

# CHARACTERIZING THE MECHANICAL PROPERTIES OF SKIN-CORE STRUCTURE IN POLYMER MOLDING PROCESS BY NANOINDENTATION

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**Abstract:** Quality of the polymer product produced by injection molding process are strongly affected by the mechanical properties of the skin-core structure formed during injection molding operation. It is desirable to know the mechanisms of the skin-core structure and the influence from process parameters and material properties to the skin-core formation in the injection molding. This paper focuses on characterisation of the hardness, modulus, elastic and viscoelastic properties in the skin-core structure of the HDPE polymers by using nanoindentation approach in order to understand the formation of mechanism of skin-core structure, and to facilitate design and dimensioning the polymer part, optimize molding process. The distribution of hardness and modulus were also measured with grid mapping technique by using sharp berkovich indenter.

**Keywords:** nano hardness, nanoindentation, skin-core, moulding, polymers.

## 1. INTRODUCTION

The final part prepared by injection moulding operation usually exhibits different morphological characteristics in outer layer and inner part, formed so called skin-core structure (Utsumi, et al., 2003). The structure in turn is influential to the mechanical properties of the part. (Ghiam and White, 1991) made an investigation on development of phase morphology of the nylon-6 (PA6)/polyethylene (PE) and they found that the phase morphology of the compression-moulded part was isotropic, while that of both screw and ram injection-moulded parts was both heterogeneous and anisotropic through the cross section and formed skin-core structure. In the skin-core structure of injection-moulded parts, the morphology exhibited its greatest level of isotropy in the core and became increasingly anisotropic approaching the mould skin (Karger-Kocsis and Csikai, 1987). There exist large differences in morphology, orientation, and stress between the skin and core layer of the material, which could have different effect on the quality of the ready product (Gao and Mackley, 1994). Different process parameters, such as speed of injection and mold temperature, which are correspondent to the cooling temperature, flow speed and cooling rate, may significantly attribute to the formation of the skin-core structure. In some cases, the skin characteristics are especially important for the thin wall products, because of the large ratio of skin layer thickness to core thickness. Although understanding the crystalline structure was the topic for previous research in this subject, characterisation of mechanical properties of skin-core structure is essential for the quality of the part. The characterisation of properties of skin-core remains difficult because of the small dimensions involved in the skin-core structure. The knowledge of the influence from process parameters of skin-core forming also is desirable for further optimization of the moulding process. In the present study, mechanical properties in the skin-core structure is characterised with the uses of nanoindentation as a testing method and the effect of the process conditions on the mechanical properties was analysed. The objective of this investigation is to characterize the mechanical properties of skin-core structure in HDPE after injection molding process for determination and verification of polymer mechanical properties at micro scale level in order to facilitate design and dimensioning the polymer part, optimize molding process.

### 1.1. Skin-core in polymer injection molding process

During injection molding, the hot polymer melt contacting cold mold walls experiences high strain, high stress and large cooling rate, and thus a skin layer with high orientation is formed near the walls (Kalay, et al., 1996). Fig. 1 displays skin-core morphologies as a result of processing (Woodward, 1995). The core is usually spherulitic, however may still exhibit an overall chain orientation (Trotignon, et al., 1982). The skin usually shows three (Mencik, et al., 1973) or more distinct layers (Karger-Kocsis and Csikai, 1987). The structure of the skin consists of highly oriented structures. The underlying reason for this typical skin-core morphology is that due to processing, the polymer is subjected to strong flows before and during crystallization. Moreover the polymer crystallizes under strong temperature gradients. This results in a strong orientation of both the crystalline and amorphous phases (Mencik, et al., 1973), (Karger-Kocsis et al., 1987). The skin-core indeed is an intrinsic problem of normal injection molding because these boundary conditions create large gradients of temperature, shear rate and stress fields (Li, et al., 2006). The residual stress produced by different levels of crystal orientation in the cross section can affect mechanical properties negative. Also different material properties will have influence on the skin-core formation. For instance a skin can be formed when low molecular chains that have higher movability than the bulk polymer merge to the surface during injection molding and form a softer skin. This will affect mechanical and surface properties in other ways than skin formed by shear flow. For semi crystalline polymers, shear flow at the mold filling stage may induce molecular orientation (Lots, et al., 1996).

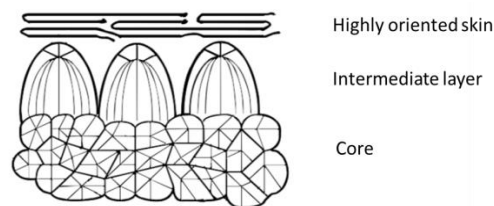


Fig. 1. Simplified schematic representation of a skin-core morphology (Woodward, 1995).

### 1.2. Nanoindentation

The nanoindentation technique has been used widely to evaluate the mechanical behaviour of polymers and their nanocomposites. It can provide the near-surface mechanical properties of materials, such as modulus and hardness, by applying a localized deformation on the surface of the material by a hard indenter. The working principle of nanoindentation is similar to that of the well established hardness test for material characterization. An indenter, such as a Berkovich diamond tip, is forced into a specimen, and the size of the residual indent in the material is measured after the indenter is fully unloaded. The maximum applied load and size of the residual indent are then used to estimate the hardness of the specimen. Nanoindentation is different from the standard hardness test in two aspects. Firstly, the magnitudes of the applied loads and resulting displacements are significantly smaller. Loads on the order of micronewtons and displacements ranging from a few nanometers to one micrometer are typical for nanoindentation. Therefore, small volumes of materials can be sampled and measured. The second difference is that the displacement of the indenter is monitored continuously during the loading and unloading cycles in nanoindentation. Therefore, nanoindentation is also referred to as depth-sensing indentation. The basic loading and unloading phase of nanoindentation are illustrated in Fig. 2. The output from such a nanoindentation test is a graph relating the applied load and the corresponding indenter displacement during the loading and unloading phases. The load displacement graphs are then analyzed to estimate the mechanical properties.

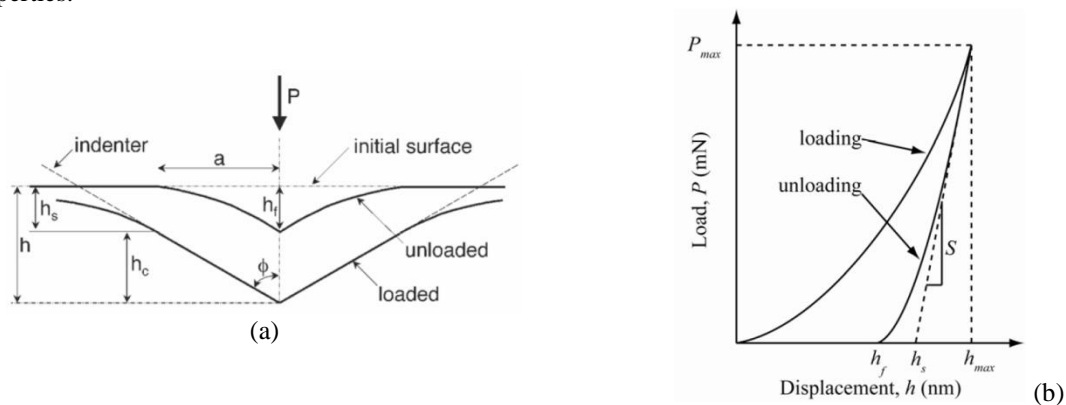


Fig. 2. (a) Illustration of the indentation geometry and (b) load-displacement curve.

The nanoindentation technique has drawn much interest recently for both its efficiency and versatility in measuring the mechanical properties of small volumes of materials and thin films. However, the application of nanoindentation to polymeric materials is still a challenging issue. Since the unloading curve of polymers depends not only on the holding time but also on the unloading rate, the widely used (Oliver & Pharr 1992) method is greatly limited. It is well known that when the unloading rate is low, the initial slope of the unloading curve, which is defined as the contact stiffness, may even become negative, causing the so-called “nose” effect. It is believed that the viscoelasticity and/or viscoplasticity of polymeric materials are responsible for this phenomenon.

The paper focuses on extracting the hardness, modulus, elastic and viscoelastic properties of polymers using nanoindentation with sharp Berkovich indenters. It is assumed that the total indentation deformation can be decomposed into a plastic component and an elastic-viscoelastic component. Samples were prepared with a predefined schedule of grinding and polishing. Nanoindents were made with a maximum depth of 1000 nm. The resolution was 10  $\mu\text{m}$  between each indent. Grid indentation was made to determine distribution of hardness and elastic modulus for the cross section of a polymer sample to assess effect of the molding process parameters on skin-core structure. The correlation between the mechanical properties and molding parameters will be addressed.

## 2. SAMPLE PREPARATION AND TEST SETUP

### 2.1. Sample preparation

*Injection moulding.* HDPE parts were produced with injection moulding according to ISO 294-5; Plate type F, a standard for material test, see Fig 3 (a). The theoretical thickness were 0,6 mm. The material flow was from the short end at the bottom of picture in Fig 3 (a) towards the top of the picture. Moulding process parameters were, melt temperature 260°C, mold temperature 60°C and flow rate 25 cm<sup>3</sup>/s.

*Sample preparation.* The specimen from injection molding was firstly embedded in epoxy or acrylic resin and followed by grinding and polishing to prepare the surface of the cross-section at a pre-selected position for nanoindentation measurements. Surface roughness should be minimized, in order to obtain satisfactory results. Specimens were cut carefully from both transverse and longitudinal direction to characterise the mechanical behaviour. To examine the cross section of the part samples were prepared with a predefined schedule of grinding and polishing. Materials and equipment were from Struers. Plane grinding and fine grinding were made with SiC paper in four steps, 500# 10N, 1000# 10N, 2000# 10N, 4000# 10N. Diamond polishing were made with 3  $\mu\text{m}$  and 1  $\mu\text{m}$  diamond particles. Fine polishing were made with silica suspension. Two samples were prepared from different direction of the part one towards the flow direction and the other perpendicular to the flow, seeing Fig 3 (a).

### 2.2. Experimental setup

*Nanoindentation.* Nanoindentation were made by using Nanotest Vantage from Micro Materials. Nanoindents were made with depth control to a maximum depth of 1  $\mu\text{m}$  using a Berkovich indenter with sharp tip (tip radius: 100 nm) in order to evaluate mechanical characteristics of different morphological layers in both the flow direction and perpendicular to the flow direction. The area function was calibrated by performing a series of indentations on quartz, a standard material of known hardness. In order to determine the best experimental settings for the material used a series of test were made with varying load, dwell period and unloading speed. The resolution was 10  $\mu\text{m}$  between each indent. Grid indentation was made to determine distribution of Hardness and Reduced Modulus with this method for the cross section of a polymer sample. Hardness and Reduced Modulus were determined by using power law with a fifth order fitted polynomial to the unloading curve. The analysing was done by using software from Micro Materials.

## 3. RESULTS AND DISCUSSION

### 3.1. Skin-core visualisation

The skin-core zones can be visualized using polarised light and optical microscopy, see Fig. 3. The skin layer was 70  $\mu\text{m}$  thick. There are surface defects occurring from flow separation, seeing Fig 4 (b). These defects are barely visible but can certainly have influence on later processes like coating.

In Fig 4 (a) the different regions in the molded part arising from separation of the flow is visualised with polarised light. This paper presents the characterization of mechanical properties in one region of the sample and in two directions that is marked with the arrows in Fig. 4 (a).

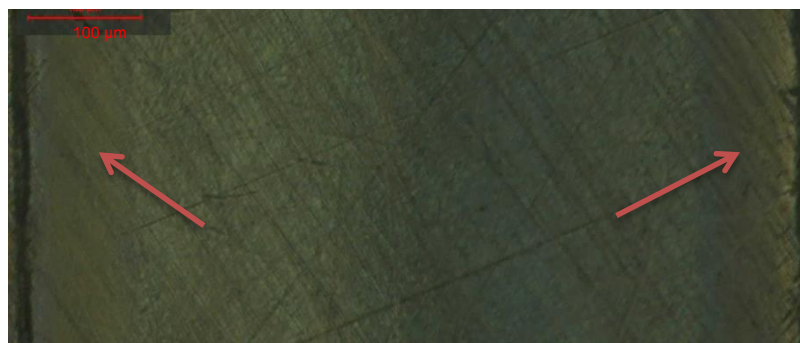


Fig. 3. Visualising the skin-core using polarised light and optical microscopy, looking at the crosssection of a 700 nm sample. Skin layers marked with arrows.

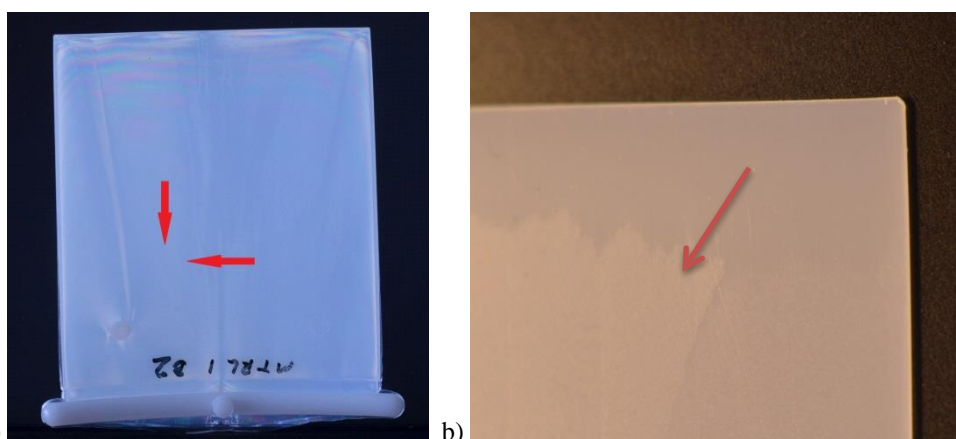


Fig 4. (a) Visualising different material regions on a molded sample using polarised light. Indents were made in two directions according to the arrows. (b) Surface defects due to flow separation. Ruff surface are visible at the arrow. The inlet is from bottom of picture the flow is towards the top.

### 3.2. Elastic-plastic behaviour

By examining the load/unload curves for a series of tests with varying load, dwell period and unloading speed the best settings for the indentation were determined. Indentation with the so-called “nose” effect when the initial slope of the unloading curve is negative is impossible to use as hardness measurements. When doing indents in the range from 0,5 – 5 mN the nose effect is seen when the dwell period is as short as 5 s. This is seen in Fig. 5 a),b) and Fig. 7 a) for the range of unloading speed from 0,001 mN/s to 0,3 mN/s. By using a longer dwell period it is possible to reduce the “nose” effect. A dwell period of 220 s gives a result with no detectable “nose” effect see Fig. 6 b). When comparing results in Fig 6 b) with Fig 7 b) the best unloading speed is 0,05 mN/s. More information of the viscoelastic behavior of the material can be withdrawn by examining the creep during the dwell period. The result of that test is shown in Fig 8. The viscoelasticity is increased with increasing load seeing Fig 8 a). Also the viscoelasticity is increased with increasing unloading speed seeing Fig 8 b).

To get a high enough resolution for the grid of indents the depth had to be maximized and correspondingly load minimized. When trying to use as low load as 0,05 mN difference in mechanical properties of the skin layer compared to core was barely detectable, seeing Fig 11. The indents were made with depth control and setting the maximum depth to 1000 nm. This gave the resolution of 10 μm between each indent.

### 3.3. Hardness and modulus

The thickness of the skin was measured by microscopy and it is corresponding to the change in material properties at around 70 μm from the edge, seeing Fig 9 and 10. There are no significant differences in Hardness and Reduced Modulus of the skin between the two directions of the measurements. A slight difference is noticed in the core between the skin layers. When examining the properties in the directions towards the flow a gradual increase in both Hardness and Reduced Modulus towards the center is noticed, seeing Fig 9. This is not the case when measuring perpendicular to the flow direction. Fig 10.

The overall distributions of both modulus and hardness supported polarized light microscopy results regarding morphology and the skin-core structure. This microstructure is formed, as a result of the thermo-mechanical history experienced by the material. Modulus and hardness increased first from the surface of the skin layer toward the core of the specimen. The increases were followed by a downturn after the skin layer and before reaching the core. The modulus and hardness in the core region were generally lower than for the skin layer and trans-crystalline layer. The low values of these mechanical properties in the core region might be due to indentation positions in the amorphous region, which would be softer than its surrounding region. Values near the edge are uncertain due to influence from the surrounding epoxy, which has higher modulus and hardness. The asymmetry in mechanical properties with regard to the middle plane of the plate was probably caused by the unsymmetrical flow, which resulted in an unsymmetrical structure in the morphology near the gate region.

To visualize the mechanical properties a mapping of the crosssection was made. The result of this is presented in Fig 12 and 13. The mapping do not cover the hole size of the sample.

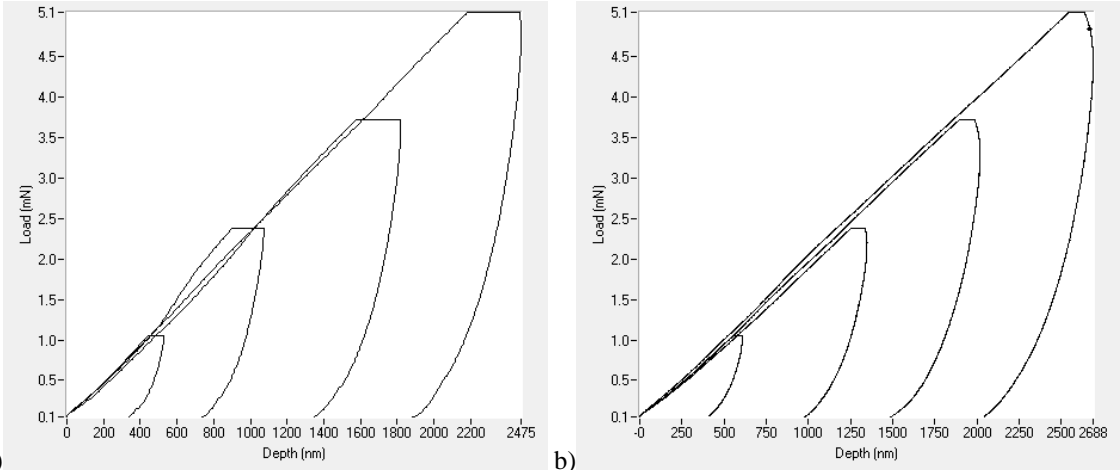


Fig. 5. (a) Loading and unloading curve for indents with a load range of 1-5 mN, dwell period of 5 s and unloading speed of 0,3 mN/s. (b) Loading and unloading curve for indents with a load range of 1-5 mN, dwell period of 5 s and unloading speed of 0,05 mN/s.

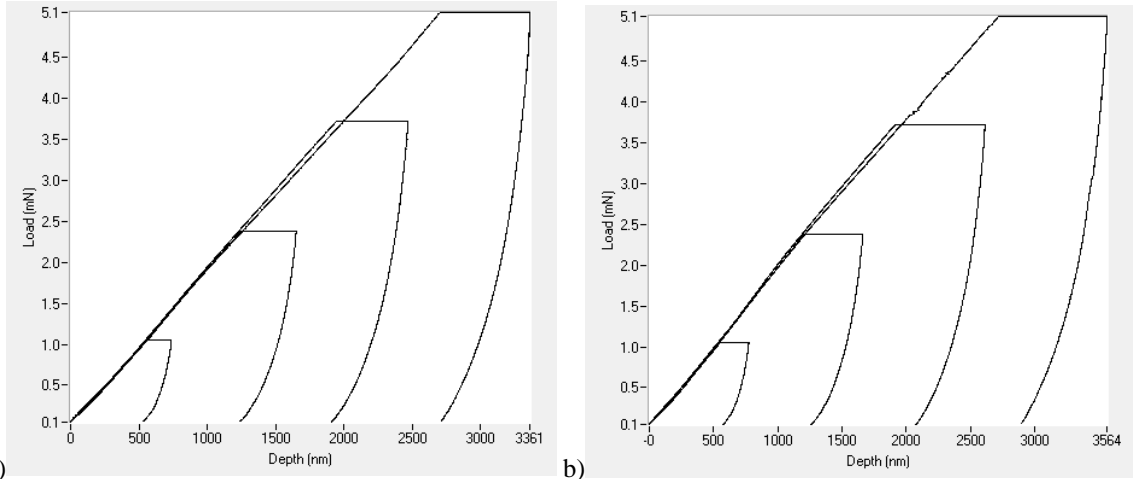


Fig. 6. (a) Loading and unloading curve for indents with a load range of 1-5 mN, dwell period of 120 s and unloading speed of 0,05 mN/s. (b) Loading and unloading curve for indents with a load range of 1-5 mN, dwell period of 220 s and unloading speed of 0,05 mN/s.

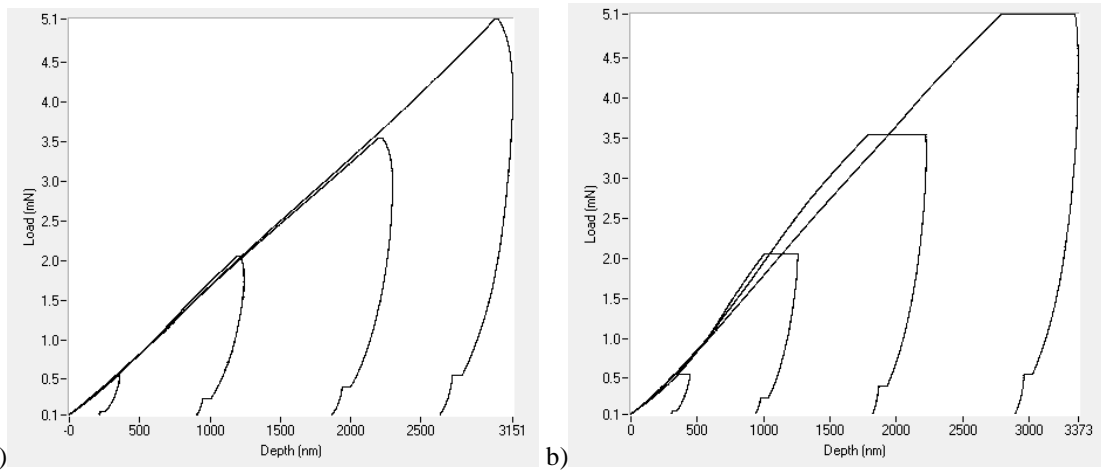


Fig. 7. (a) Loading and unloading curve for indents with a load range of 0,5 - 5 mN, dwell period of 5 s and unloading speed of 0,01 mN/s. (b) Loading and unloading curve for indents with a load range of 0,5 - 5 mN, dwell period of 220 s and unloading speed of 0,01 mN/s.

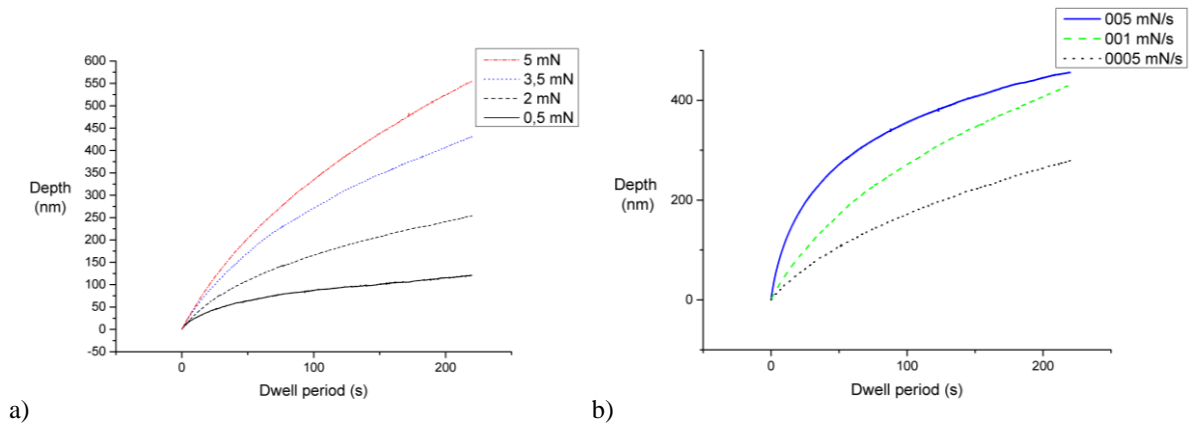


Fig. 8. Shows the effect of visco-elasticity of the sample during the test. (a) Progression of indentation depth during holding period under different load; (b) Progression of indentation depth under different loading rate.

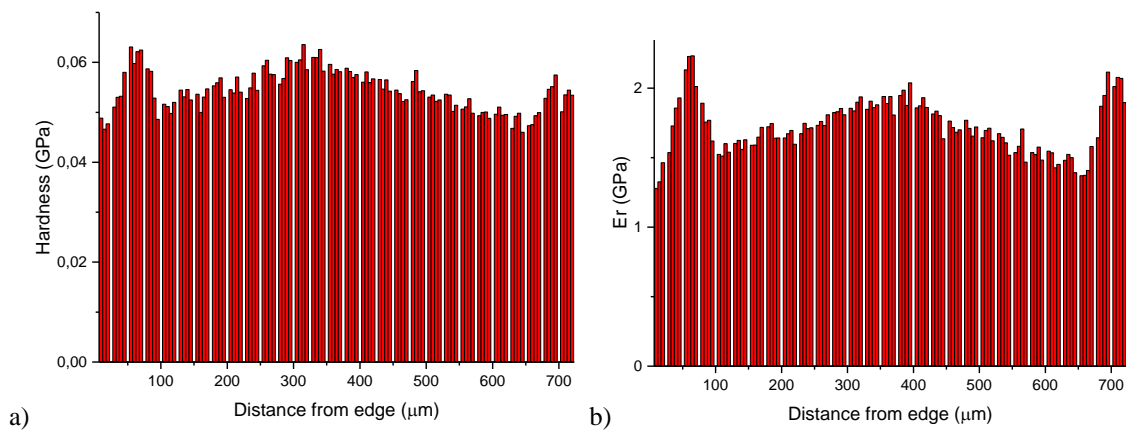


Fig. 9. a) Hardness distribution towards the flow direction. b) Distribution of Reduced Modulus towards the flow direction.

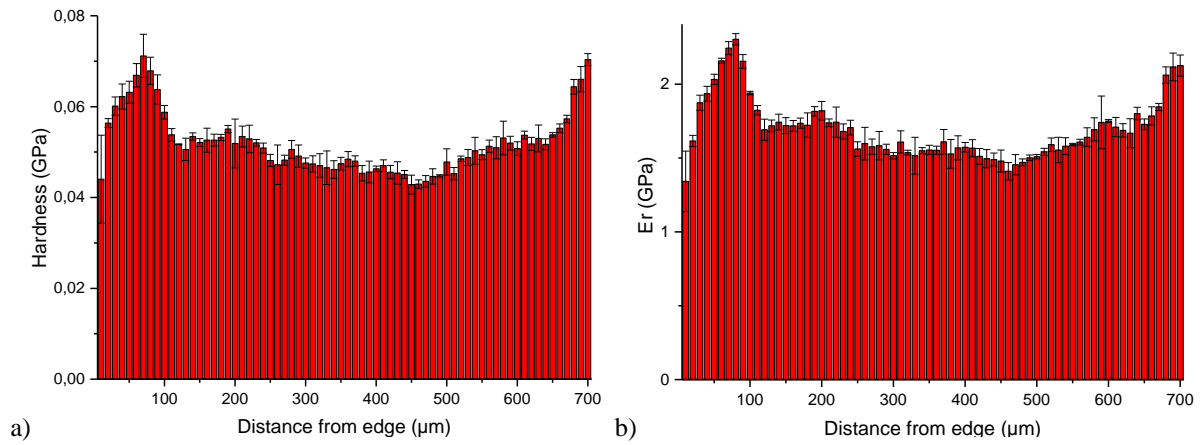


Fig 10. (a) Hardness distribution perpendicular to the flow direction.  
 (b) Distribution of Reduced Modulus perpendicular to the flow direction.

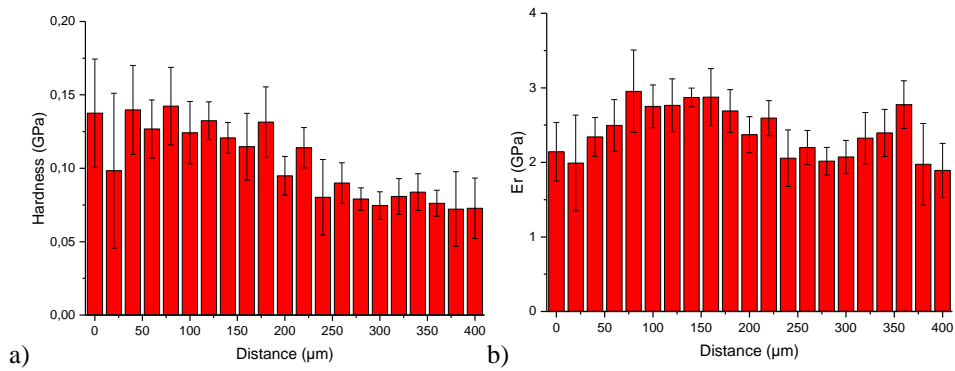


Fig 11. Indentation made with low load from the edge towards the center of the sample covering half the thickness. The load was 0,05 mN.

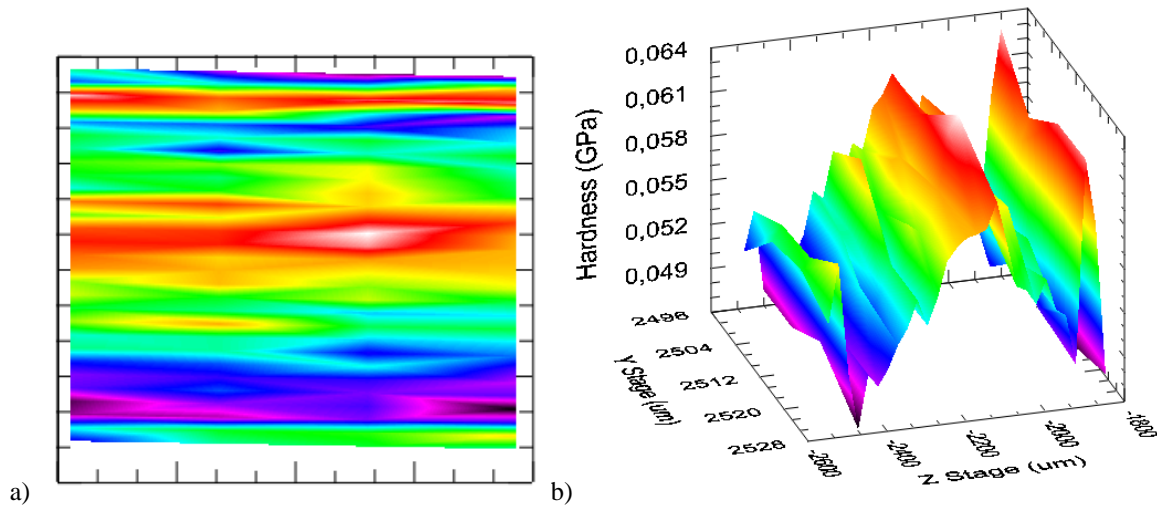


Fig 12. (a) Mapping of Hardness for the crosssection. (b) 3D view of Hardness mapping.

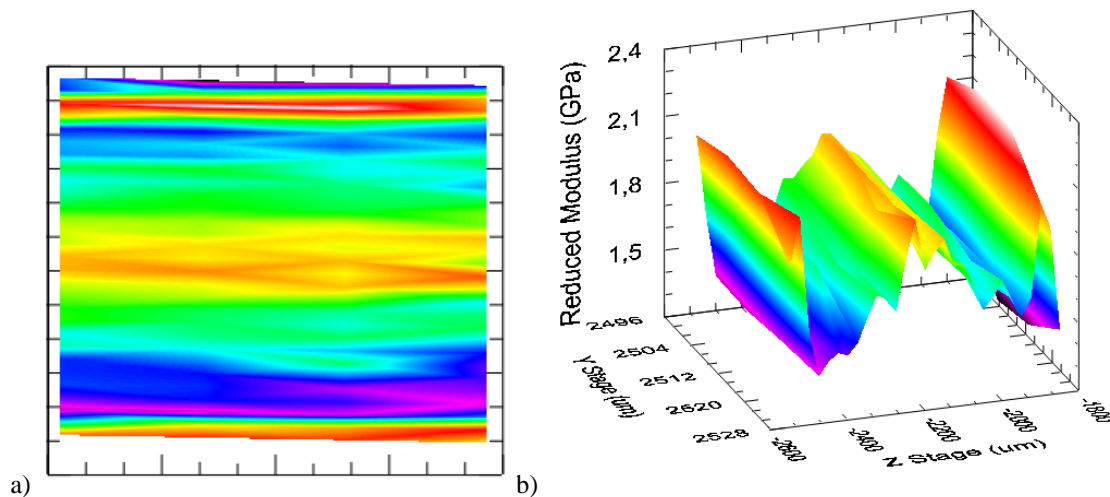


Fig 13. (a) Mapping of Reduced Modulus. (b) 3D view of Reduced Modulus mapping.

#### 4. CONCLUSION

An apparent skin-core structure was observed in the HDPE specimen produced by injection molding process. Three layers with different mechanical properties were identified in tested samples, which include skin layer, intermediate layer and core layer. Higher hardness and reduced modulus were found on the skin section of HDPE produced by injection molding. The hardness and modulus were lower in the core section than skin section with variance from edge to the center area of the core. Minimum value in hardness and reduced modulus was identified in the intermediate layer. This mechanical behaviour was thought to be relate with the phase morpholoy formed in the injection molding process. The proposed method for mapping the Hardness and Reduced Modulus gives relative values that could be used for comparision of injection molded HDPE parts poduced with different process parameters.

#### 5. FUTURE WORK

Future investigation will focus on the more comprehensive test of mechanical behaviour of the specimens produced with difference process parameters in the injection molding. In addition, morphorlogy and crystalline structure of skin-core structure and their correlation with mechanical properties will also be studied.

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