strength and transparency and impact strength and stress whitening is desired and are areas of continuous research.

A detailed knowledge of the phase morphology is believed to be a key parameter for the improvement of mechanical and optical properties, and to be able to obtain a proper balance between these properties for different applications. The impact properties will in general be dependent on the matrix ligament thickness and thickness distribution, the rubber dispersions and particle sizes, and finally, the matrix crystallinity. The optical properties will in general be dependent on the crystallinity and crystal sizes, the rubber particle sizes and rubber composition. The phenomenon of stress whitening, often described as blushing, is dependent on the amount and composition of the dispersed phase, as well as on the crystallinity of the matrix.

High-impact PP, produced either by multi-stage copolymerisation of propylene with other α-olefins or by blending PP with various elastomers, show bi-phasic or multi-phase morphology. In the processing step, mechanism of breaking up and coalescence between domains of the elastomer will be in play, depending on the initial distribution, the viscosity ratio between the components, and the processing conditions. For instance, domain sizes and shapes will depend on the relative viscosity of the components, the interfacial tension as well as on the shear rate applied in melt processing. On a

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Table 1
Samples used in this work together with relevant information

Sample	Composition
PP-1	PP/Rubber/PE—85/15/0
PP-2	PP/Rubber/PE—82/13/5
PP-3	PP/Rubber/PE—70/0/30
PP-4	PP-Rubber/PE—85/15/0

small length scale, details of the morphology depend on the compatibility of the components [1].

A wide range of characterisation methods has been applied to the study of PP copolymers and blends. A number of these techniques are suited to give information on the rubber particle distribution, inter-particle distances, etc. where elastomer domains typically extend from a few hundred nanometers to a few microns in size. In particular, knowledge on volume fraction and particle size distribution of the rubber phase is important for the development of new high-impact grades and direct control of these parameters are not obtained, neither in reactor made materials nor in blends.

Scanning electron microscopy (SEM) has frequently been applied to study the rubber distribution in PP copolymers and blends [1–16]. Samples to be studied in a conventional SEM require coating to avoid charging. Since the components have similar chemical compositions and density, the rubber particles are not visible in backscatter SEM images without additional preparation. Selective staining with RuO_4 [1–6], or OsO_4 [3,4] combined with ultramicrotomy is frequently used. Ultramicrotomy combined with etching by 1,1,2,2-tetrachloroethane [7,8], hexane [3,5,6] or heptane [9] has furthermore been employed. Information on the structure of the rubber phase is then consequently lost, however, a topographic contrast due to the remnants of the rubber phases is present. Similar topographic effects are generated by xylene [10–12] extraction. Brittle fracture under liquid nitrogen [3,10,13,14], other cold environments [3,15], or examination of surface fractures by mechanical testing [12,16] has been employed, also combined with etching in cyclohexane [3]. To reveal information on crystalline structure, etching in solution of $KMnO_4$ in 2:1 (v/v) of concentrated H_2SO_4 and orthophosphoric acid is also employed [7,8].

Low-voltage SEM is advantageous in that the sample does not require coating, however, staining is still necessary. This SEM variant has been shown to give information on EPR distribution in the near surface region of painted, injection moulded PP/EPR blends [11].

TEM is another technique that has been widely applied to study the morphology in PP copolymers and blends [2,5,11,13,17–24]. This technique requires elaborate sample preparation, involving staining and ultramicrotomy. Successively prepared TEM samples show clear contrast between matrix and rubber inclusions. Furthermore, this technique has the advantage that the lamellae structure of the matrix as well as the rubber part can be studied [5,13,20,21]. TEM may also give information on the structure of the particle–matrix interface. Furthermore, in deformed samples, TEM micrographs are able to show details of the microdeformation process [13]. High-voltage TEM has been observed to better reveal larger particles [20,24].

Atomic force microscopy (AFM) is a convenient method compared to SEM and TEM in the sense that less sample preparation could be necessary and several works have employed AFM in morphology studies in rubber-modified PP [7,8,19,22,23,25–29]. AFM can directly reveal the presence of rubber inclusions directly on the surface [19,23,26,27] or on microtomed surfaces [7,8,25,28], however, etching techniques described for SEM [7,8,29] and examination of surfaces generated by breakage in liquid nitrogen is also used for AFM [22].

In this work, cryomicrotomation is applied to obtain 2D plane sections from the bulk of the samples, and an effort is made to enhance the quality and the amount of information that could be gathered from AFM observations, without any further treatment. Topographic and phase information of the 2D plane sections is obtained simultaneously in tapping mode. The local mechanical response of the material will be pictured through the phase imaging, and thus easily distinguishing between the PP matrix and the rubber inclusion

2. Experimental

2.1. Samples

The samples used in this work are four different heterophasic PP copolymers. These are listed in Table 1 together with relevant information. PP-1 and PP-4 are commercial available samples from Borealis (known as BE170MO and BJ360MO, respectively). PP-2 and PP-3 are model polymers.

2.2. Sample preparation

To gain access to the bulk structure in heterogenic PP systems and to do AFM analysis it is convenient to use ultramicrotomy, a preparation technique that is suited to obtain a smooth surface for AFM analysis. To reduce the deformation on the PP samples during microtomy, it is necessary to perform the cutting at cryogenic temperature [30]. This requires first of all a careful trimming and embedding before the sample is cut.

The PP system to be studied could exist in a wide range of different shapes, e.g. pellets, tensile bars, disks, etc. depending on the application. A convenient shape of the sample for microtomy is an object that fits into a sample holder in the microtome and also meets the size limitations for AFM analysis, without further trimming after the cutting. To obtain such geometry from, e.g. a tensile bar,

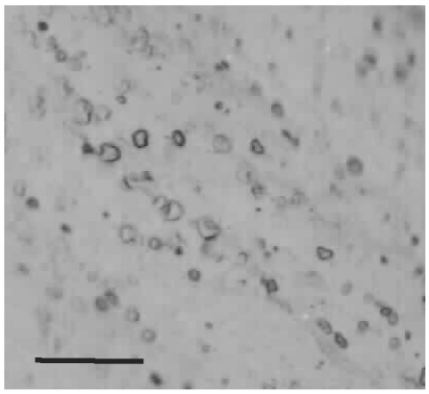
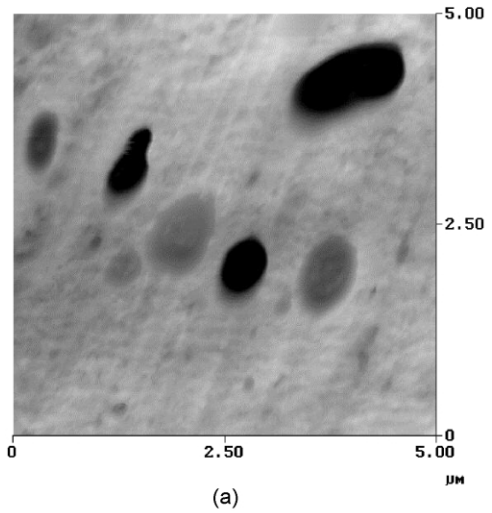


Fig. 1. Optical microscopy image of a cryomicrotomed surface in PP-1. The scalebar in the picture is 20 μm.



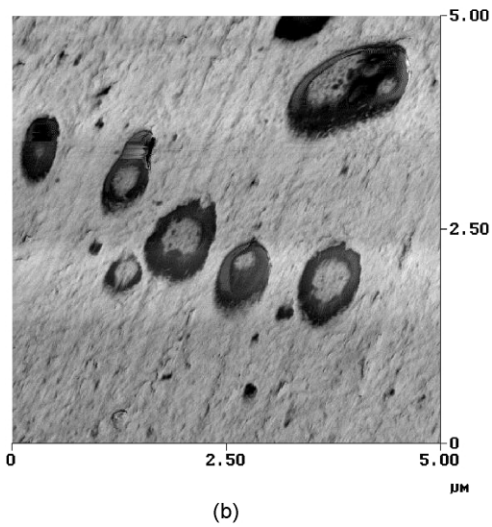


Fig. 2. (a) AFM topography image of PP-1, showing the presence of grooves in the sample. (b) AFM phase contrast image of PP-1 showing segregated soft rubber phases.

small samples have to be cut from the larger pieces and trimmed. A small handsaw was employed for sample take-out and further trimming was performed with a grinding device equipped with a water-cooling unit. A minimum of forces was applied to avoid cracks, stress whitening, heating with melting of low-crystalline regions and orientation of structures within the samples. The samples were thereafter embedded in epoxy and mounted in the cryomicrotome.

For AFM analysis, the available surface should preferentially be as large as possible, however, the cut surface should be made significantly smaller than the size of the original trimmed sample that is embedded. This is necessary in order to reduce the forces on the diamond edge during cutting. A convenient procedure to reduce the size of the surface is to prepare a smaller rectangular surface that protrudes from the rest of the surface. The cut surface should not be broader than ~ 100 μm, preferentially smaller. Broader cut surfaces tend to make it much more difficult to obtain a continuous cut over the whole surface during each cycle in the cryomicrotome. This could lead to edges across the cutting direction, which often are associated with smearing of the surface structure.

In addition, broad cut surfaces increase the number of flaws along the cutting direction.

The temperature applied during cutting should be below the glass temperature or other transitions of the sample, and this temperature should be optimised for each sample. Another important parameter during cutting is the cutting speed. The effect of this parameter has not been thoroughly studied, however, a low cutting speed (below 0.5 mm/s) seems to give more uniform thickness of the slices that are cut and a more regular cutting and the surface is believed to be more preserved, than if a higher cutting speed (above 0.5 mm/s) is employed.

2.3. AFM

The AFM measurements were performed with a Nano-Scope IIIa, Multimode™ SPM from Digital instruments. Calibration of the instrument was performed by scanning a calibration grid with precisely known dimensions. All scans were performed in air with commercial Si Nanoprobes™ SPM tips for tapping mode and commercial SiN_4 tips for contact mode.

Height- and phase imaging were performed simultaneously in tapping mode at the fundamental resonance frequency of the -Si cantilever with typical scan rates of 0.5–1.0 line/s using j-type scan head. The free oscillating amplitude was 3.0 V, while the setpoint amplitude was chosen individually for each sample. In addition for certain samples, height and friction force imaging were performed in contact mode, with typical scan rates from 0.5 to 2 lines/s.

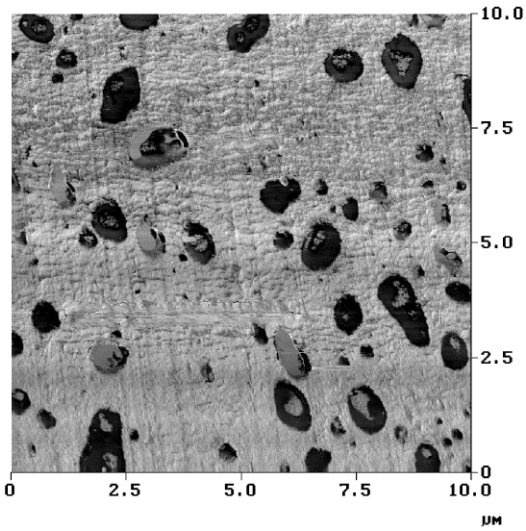


Fig. 3. AFM phase contrast image of PP-1 on larger scales. Contrast is lost in parts of the rubber phases, probably as a result of soft material periodically adhering to the tip.

3. Results and discussion

Optical microscopy is found to be a valuable technique to evaluate the quality of the surfaces after cryomicrotomation. Fig. 1 shows part of a cryomicrotomed surface from PP-1 where the cutting followed the prescriptions in the experimental part. Segregated phases are clearly visible as dark rings in the picture. As long as the segregated phases are large enough, optical microscopy is also found to be an easy and useful tool to evaluate the distribution of the larger segregated domains over the whole area defined by the cut surface.

Fig. 2(a) shows AFM topography contrast picture in tapping mode obtained from PP-1, following a premature methodology involving the use of glass knifes, and where other parameters such as cut surface, temperature during cutting and the cutting speed were not optimised. The topography image indicates the presence of grooves in the sample surface. The corresponding phase contrast image picture is shown in Fig. 2(b). The phase contrast is obtained due to the sensitivity of the phase lag and frequency shift of the cantilever oscillation relative to the drive signal of the cantilever. The reason for the phase lag/frequency shift of the cantilever while scanning the sample surface and the interpretation of the phase images is complex and not yet completely understood, and much work has been devoted to it [31–45].

The dark circular areas in Fig. 2(b) are believed to be segregated soft phases, probably ethylene–propylene rubber (EPR) phases [7]. Inside the soft EPR phases, there are islands of harder material, whose contrast is very similar to the matrix, giving a core-shell morphology. When the topography image and the phase contrast images are compared, it is clear that the segregated phases, clearly visible from the phase contrast image are submerged

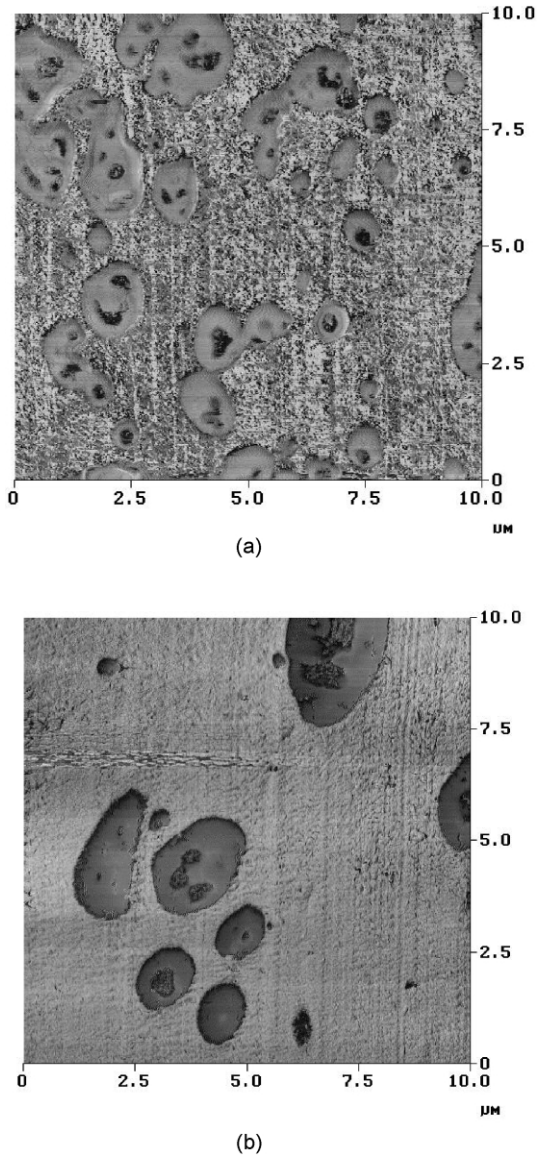


Fig. 4. (a) AFM phase contrast image of PP-1, where ‘hard tapping’ has been employed. The phase contrast between the rubber inclusions and the matrix is significantly reduced compared to light tapping. (b) AFM phase contrast image of PP-1 where the setpoint value has been set to optimise the contrast between the rubber phase and the matrix.

compared to the matrix. Height differences between the matrix, the EPR part and the more crystalline part in the segregated phases are most probably related to different expansion of the different phases during heating from cryotemperatures.

A larger phase contrast scan from PP-1 is shown in Fig. 3. The quality of the images is good enough for measuring the sizes of the rubber inclusions and also the size distributions, which are important to understand the properties. This information is readily obtained following a very direct and simple sample preparation, without considering optimising details during sample preparation.

It might be a problem to obtain correct scan parameters for these samples, since the tip/sample interactions are very

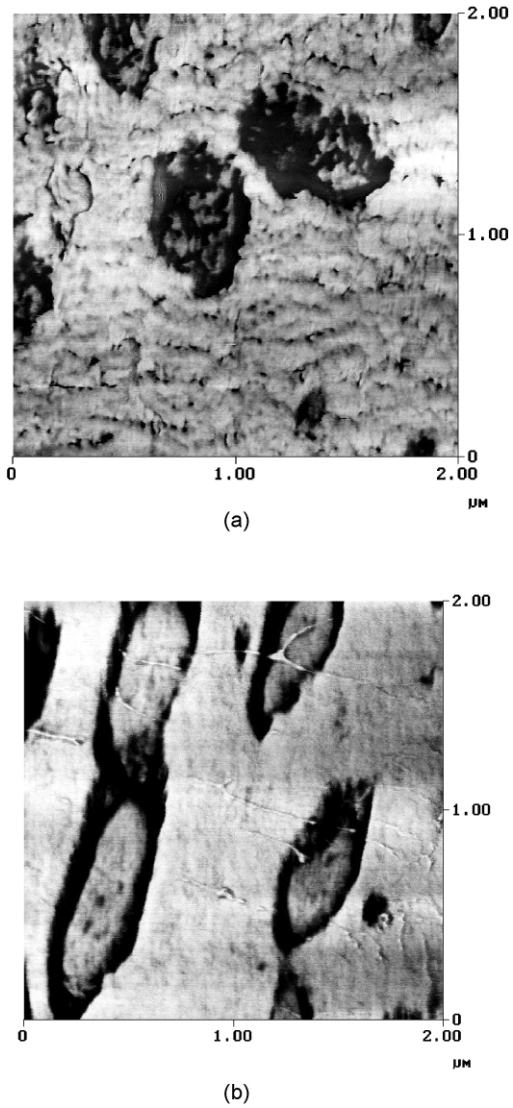


Fig. 5. (a) AFM phase contrast image of PP-2. (b) AFM phase contrast image of PP-2 obtained after a refined sample preparation procedure.

different in the matrix compared to the segregated soft phase. Material from the EPR part of the segregated phases tends to adhere to the tip for a short period, and no information is obtained in this period. In addition, the required gain values tend to be different in different phases. A typical example of such problems is seen in Fig. 3. The signal is lost at different regions within the segregated phases, and these regions might look very similar to regions with crystalline inclusions. It is difficult to completely avoid such artefacts; however, the problem could be significantly reduced by reducing the scan rate.

In addition to the scan rate, other parameters such as the setpoint ratio and the gain values are important during scanning [46]. Especially, the setpoint ratio is found to be a very important parameter to optimise when studying these samples. If the value is too low, i.e. hard tapping, the difference in contrast between the rubber phases and the matrix is significantly reduced, and a further increase in setpoint will even invert the colour contrast. An example of the contrast obtained in hard tapping is shown in Fig. 4(a). The contrast between the rubber phase and the surrounding matrix is limited, and the matrix itself has suffered from the hard tapping. In addition, the crystalline inclusions in the segregated phases are almost black, indicating a soft material.

Invertation of phase contrast during systematic changes in the setpoint ratio has also been reported earlier in polyethylene samples [32,33,46,47], in studies of phase separated blends [43] and in studies of self-assembled molecules on a substrate [42].

During hard tapping, the tip to sample contact area is larger on a soft surface than on a harder surface, and the time the tip spends in contact with the different areas is different. This might give an effective increase in stiffness of the soft layers, explaining the inversion of the phase contrast [47].

Moderate tapping facilitates correlation of contrast in phase images to local stiffness variations [32,33,46,47], and as shown in Fig. 4(b), the contrast between the EPR fraction and the matrix is significantly increased compared to Fig. 4(a) (hard tapping). Variations in the tip–sample force interactions through variations in the setpoint ratio is therefore of importance when studying rubber-modified PP systems, which has also been demonstrated for other systems, e.g. polyethylene systems [47], poly(diethylsiloxane) [48], poly(ethylene oxide) [49,50] and diblock copolymers [51].

PP-1, shown in Fig. 2(a) and (b), has good impact strength together with high stiffness.

PP-heco-2 is known to have a better balance between impact strength and transparency and between impact strength and stress whitening. In order to understand the enhanced properties of PP-2 it is of fundamental interest to be able to explore the morphology on this sample and compare it to the morphology observed in PP-1. When the morphology of the PP-2 material is explored it is

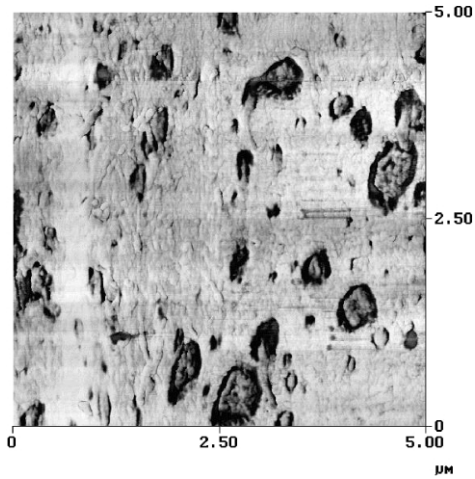


Fig. 6. AFM phase contrast image of PP-2 obtained when microtomed at −50 °C. This temperature is probably too low to preserve the structures during cutting.

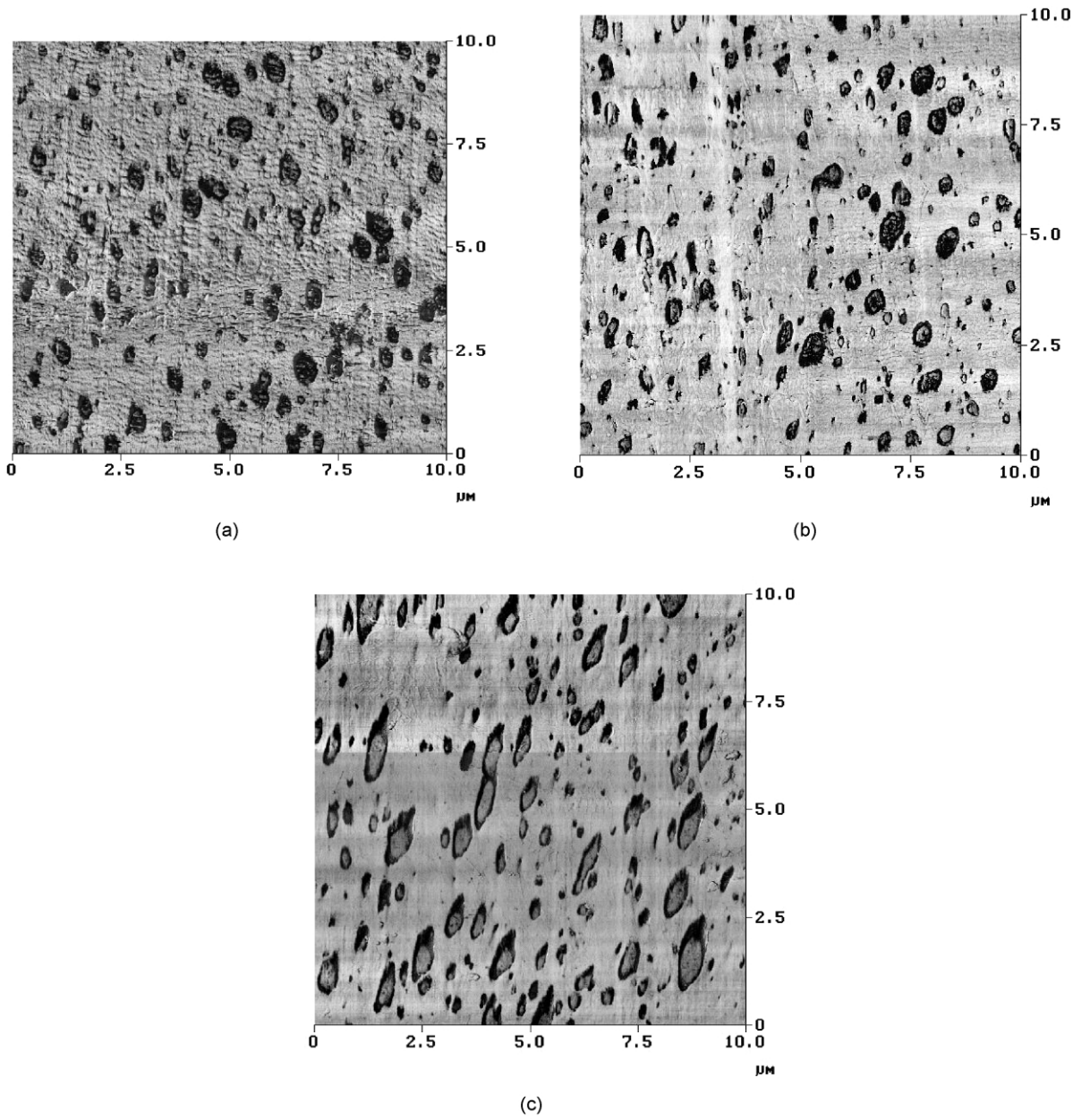


Fig. 7. (a) AFM phase contrast image of PP-2 obtained without optimising preparation procedures. (b) AFM phase contrast image of PP-2 obtained when too low temperatures are employed. (c) AFM phase contrast image of PP-2 after optimising preparation procedures.

immediately clear that the rather rough and quick sample preparation used for PP-1 does not work.

Fig. 5(a) shows AFM phase contrast picture from PP-2. The boundary between the soft rubbery phase and the matrix seems to be heavily deformed which is also the case for the matrix. The matrix is furthermore found to be dominated by edges across the cutting direction. Based on this it is clear that the sample preparation utilised to obtain relatively good-quality images from PP-1 will not give good enough results for PP-2. For this sample it was therefore necessary to consider the temperature during cutting in more detail, as well as the size of the cut surface and the cutting speed.

Fig. 5(b) shows AFM phase contrast picture in tapping mode on PP-2 obtained following a refined methodology described in Section 2. The segregated rubber phases are now much better visualised, and the presence of crystalline inclusions within the segregated rubber phases is far more clear. Edges across the cutting direction are not present. In addition, these images indicate the presence of softer islands within these crystalline inclusions, which were hard to see in the previous image. Furthermore, the boundary between the matrix and the rubber phases seems to be more preserved.

Another advantage is that smaller phases are much easier to be seen in Fig. 5(b) compared to Fig. 5(a), due to a more preserved matrix. However, it should be pointed out that the small phases might originate from the cutting plan, i.e. the

small phases might be the top of a larger phase that was cut. However, due to the mechanical deformation during cutting (smearing), it is not possible to extract any detailed information from the matrix structure.

It is furthermore interesting to see how the quality of the images is dependent on the cutting temperature. For PP-1, the quality of the results did not seem to be very dependent on the temperature in the cryomicrotome, as long as the temperature was −50 °C or lower. The cutting temperature for PP-2 was varied in the range from −50 to −150 °C. The lowest achievable temperature that could be reached on the cryomicrotome employed in this work was −150 °C. However, the experience from this work was that microtomy at such low temperatures was very difficult. It was hard to achieve a stable process where a slice was generated for every cycle in the microtome and where the thickness of the slices generated in the cycles was uniform. This will have a negative effect on the quality of the surface. An increase in the temperature will significantly reduce this problem. On the other hand, if the temperature is too high, e.g. −50 °C, the quality of the surface for PP-2 was found to be poorer. An example of this is shown in Fig. 6, where there are large matrix deformations that influence the segregated rubber phases. By reducing the cutting temperature down to −100 °C, the quality of the surface and the subsequent AFM scan will be as shown in Fig. 5(b). It should also be pointed out that the cutting speed applied is low (below 0.5 mm/s), giving a more stable process, as recommended elsewhere [52]. The reason for the different behaviour of PP-1 and PP-2 during sample preparation is most probably due to the LDPE phase in PP-heco-2 that will lower the glass temperature of the sample. On larger scales the difference between the quality of the pictures is clearer, as shown in the phase contrast pictures shown in Fig. 7(a)–(c). The quality of AFM images (e.g. Fig. 7(c)) after a refined cutting procedure is believed to at least equal to or even better than reported for stained microtomed surfaces examined by SEM [1–6].

Furthermore, the rather good quality of the images enables extraction of quantitative data through image processing. During image processing the contrast between the matrix, the EPR part of the segregated phases as well as the crystalline inclusions in the segregated phases is further enhanced. An example of this is shown in Fig. 8. Software facilities enable the calculation of area fraction of the different phases. The origin recipe of this sample is 82% PP-random matrix, 13% rubber and 5% LDPE. AFM combined with image processing gives 84% PP random matrix, 16% rubber and 3.5% LDPE. These results might indicate that parts of the LDPE are distributed not only in the crystalline inclusions in the segregated phases, but also in the matrix. However, more elaborate analysis is needed (large number of areas) to verify this. By utilising larger scan areas and several images, it is possible to get a very nice distribution of the different phases on a large scale. Another important

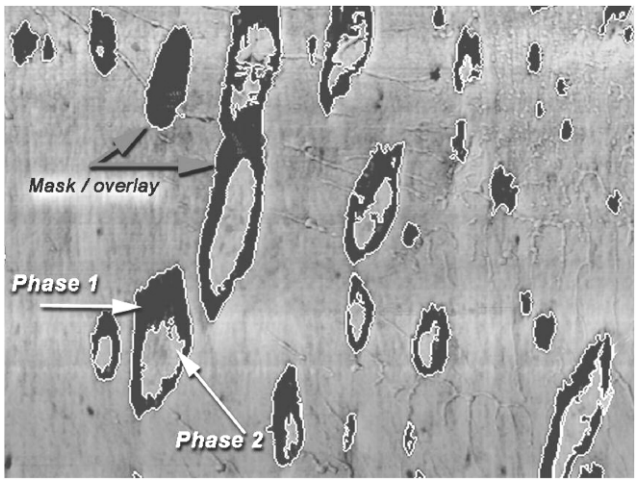


Fig. 8. Image analysis on PP-2. The contrast between the matrix, the EPR part of the segregated phases as well as the crystalline inclusions in the segregated phases is enhanced and masks are defined.

information that easily could be extracted from these data is the size distribution of these phases.

The results presented so far were gathered from PP-1 and PP-2, where most of the emphasise were put, both on sample preparation and correlation with properties. The methodology developed for PP-2 is, however, not directly transferable to other systems. An example of this is AFM applied on PP-3, which contains significantly higher amounts of PE (~30%), a significant increase in the PE part compared to PP-2. A typical result obtained for this sample is shown in Fig. 9, where a phase contrast picture from PP-3 is presented. Both the matrix and the segregated phases are found to be deformed. The high amount of polyethylene in this sample will probably demand for a lower cut temperature, and there is probably a closer interconnection between the matrix and the segregated

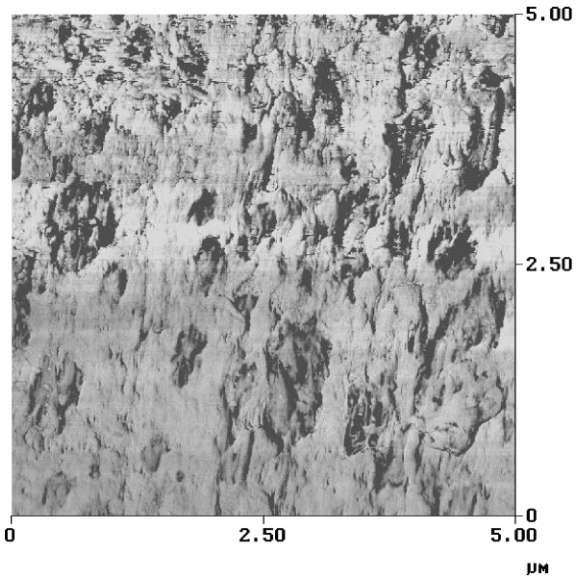
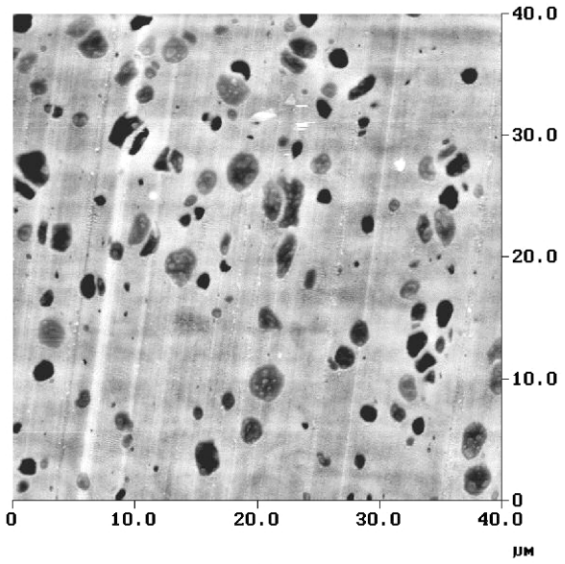
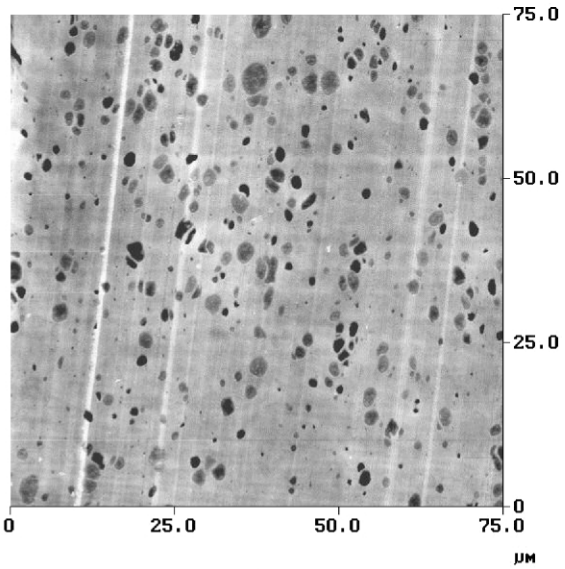


Fig. 9. AFM phase contrast image of PP-3 containing relatively high amounts of PE.



(a)



(b)

Fig. 10. (a) AFM $40 \times 40\ \mu m^2$ topography image of PP-4, generated in contact mode. (b) AFM $75 \times 75\ \mu m^2$ topography image of PP-4 generated in contact mode.

phases. However, a reduction in temperature did not improve the results considerably. For this sample, it might probably be necessary to perform some light etching to reveal the structures in this sample in more detail. This is necessary because of the relatively high content of PE in this sample. This example illustrates the necessity to optimise the sample preparation procedure for each sample that is to be studied in detail.

The work presented so far is based on tapping mode AFM. Tapping mode enables phase information in addition to topography and is a convenient mode to work with in the AFM on the polymer systems employed here. However, contact mode is normally a must quicker method to generate topography pictures, i.e. this mode allows higher scan rates than the tapping mode normally does. Additional information could also be obtained in contact mode by measuring the lateral tip–sample forces [46]. However, phase contrast information is not available in contact mode and the forces between the tip and the surface is generally larger, which might be harmful to the surface [53]. It is easier though to obtain larger scans with contact mode than in tapping mode, and this mode could therefore be useful when large-scale variations are important, e.g. for studies of impact properties of samples. Fig. 10(a) and (b) demonstrate this on PP-4, a sample that combines low temperature impact strength with good stiffness. By utilising contact mode, $75 \times 75\ \mu m^2$ scans are readily obtained, and by combining several scanned areas, information from mm-size areas are readily obtained within reasonable tine. It should also be pointed out that detailed information about the segregated phases also is possible from contact mode analysis, as shown in Fig. 11, where detailed structures in the phases in PP-4 are studied.

4. Conclusions

This paper describes the use of AFM to explore the morphology in heterophasic PP materials and the sample preparation necessary to generate such information. The method described is shown to give valuable information about the morphology in these samples, i.e. size- and size distribution of rubber phases as well as detailed information of the phases on sub-μm scales. The method is considered to be faster than traditional work based on TEM and SEM. The technique do not allow for the same level of details as good

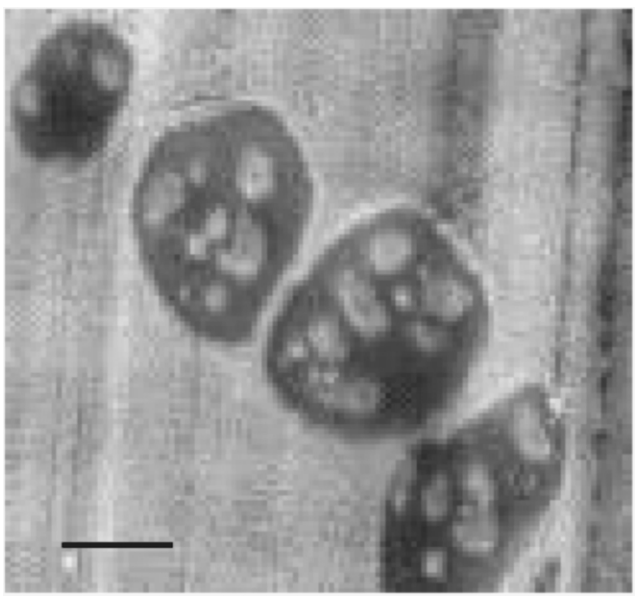


Fig. 11. AFM topography from contact mode in PP-4 showing segregated rubber phases with islands of harder material. The scale bar in the image is 1 μm.

TEM samples might do, however, it is considered equal to or even better than samples prepared for SEM. Optimalization of sample preparation might be needed for each type of material to get the necessary quality of the pictures. However, once sufficient quality of the prepared surfaces is obtained, the corresponding AFM images allow for image analysis, where compositional information could be gained.

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