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Spatial resolution and property contrast in local mechanical mapping of polymer blends using AFM dynamic force spectroscopy

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ABSTRACT A R T I C L E I N F O Keywords: The spatial resolution and the contrast in mechanical property mapping by atomic force microscopy (AFM) Atomic force microscopy modes based on dynamic force-curve acquisition, HarmoniX™(HMX) and Peak-Force-Tapping-QNM™(PFT-QNM) Polymer blends modes, are discussed in terms of contact radius, probe type and imaging parameters. The study is based on model Elastic modulus polymer samples including elastomers, thermoplastics and thermoset resins and on contact mechanics con-Adhesion siderations to provide a better understanding of the main parameters governing spatial resolution and property Spatial resolution contrast in AFM-based nanomechanical mapping. The tip-sample interaction area and volume characterized by Property contrast the contact radius are the key parameters governing the spatial resolution in adhesion force and elastic modulus images, respectively. The contrast in mechanical properties depends on the proper choice of the probe and on the control of the pixel size and the imaging force. The study also demonstrates that all these parameters are mu-

tually interconnected and may have contradictory influences.

1. Introduction

Mapping at the local scale the mechanical properties of polymers and soft matter has been a major subject of interest since the introduction of atomic force microscopy (AFM) in 1986 [1]. Besides imaging surface topography with nanoscale resolution, the possibility of probing a very small volume of materials (few nm³) offers a great depth of knowledge about polymer mechanical properties at the level of interfaces and interphases. However, when imaging of mechanical properties is concerned, the generation of numerous data pixels with conventional (quasi-static) force-distance spectroscopy appears to be a very tedious and time consuming task.

The emergence of vibrating probe AFM modes [2-4] was a great step toward simultaneous topography and property mapping at reasonable imaging speed with a lower risk of tip or sample damage. In these modes, the probe is made to vibrate at one or multiple frequencies that may be resonant or non-resonant frequencies. The vibration mode and the observable parameters that are tracked using the feedback system (amplitude, phase or frequency response of the probe) define a variety of AFM modes.

Reliable mapping of the mechanical properties using AFM is possible provided the tip-sample interaction force is measured as a function of the mutual distance during the full approach-retraction cycle. To achieve this measurement, there are two main approaches depending

on the used AFM mode: either the reconstruction of the force curve using the vibration spectrum of the cantilever response or using directly the relation between the cantilever deflection and the piezo displacement. AFM modes based on the first approach are referred to as multifrequency modes [5]. The second approach is similar to conventional AFM-based force spectroscopy adapted to vibrating probes. In this study, one mode form each group was chosen, the HarmoniX™(HMX) mode [6] from the multifrequency group and the Peak Force Tapping QNM[™](PFT-QNM) mode [7].

AFM-based mechanical mapping can also be performed by monitoring the variation of probe response parameters, e.g. the amplitude, phase or probe resonance frequency resulting from variations in materials properties. However, mechanical characterization without knowledge of the interaction force provides a qualitative contrast of properties.

Regardless of the used AFM mode and beside the important question on the accurate quantitative determination of the mechanical properties, two other major questions may be raised about the spatial resolution and the property contrast in AFM mechanical property imaging. How far can AFM allow visualizing small phases? Can it resolve phases with closely similar mechanical properties?

In one of the early works, Krausch et al. [8] used a home-built AFM system with the probe vibrating at 6 kHz for elasticity measurement. They reported on the generation of a qualitative elasticity contrast in a

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blend of polystyrene (PS) and poly(methyl methacrylate) (PMMA). They concluded that even though the bulk mechanical properties of both components are closely similar, they can be well distinguished based on their surface nanomechanical properties.

Phase imaging in Tapping™mode became a popular application of AFM for materials property imaging [9,10] since the phase shift between the cantilever drive and its response signal shows materials property sensitivity. Magonov et al. [11] studied styrene-butadienestyrene (SBS) triblock copolymer using phase imaging at different tapping forces and were able to visualize the pattern of microphase separation beneath the topmost sample surface with a wormlike structure of 15–20 nm wide. Using the same technique. Chen et al. [12] studied biodegradable blends of poly(sebacic anhydride) and poly(DLlactic acid) (PSA-PLA blend). They investigated the effect of tapping force on the contrast generation in phase images and reported a resolution of 5 nm revealing PSA spherulites. Similarly, a phase contrast with a resolution of 15 nm revealing the nanostructure and phase separation phenomena was reported by Bar et al. [13] in blends of polypropylene (PP) and poly(styrene)-b-poly(ethene-co-but-1-ene)-bpoly(styrene) (SEBS).

However, the phase signal is related to the dissipated energy in each tapping cycle [14], which is a complex function of various contributions from different tip-surface interactions as well as AFM operation parameters [9]. Hence, the non-selectivity of this signal for a specific surface property like adhesion or elastic modulus makes it prone to misinterpretation and less likely to be used as a robust surface characterization technique.

Several approaches have been introduced more recently for the force measurement in vibrating probe AFM modes. Modes belonging to the multifrequency AFM group, including bimodal AFM [15], intermodulation AFM [16], dual frequency resonance tracking (DFRT) [17] and the HMX mode [6] as well as force-controlled modes like PFT-QNM [7] are some examples.

Sahin et al. [18] developed the HMX mode to study different samples with nanoscale features and with large modulus variation within one sample. They reported on a spatial resolution around 10 nm and a modulus resolving capacity over four orders of magnitude (1 MPa–10 GPa) in one scan (same probe and feedback settings).

Using bimodal AFM, Herruzo et al. [19] reported on a modulus contrast of 1 MPa in two separate tests on different polydimethylsiloxane (PDMS) samples under the same experimental conditions. Furthermore, they reported on a modulus spatial resolution of 17 nm on the surface of a polystyrene-b-poly(methyl methacrylate) (PSb-PMMA) block copolymer. The authors pointed out that the bimodal AFM approach has some advantages over force spectroscopy techniques, including the insensitivity to the imaging parameters as well as to the probe and cantilever choice, which allow mechanical mapping of materials with almost four orders of magnitude of modulus difference at low applied forces and without cross-talk between the surface topography and measured properties.

Lorenzoni et al. [20] studied several thin films of polystyrene-b-poly (methyl methacrylate) (PS-b-PMMA) using PFT-QNM. The size of the resolved features (pitch size) was 22 nm and the difference of elastic modulus between the components was 600 MPa. They reported on the successful detection of different phases and even on the sensitivity to local variations of the morphology since vertical domains presented a higher modulus than the horizontal ones.

However, most of the previous works only demonstrated the limits for the spatial resolution and/or the property contrast for a specific case study and without more considerations on the fundamental origin of the observations. The object of this work is thus a systematic study of the parameters determining the spatial resolution and the property contrast, especially in the case of adhesion and elastic modulus. The objective is also to provide tracks to optimize the identified parameters in order to improve the AFM property imaging capabilities.

Different model blends based on elastomers, thermoplastics and

thermoset resins were designed to cover a wide range of mechanical property values and to present well defined nanoscopic phases. First, PFT-QNM and HMX modes were used for mechanical property mapping on CSR-Epoxy blends that presented multiple phases with large variability of modulus and physical properties and forming a very fine microstructure. In that case, the objective was to assess the contrast capacity and the spatial resolution of these AFM-based modes when imaging complex polymer blends. These samples were nice candidates to compare both modes in terms of their ability to resolve spatially and in terms of modulus different phases with quite different values of elastic modulus, i.e. the bandwidth of both modes. The phenoxy-epoxy blends with a relatively coarse microstructure and much less contrasted phases properties were analysed with the PFT-ONM mode to study the influence of the pixel size on the ability of resolving phases with similar values of modulus. The results are analysed in terms of contact mechanics considerations, proper control of the imaging parameters including the probe choice and the applied force. The main factors influencing the spatial resolution and the property contrast are discussed and suggestions for further improvements are made.

2. Theoretical background

Mechanical property mapping in most commercial AFM modes is based on the Derjaguin-Müller-Toporov (DMT) contact model [6,21]. This is mainly due to the mathematically simple implementation of this model for real time calculation of different mechanical properties. The existence of a direct relationship between the elastic modulus and the measured parameters like the applied force, the adhesion force and the tip radius makes the application of this model much faster and easier. Furthermore, the DMT model is an adhesive elastic contact model valid for small indenter that is supposed to successfully describe the tipsample contact in AFM experiments.

However, the tip-sample contact in AFM may often correspond to an intermediate case between different models [22,23]. That is why a better understanding of the results can be achieved through further interpretations based on other models. Another widely used adhesive elastic contact model is the Johnson-Kendall-Roberts (JKR) model.

Both models derive from the Hertz model [24] which describes the non-adhesive contact between elastic bodies and relates the applied external load (F_0), the radius of the contact area (a) and the mutual penetration or distance between the surfaces of the undeformed solids (δ).

$$a^3 = \frac{RF_0}{K} \tag{1}$$

$$\delta = \frac{a^2}{R} \tag{2}$$

In these expressions, R is the reduced contact radius given by

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$
(3)

with R_1 and R_2 the radii of curvature of both contacting bodies. *K* is the contact reduced modulus given by

$$\frac{1}{K} = \frac{3}{4} \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)$$
(4)

with E_1 and E_2 the Young's moduli of both solids and ν_1 and ν_2 their Poisson's ratio. In the case of an infinitely stiff sphere indenting a flat compliant surface, the reduced contact radius is equal to the indenter radius of curvature and the contact reduced modulus is equal to the surface reduced modulus. Equations (1) and (2) are only valid if the contact radius *a* and the penetration δ are much smaller than the contact radius *R*.

The DMT and JKR models are extensions of the Hertz model that take into account the adhesion force between the contacting bodies. A

brief review of both models is presented hereafter.

2.1. DMT model

In the DMT model, directly based on the Hertz contact model, the long-range adhesion forces are considered to act outside the contact zone and are considered as a force offset [25,26]. More precisely, surface displacement is only due to the contact stresses and not to the interaction stresses arising from the adhesion force. Thus, adhesion only increases the contact radius, which means that it simply adds up to the external applied force.

Thus the total force acting on the contact is

$$F = F_0 + F_{adh} \tag{5}$$

with F_{adh} the adhesion force.

The contact radius is given by

$$a_{DMT}^3 = \frac{R}{K}(F_0 + F_{adh}) \tag{6}$$

and the penetration depth by

$$\delta_{DMT} = \frac{a_{DMT}^2}{R} \tag{7}$$

In this model, F_{adh} is the maximum force measured at pull-out when $F_0 = -F_{adh}$, which means when the contact radius is zero. The expression of the adhesion force is

$$F_{adh}^{DMT} = 2\pi R W \tag{8}$$

with *W* the Dupré's work of adhesion related to the contacting body surface energies and interfacial energy.

2.2. JKR model

In this model only short-range forces acting inside the contact zone are considered. Furthermore, it is assumed that the interaction stresses due to adhesion result in displacement of the surface [27]. The equations [23] related to the JKR model for a spherical tip that forms a relatively small contact radius with the sample are presented in the following. The contact radius a_{JKR} , the total penetration δ_{JKR} , the adhesion force and the contact radius at zero applied load a_0^{JKR} in the JKR model [23,28,29] are given by

$$a_{JKR}^3 = \frac{R}{K} [F_0 + 3\pi RW + \sqrt{6\pi RWF_0 + (3\pi RW)^2}]$$
(9)

$$\delta_{JKR} = \frac{a_{JKR}^2}{R} - \frac{2}{3}\sqrt{\frac{6\pi a_{JKR}W}{K}}$$
(10)

$$F_{adh} = \frac{3}{2}\pi R W \tag{11}$$

$$a_0^{JKR} = \sqrt[3]{\frac{6\pi R^2 W}{K}}$$
(12)

The characteristic of the JKR theory is the formation of a neck during unloading which is ruptured when the external applied load compensates the maximum adhesion force. Usually large tip radius and adhesive nature of the surface favour the formation of a neck and hence the application of the JKR model. The contact radius and displacement at pull-out, i.e. rupture of the neck ($F_0 = -F_{adh}$), are [29]:

$$a_{min}^{JKR} = \sqrt[3]{\frac{3\pi R^2 W}{2K}}$$
(13)

$$\delta_{\min}^{JKR} = -\sqrt[3]{\frac{\pi^2 R W^2}{12K^2}}$$
(14)

The adhesion force in AFM is measured at pull-out, i.e. the point of tip-surface contact rupture. The spatial resolution of adhesion force channel should thus depend on the contact radius at rupture, which is not predicted in the DMT model where the snap-out contact radius is considered to be equal to zero. This value can be estimated for the JKR model after some basic modifications and rearrangements of the equations.

Equation (13) for the contact radius at rupture can be written to include the adhesion force as follows

$$a_{min}^{JKR} = \sqrt[3]{\frac{RF_{adh}}{K}}$$
(15)

But the reduced modulus value, which is calculated based on the DMT model in this work, cannot be fed into this equation. Thus, *K* should be first calculated based on the JKR model.

Equation (9) for the contact radius can be written in terms of the adhesion force

$$a_{JKR}^3 = \frac{R}{K} [F_0 + 2F_{adh} + 2\sqrt{F_{adh}(F_0 + F_{adh})}]$$
(16)

Since the applied force (F_0) and the adhesion force (F_{adh}) are known, we can define $F^* = F_0 + 2F_{adh} + 2\sqrt{F_{adh}(F_0 + F_{adh})}$ and get

$$a_{jKR}^3 = \frac{RF^*}{K} \tag{17}$$

The equation of the penetration depth may also be rearranged to include the adhesion force

$$\delta_{JKR} = \frac{a_{JKR}^2}{R} - \frac{2}{3}\sqrt{\frac{4a_{JKR}F_{adh}}{RK}}$$
(18)

Substituting the expression of K obtained from equation (17) into this equation gives

$$\delta_{JKR} = \frac{a_{JKR}^2}{R} - \frac{4}{3}\sqrt{\frac{F_{adh}}{F^*}}$$
(19)

2.3. Elastic indentation stress fields

A better understanding of the spatial resolution in mechanical property mapping using AFM requires a good knowledge of the elastic indentation stress fields. The volume of material under the indenter influenced by the contact stresses indeed determines the contribution of the different phases to the overall mechanical response in a polymer blend or nanocomposite.

The study of the indentation stress fields was initiated by Hertz [24]. He was interested in determining the pressure distribution and the localized deformation in two contacting elastic bodies. To allow the mathematical description of the problem, he defined various boundary conditions, among which the condition that the integral of the normal pressure distribution within the contact area is equal to the contact force between the bodies. This is the basis of the Hertz elastic contact model. Hertz only proposed the normal stress distribution on the surfaces of the contacting bodies. In the case of two contacting spheres it is given by

$$\frac{\sigma_z}{p_m} = -\frac{3}{2} \left(1 - \frac{r^2}{a^2} \right)^{1/2} \text{ for } r \le a$$
(20)

with p_m the mean contact pressure, i.e. the applied load F_0 divided by the contact area πa^2 .

However, knowing the complete indentation stress fields at the surface and in the bulk of the sample associated with specific indenter geometries is of practical interest because it would allow the estimation of the overall material volume affected by the indenter and responsible for the measured mechanical response. Their determination starts with the analysis of a point contact initially studied by Boussinesq [30,31]. Afterwards, the stress distribution for any desired indenter geometry like sphere, cone or flat-punch may be determined using the principle of superposition. More precisely, any contact configuration can be seen as

a distribution of point loads with varying intensity and the stress distribution in the bulk of the sample can be determined by the superposition of the indentation stress fields for each point load. The point loading stresses were calculated by Boussinesq [30] and formulated in cylindrical polar coordinates by Timoshenko and Goodier [31]. Analytical expressions of the 3D stress distributions inside the elastic half-space were first proposed by Hüber [32]. Based on these expressions, the stress distributions on the surface (z = 0) for r < a are given by

$$\frac{\sigma_r(r)}{p_m} = -\frac{3}{2} \left[\frac{1-2\nu}{3} \frac{a^2}{r^2} \left[1 - \left(1 - \frac{r^2}{a^2} \right)^{3/2} \right] - \left(1 - \frac{r^2}{a^2} \right)^{1/2} \right]$$

$$\frac{\sigma_\theta(r)}{p_m} = -\frac{3}{2} \left[\frac{1-2\nu}{3} \frac{a^2}{r^2} \left[1 - \left(1 - \frac{r^2}{a^2} \right)^{3/2} \right] + 2\nu \left(1 - \frac{r^2}{a^2} \right)^{1/2} \right]$$
(21)

The distribution of σ_z inside the contact area is given by the expression proposed by Hertz (Eq. (20)). Outside the contact area (r > a), the surface stress distributions are given by

$$\frac{\sigma_r(r)}{p_m} = -\frac{\sigma_{\theta}(r)}{p_m} = \frac{3}{2} \frac{1-2\nu}{3} \frac{a^2}{r^2} \\ \sigma_z(r) = 0$$
(22)

Inside the material below the tip apex (r = 0), the stress distributions are given by

$$\frac{\sigma_r(r)}{p_m} = -\frac{\sigma_\theta(r)}{p_m} = \frac{3}{2}(1+\nu) \left(1 - \frac{z}{a} \arctan\left(\frac{a}{z}\right)\right) - \frac{1}{2} \left(1 + \frac{z^2}{a^2}\right)^{-1}$$

$$\frac{\sigma_z(r)}{p_m} = -\frac{3}{2} \left(1 + \frac{z^2}{a^2}\right)^{-1}$$
(23)

Fig. 1 presents the profiles of the principal stresses on the sample surface (Fig. 1a) and along the z-axis (Fig. 1b). One clearly see that the principal stresses at and beneath the surface remain non-negligible at distances equal to several times the radius of the contact circle [28,33]. However, the stress value decreases rapidly at a certain range, depending on the material properties and the contact configuration.

It can be seen from these graphs that the principal stresses become negligible both on the surface and underneath the sample surface at distances larger than three times the radius of contact circle. Thus, the interaction radius during indentation experiments is at least three times the contact radius.

3. Materials and methods

3.1. Materials

Core-shell rubbers. Industrial grade core-shell rubbers (CSRs) were provided by Kaneka Corporation under the trade name Kane-AceTM-MX. Batches consist of polybutadiene-based CSRs dispersed in bisphenol A diglycidyl ether (DGEBA) carrier resin at 30–40 wt% of CSR loading with a monodisperse diameter of 100 nm. CSRs blended with epoxy form a fine interface between the rubber particle and the matrix as well as a wide range of difference in the mechanical properties of the phases. These CSRs are specifically designed for epoxy toughening, thus the interface is relatively stable, which improves the quality of surface preparation with microtomy and avoids interface debounding.

Epoxy resins. Two different epoxy resins were used in this work: (1) bisphenol A diglycidyl ether (DGEBA) from MOMENTIVE under the trade name EPIKOTETM Resin 827 with a number averaged molecular weight $M_n = 700 \text{ g/mol}$ and (2) N,N,Y,Y-tetraglycidyl-4,4'-diaminophenylmethane (TGDDM) epoxy from HUNTSMAN with the trade name Araldite[®] MY721-CH.

Epoxy hardener. Both epoxy resins were cured with a diaminodiphenyl sulfone (DDS) curing agent from HUNTSMAN with the trade name Aradur^{*} 9664-1 NL.

Phenoxy. A PKHH-grade polyhydroxyether of bisphenol A (phenoxy) from GABRIEL Co. with a weight average molecular weight M_w = 52000 g/mol and a glass transition temperature T_g = 92 °C was used for the preparation of phenoxy-epoxy blends.

This blend is expected to be an interesting model sample. Indeed, the formation of spherical nodules of phenoxy in the epoxy matrix after phase separation provides a blend with phases of relatively similar values of elastic modulus and a smooth interface width of few tens of nanometres.

3.2. Experimental procedures

CSR-Epoxy blends. The CSR wt% in the blend was adjusted to 30 wt % by addition of DGEBA epoxy before addition of the DDS hardener. The batch was stirred and degassed at 80 °C for 30 min and then poured in moulds for the curing process. The curing cycle included a heating ramp up to 180 °C at 2 °C/min and an isothermal step at 180 °C for 2 h.

Phenoxy-epoxy blends. Phenoxy proportion in the binary system was varied by preparing several blends with 5–20 wt% phenoxy. TGDDM (epoxy), PKHH (phenoxy) and DDS (hardener) were blended at 100 °C in a container placed in a heated oil bath. The mixture was stirred for 30 min and degassed for another 30 min before curing. The curing program proposed by HUNTSMAN was applied: 2 h at 80 °C, 1 h at 100 °C, 4 h at 150 °C and 7 h at 200 °C. The heating rate between each isothermal step was 2 °C/min.

Ultramicrotomy. Flat surfaces for AFM studies and thin cuts for TEM observations were prepared with diamond knives from DiATOME on a Leica EM FC6 microtomy machine equipped with a liquid nitrogen cooling system.

Transmission electron microscopy. In the case of the CSR-Epoxy blend, thin cuts approximately 90 nm thick collected on copper grids of 300 mesh were observed without staining using a LEO922 TEM operated at 200 kV in order to have an estimation of CSR dimensions.



Fig. 1. Variation of principal stresses at (a) the surface (equations (21) and (22)) and (b) along the z-axis (equation (23)) of an elastic body indented with a spherical punch.

Atomic force microscopy. Most of the experiments were realized using the PFT-QNM mode. However, the CSR-Epoxy blend was also studied using the HMX mode for comparison between both modes. The analyses in the HMX mode were realized using the procedure extensively described elsewhere [34].

The PFT-QNM studies were realized on a Dimension Icon system (Bruker). Probe vibration frequency of 2 kHz, peak force amplitude of 150 nm and variable force set-points were used. In order to have a reliable AFM mechanical property measurement of samples with different modulus values, the probe spring constant should be selected accordingly. If the probe is too soft, the cantilever deflects too much at a given force without sufficiently indenting the sample surface. On the contrary, a very stiff probe will barely deflect at equivalent forces. In both cases the precision of the modulus measurement is low. Thus, the ratio between cantilever deflection and penetration depth should be optimized for each probe-sample combination [35]. Standard probes with an axial spring constant in the range 20-50 N/m offer a good compromise in this respect taking into account the range of applied force used in our experiments (5-150 nN). Therefore, unless otherwise mentioned, TESPA probes (Bruker) were used for all measurements. The spring constant, k, for each probe was determined via the measurement of the thermal noise spectrum and varied between 35 and 45 N/m.

For all the DMT modulus images, the minimum and maximum force fit boundaries of the unloading curve were kept equal to 10 and 80% of the peak force, respectively. A relative calibration process was first used to calibrate the tip radius of curvature, *R*. The calibration was done on a polystyrene (PS) sample and the parameters were adjusted in order to obtain ≈ 2.7 GPa for the elastic modulus of PS at ≈ 2 nm penetration depth. These parameters were kept constant for further mapping on the test samples. For most samples, the exact tip apex radius of curvature was also measured afterwards by imaging the polycrystalline titanium sample (roughness sample from Bruker).

Image analysis. Image analysis and data processing were carried out using in-house developed routines under IGOR Pro (Wavemetrics). The variations of the mechanical properties (adhesion force and elastic modulus) were determined using line profiles. Histograms were generated from the property images to estimate the property resolution on the different systems. These histograms were fitted with gaussian probability distribution functions for the determination of the mean value, variance and peak area.

Bulk compressive modulus. The macroscopic compressive modulus of cured CSR-Epoxy blend was measured using uniaxial compression test on a screw-driven Zwick-Roell universal testing machine. Tests were performed at room temperature using a 250 kN load cell at a constant crosshead speed of 1 mm/min. Cylindrical specimens with equal height and diameter of 6 mm and solid lubrication were used.

4. Results

4.1. CSR-epoxy blends

The average diameter and the shell thickness of the dispersed CSRs in epoxy are equal to 95 nm and 12 nm respectively based on TEM images (Fig. 2). Despite the monomodal size distribution of the CSR particles, variations in CSR diameter are apparently observed on the TEM image due to the different spatial location where the spherical particles were cut.

DMT modulus and adhesion force images of a CSR-epoxy blend obtained in PFT-QNM mode with two different peak force values are presented in Fig. 3. The mechanical property contrast is different depending on the data channel. In the DMT modulus images, only two major contributions are detected, while in the adhesion force channel, the core, the shell and the epoxy matrix are clearly resolved. Additionally, the average CSR shell thickness based on the AFM adhesion images is equal to 20 nm, a value larger than the one measured on the



Fig. 2. TEM image of CSR-Epoxy system revealing the average diameter and shell thickness values equal to 95 nm and 12 nm, respectively.

TEM images.

The spatial resolution on the different mechanical properties is defined as the minimum lateral distance between two different resolved phases. It was measured at the CSR-epoxy interface using line profiles as shown schematically in Fig. 4. An average of at least 10 line profiles was used on different CSR particles.

Table 1 summarizes the results of this analysis on adhesion force and DMT modulus images recorded with different peak force values. The contact radius, *a*, at the interfacial zone was calculated based on the DMT model and the JKR model at the maximum penetration and based on the JKR model at the snap-out or the tip-sample neck rupture.

Initially, the epoxy and CSR elastic modulus values were extracted from the corresponding images. After calculating the contact radius on both phases, values of the elastic modulus could be recalculated based on the DMT model (Eq. (6)) and compared to the values obtained from the images (Fig. 5). The recalculated values are systematically higher than the ones obtained directly from the images but depend much less on the peak force setpoint.

Values of the elastic modulus were also calculated based on the JKR model using equation (17) and compared to the values obtained with the DMT model (Table 2).

Fig. 6 shows modulus histograms calculated from the DMT modulus images obtained in PFT-QNM mode on the CSR-epoxy system at increasing peak force values. None of the histograms show three clearly resolved peaks as expected from the blend composition, i.e. contributions from the CSR particle core, from the CSR particle shell and from the epoxy matrix. Only at low peak force values a low modulus contribution, apparently corresponding to the CSR particles, is observed. This contribution (peak) disappears at higher peak force values. Furthermore, the peak corresponding to the epoxy matrix shifts progressively to higher modulus values when the peak force setpoint increases and approaches the expected modulus value for epoxy at high applied forces.

In order to check the validity of the modulus values reported in the images, force-distance curves were recorded and analysed off-line. Typical curves obtained on the epoxy matrix and on the CSR core are presented in Fig. 7. The curves obtained on the epoxy matrix present an elastic behaviour with a low adhesion and were well fitted with either the DMT or the JKR model giving for a peak force of 50 nN a value of the elastic modulus around 1.6 GPa. The curves obtained on the CSR core present a larger adhesion and a clear hysteresis. They were hardly



Fig. 3. PFT-QNM images of a CSR-Epoxy blend at different peak force values: DMT modulus and adhesion force images at 25 nN (a–b), DMT modulus and adhesion force images at 100 nN (c–d).



Fig. 4. Scheme of the way line profiles were used to determine the spatial resolution in DMT modulus and adhesion force images.

Table 1

Contact radii and property resolution for different peak force values: a_{DMT} and a_{JKR} are the contact radii at maximum penetration calculated with the DMT and JKR models respectively, a_{min}^{JKR} is the contact radius at pull-out calculated with the JKR model, adhesion and modulus resolution were determined with the procedure depicted in Fig. 4.

Peak force (nN)	a _{DMT} (nm)	a _{JKR} (nm)	a _{min} (nm)	Adhesion Resolution (nm)	Modulus Resolution (nm)
15	6.3	8.3	3.8	10	22
25	7.4	10.0	4.3	10	28
50	8.9	11.0	4.4	12	28
100	12.2	14.7	5.5	14	30
150	12.6	15.3	5.8	15	40



Fig. 5. Comparison between the values of the elastic modulus of CSR and epoxy obtained from the images and calculated separately based on the DMT model (denoted here as corrected modulus).

Table 2

Comparison between the values of the elastic modulus of the epoxy matrix and the CSR particles calculated based on the DMT and JKR models for different peak force values.

Peak force (nN)	E_{epoxy}^{DMT} (GPa)	E ^{JKR} (GPa)	E_{CSR}^{DMT} (GPa)	E_{CSR}^{JKR} (GPa)
15	3.2	3.3	0.50	0.47
25	2.9	1.9	0.50	0.40
50	2.8	2.0	0.53	0.50
100	2.8	2.7	0.53	0.40
150	3.0	2.9	0.53	0.50

fitted with the DMT or the JKR model, giving for a peak force of 50 nN a value of the elastic modulus around 0.4 GPa. In fact, fitting this curve with a power law lead to an exponent much larger than 2. This strongly suggest that creep still occurs during the unloading.



Fig. 6. Histograms obtained from the DMT modulus images captured in PFT-QNM mode on the CSR-epoxy system at different peak force values.

The HMX mode was also used to analyse the same system. Fig. 8 shows examples of DMT modulus images recorded at three different values of the tapping ratio, equivalent of different applied forces. The corresponding histograms are presented in Fig. 9. At high tapping ratio (t. r. = 0.8), i.e. soft tapping conditions equivalent to a weak imaging force, three main peaks are observed in the histogram, supposedly corresponding to the matrix, particle core and particle shell. A shoulder at higher modulus values is also observed. At lower tapping ratios, i.e. harder tapping conditions, only two peaks are clearly observed with the

modulus value of the maximum of the second peak appearing at a modulus value larger than the one of the high modulus peak observed at *t*. r. = 0.8. For the two lower tapping ratios (*t*. r. = 0.6 and 0.4), the value of the modulus of the high modulus peak do not vary significantly.

4.2. Phenoxy-epoxy blends

To investigate the parameters influencing the contrast of mechanical properties in AFM, images were acquired on the epoxy/phenoxy blends and histograms were generated from these images. Fig. 10 shows an example of topography and DMT modulus images of this system at two different phenoxy content (9 and 18 wt%).

The peak force value used to analyse all epoxy/phenoxy blends was fixed at 100 nN resulting in a penetration depth of approximately 2 nm. The variable parameters in this study were the phenoxy content in the blends and the pixel size. The pixel size determines how close the indented points in an image are located, which itself can influence the resulting histograms. The peak separation level in each histogram was measured using the following equation [36].

$$S = \sqrt{\frac{(\mu_1 - \mu_2)^2}{\sigma_1^2 + \sigma_2^2}}$$
(24)

where μ and σ^2 are the mean value and the variance for each peak obtained from gaussian fit of the peaks. Fig. 11 present the variation of the separation level (*S*-factor) as a function of the pixel size. When the pixel size is smaller than 20 nm (indented points are closer than 20 nm)



Fig. 7. Typical force curves obtained in PFT-QNM mode with a peak force of 50 nN on (a,b,c) the epoxy matrix and on (d,e,f) the CSR core. (a & d) Deflection *vs* displacement curves; (b & e) force *vs* distance curves; (c & f) retraction force-distance curves fitted with the DMT and JKR models.



Fig. 8. HMX mode DMT modulus image of the CSR-epoxy system obtained at three tapping ratios.



DMT modulus (MPa)

Fig. 9. Modulus histograms corresponding to the HMX mode images of CSR-Epoxy system at three different tapping ratios (*t. r.*) showing different number of peaks as the imaging force (related to the tapping ratio) is changing.



Fig. 10. Topography (a & b) and DMT Modulus (c & d) images obtained in PFT-QNM at a peak force value of 100 nN on two epoxy/phenoxy blends with different phenoxy content: 9 wt% phenoxy (a & c) and 18 wt% phenoxy (b & d).



Fig. 11. Variation of the separation factor (S-factor) as a function of the pixel size.

the separation level between the phenoxy and epoxy peaks is considerably reduced.

5. Discussion

5.1. Spatial resolution in mechanical property mapping

The tip-surface interaction force in AFM measurements results from the response of the sample material within an effective finite interaction zone, which introduces an inherent resolution limit to topography and mechanical mapping by AFM [37]. Knowing and controlling the parameters that influence the size of this interaction zone should allow the improvement of the spatial resolution.

As shown in Fig. 3, the adhesion image at low peak force value reveals the CSR particle structure with the core and the shell clearly visible in the epoxy matrix. The adhesion force is measured at the moment of separation of the probe from the surface (pull-out). Thus, the radius of the contact circle at rupture is the suitable parameter to better describe the spatial resolution of adhesion. The DMT model only provides a value of the contact radius when a load is applied to the tip-surface contact (Eq. (6)). At the pull-out, the applied load compensates for the adhesion force and the DMT model predicts that the contact radius *a* = 0. In the case of the JKR model, the contact radius at pull-out is finite (Eq. (13)). The values of the contact radius based on the DMT (at the peak force) and the JKR (at the peak force and at the pull-out) models are presented in Table 1 and are compared with the spatial resolution observed on the mechanical property images.

The pixel size in all the images acquired on the CSR-epoxy blend was approximately 4 nm (1 µm scan size with 256 pixels/line). The estimated contact radius at rupture a_{min}^{KR} varies between 4 and 6 nm as a function of the peak force. The spatial resolution of the adhesion image varies between 10 and 15 nm. It is slightly larger than twice the contact radius at rupture.

The DMT modulus images reveal fewer details about the

morphology of the CSR-epoxy blend compared to the adhesion images (Fig. 3). Only two peaks are systematically detected on the modulus histograms generated from the images corresponding to the epoxy matrix and the CSR ensemble without a clear separation between the core and the shell. The measured elastic modulus results from the mechanical response of the material within the interaction range (volume). As explained in the theoretical background, the interaction volume extends over a radial distance equal to several times the value of the contact radius, at least three times.

The maximum contact radius predicted with the JKR model is slightly larger than the value obtained with the DMT model (Table 1). The difference is however negligible and the spatial resolution on the modulus images at different peak forces is 3–4 times larger then the contact radius. This is in agreement with the expectations resulting from the stress field calculation using the Hertz model. Reducing the peak force, i.e. performing superficial indentation favours the spatial resolution due to the smaller contact radius. However, this may affect the quantification aspects as discussed in the section 5.3.

Adhesion force as a surface dependent parameter can offer a better spatial resolution of the different phases due to smaller interaction range of the adhesion force and the lower sensitivity to the neighbouring phase or spatial confinement effects [20]. However, the finite contact radius may still affect the determination of the lateral size of the phases leading here to an apparent broadening as illustrated by the discrepancy between the values of the thickness of the shell of the CSR particles as determined by TEM and by AFM respectively. The influences on the measured modulus will also further be discussed in the section 5.3.

5.2. Contrast in local mechanical properties

5.2.1. Peak force and probe

Fig. 6 shows that for low peak force values (15 and 25 nN) a peak at low modulus values corresponding to the CSR ensemble is observed. This peak disappears when the peak force increases. Increasing the applied force may have two objectives: first, evaluate the material mechanical response over different length scales and minimize surface dependent effects, second obtain a more reliable quantitative mapping in the relative calibration process.

Quantitative modulus mapping using the relative calibration process can be reliable as long as the penetration depth obtained on the tested sample is comparable to the one obtained on the reference sample. In the case of the experiments on the CSR-epoxy, the penetration depth on the epoxy matrix reaches the expected range (2–3 nm) only at high peak force values, above 100 nN. The contact radius at these force levels is approximately equal to 15 nm (Table 1). This results in a size of the interaction volume (45–60 nm) comparable to the CSR particle dimensions (95 nm). The measured modulus around and on the CSR particles is thus averaged with the one of the epoxy matrix. This results in a loss of contrast between the different phases in the modulus images as revealed by the histograms. Increasing the applied force or peak force thus results in an increase of the interaction volume and in interferences of the indentation stress fields between the different phases.

Another parameter that seems to influence the property contrast is the probe, more precisely its force sensitivity and bandwidth. High force sensitivity means that the probe generates a large response as a result of force differences. High bandwidth means that the probe can detect a wide range of different forces. In PFT-QNM mode the ratio between the probe spring constant and the elastic and adhesive stiffnesses of the sample has an important influence on the force sensitivity. To optimize the property resolution, the probe has to be carefully chosen as a function of the sample properties, i.e. the spring constant has to be similar to the expected contact stiffness. However, this is impossible to achieve when imaging samples with phases presenting very different values of elastic modulus. Alternative probe designs like the torsional harmonic cantilever (THC) in the HMX mode can offer a larger bandwidth and improve the probe response in case of complex samples.

Force spectroscopy in the HMX mode relies on the vibration spectrum of THC probes that can detect different force levels over a wide frequency range. This results in the possibility to better resolve the different phases in the case of systems where materials of very different rigidity are blended as demonstrated in Figs. 8 and 9. At low tapping ratio values, i.e. high interaction forces, the histograms show two major peaks corresponding to the epoxy matrix and to the CSR particle. At high tapping ratio, i.e. low interaction force, three major peaks are even resolved, corresponding to the epoxy resin and to the core and the shell of the CSR particle. This demonstrates the better capacity of the HMX mode to resolve phases with very different elastic modulus values compared to the PFT-QNM mode.

5.2.2. Pixel size and phase content

Numerous data pixels are necessary for high resolution mechanical characterization. However, an important factor that can influence the contrast in mechanical properties is the pixel size or the spacing between two adjacent indented points. As shown in Fig. 10, phenoxy forms well-defined nodules dispersed in the epoxy matrix in the epoxy/ phenoxy blends. The very low surface roughness ($R_a \approx 1$ nm) minimizes the data scattering in the calculated modulus.

As shown in Fig. 11, the separation factor S decreases when the pixel size is reduced below 20 nm. This corresponds to a widening of the peaks in the corresponding histograms and the loss of a clear bimodal distribution. The phenoxy content do not have an important influence on the *S*-factor.

In all the experiments on the epoxy/phenoxy blends, the maximum applied force was constant at 100 nN leading to low variations of the contact radius that was estimated around 5 nm. This results in an interaction volume extending at least 15 nm under and around the tip. Thus, once the pixel size gets comparable to the interaction volume size, the probe response on one pixel is influenced by the material previously indented during the acquisition of the previous pixel. This overlap between adjacent indented points reduces the *S*-factor or property contrast.

5.3. Quantitative modulus mapping

The elastic modulus values of the epoxy matrix deduced from the PFT-QNM images increase when increasing the peak force (Figs. 5 and 6). When the peak force reaches 100 nN, the penetration depth on the epoxy matrix is approximately 3 nm, a value similar to the conditions used for the calibration on the polystyrene reference sample. It is only at this point that the value of the matrix modulus approaches the value measured for the bulk compressive modulus (2.6 GPa). The value of the elastic modulus of the CSRs shows a similar trend. However, the values are higher than expected even at low peak force.

As explained previously, the drawback of the relative calibration is that the measured values for the elastic modulus are only reliable as long as the test conditions are similar to those used during the calibration. This may explain why the value of the modulus measured on the epoxy matrix on the DMT modulus images is evolving when increasing the peak force and only approaches the expected value when the force is higher than 100 nN, i.e. when the penetration depth becomes similar to the one used for the probe radius calibration. It also explain why the modulus on the CSR particles is overestimated because on the particle, the penetration depth and hence the contact radius is larger than on the calibration sample.

The values of the elastic modulus calculated taking into account the contact radius at the different peak force values is almost independent on the peak force and thus on the maximum penetration depth (Fig. 5). However, the average modulus value is higher in this case, around 3.0 GPa. The comparison of elastic modulus values calculated based on

the JKR model with those obtained with the DMT model (Table 2) shows that at moderate peak force values the JKR model gives a better estimation of the modulus. Both models give very similar results for the elastic modulus of the CSRs with negligible penetration depth dependency. Nevertheless, the values are much higher than expected.

Comparing mechanical properties values obtained with the AFM with bulk values is only possible when local effects are minimized by increasing the interaction volume. However, this results in a decrease of the spatial resolution as explained above.

Two major deviations in quantitative modulus values are expected and may explain the observations in this work. First, overestimation of the modulus measured on rubbery polymers, which is also reported in the literature [18]. This overestimation may be related to the dynamic effects associated with the force curve acquisition. While the tip-sample contact time for each data pixel is in the millisecond range for these AFM techniques, the frequency dependent behaviours are not considered in the contact models used to analyse the data. The second deviation is the underestimation of the modulus for rigid samples. In the case of the PFT-QNM mode, once the proportion of the penetration depth to the probe deflection reduces the confidence in the measured moduli drops [35]. The tip-sample contact time is also reduced when the sample rigidity increases. In the case of the HMX mode, above a certain rigidity threshold, the probe vibrations cannot follow the timevarying forces fast enough. The probe finite bandwidth is saturated and higher modulus values are not measured precisely [18].

Eventually, the observed deviations between the values of the elastic modulus reported in the DMT modulus images and the expected ones for the various phases can be explained by the two following facts [38,39]. First, the DMT model is probably not well suited to analyse the force-distance curves, especially in the case of the soft rubber core of the CSR particles where a large adhesion force is measured. Second, both the DMT and the JKR models do not take into account the viscoelastic and/or viscoplastic behaviours of polymers. This inaccuracy of these models, particularly for the soft rubbery core of the CSR particles, is illustrated by the force-distance curves presented in Fig. 7. The curves obtained on the elastic epoxy matrix may be rather well fitted with the DMT or JKR models. On the contrary, the curves obtained on the core of a CSR particle present viscoelastic behaviours that clearly cannot be fitted nor by the DMT model neither by the JKR model. This raises the question of the reliability of the modulus values reported in the DMT modulus images obtained by on-line fitting with the DMT model.

6. Conclusions

A systematic study of the major factors influencing the spatial resolution and the property contrast in quantitative AFM mechanical property mapping of polymer blends was carried out with the help of carefully chosen model samples and contact mechanics considerations.

The spatial resolution and the contrast of the mechanical property mapping are in fact influenced by interconnected parameters. Imaging the mechanical properties of small scale phases requires a better control over the interaction area in the case of the adhesion force or on the interaction volume in the case of the elastic modulus to avoid data overlap caused by the interference of indentation stress fields. Imaging and clearly discriminating phases with closely similar properties in polymer blends is possible if the data overlap determined by the ratio between the radius of the contact area and pixel size is minimized. The force sensitivity of the probe and its effective bandwidth are also influencing the property contrast between the different phases.

The spatial resolution in adhesion force images is approximately proportional to twice a_{min} with a_{min} the contact radius at tip-surface pull-out. The spatial resolution in elastic modulus images is approximately proportional to three to four times a_{max} with a_{max} the maximum contact radius. To improve the spatial resolution, the size of the contact area has to be reduced by reducing the peak force or maximum interaction force. Concerning the property contrast, when the pixel size or

the distance between adjacent indented points is comparable to the interaction volume size, the data overlap and hence the scattering in measured properties increases and the contrast between the phases decreases.

A correctly chosen probe based on the sample adhesive and/or elastic properties can offer a high force measurement sensitivity, which will improve the contrast as well. In this respect, probe designs like in the HMX mode can offer even better contrast thanks to a larger bandwidth, which is more adapted in the case of complex blends with phases having very different properties.

Quantitative determination of the elastic modulus values could be reliable as long as the test conditions are similar to those used during the modulus calibration process on the reference sample. However, the use of the DMT model for the generation of the modulus images can cause deviations from the actual values because this model is only valid for stiff contact with low adhesion and do not take into account viscoelastic and/or viscoplastic behaviours.

It should be noted that while improvement and optimization of the spatial resolution and of the property contrast are feasible by optimizing the values of the above discussed parameters, these parameters are mutually interconnected and may have contradictory effects. The imaging parameters or the AFM modes should thus be selected or adapted according to the type of information that is searched for.

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