VISCOELASTIC EFFECTS ON ELASTIC MODULUS OF POLYMERS

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Abstract. The nanoindentation test is used to determine the viscoelastic parameters of a thermoplastic polymer at ambient temperature. The aim of the study is to obtain a mean representative value taking into account the influence of the viscosity on the elastic modulus of the poypropylene. For that, Berkovich indenter has been chosen and applied load equal to 100mN. We used poypropylene as a prototype of viscoplastic material, having a creep more important than the others thermoplastic polymers. It was found that, during nanoindentation, the Young's modulus estimated by the Oliver-Pharr method is several times higher than that which is suitable. The Pile-up and viscoelasticity are usually at the cause of this failure and an analysis of their influences is attempted in this work. The loading and unloading curve obtained from FE simulation results by the nanoindentation test is then undertaken to complete the work. The various results have enabled to analyze the influence of viscosity on the elastic modulus of the polypropylene matrix.

Keywords: thermoplastic polymer, nanoindentation, viscoelasticity, finite elements

1) INTRODUCTION

Polymers, and particularly thermoplastic polymers, have singular characteristics which can be a source of difficulties in the experimental characterization. They can indeed be considered as anisotropic and heterogeneous materials at the nanoscale, thus opposing the homogeneous bulk polymers considered in the theory of elastic contact. Considering the indentation technique, it is the formation of pile up and the effect of the viscosity that complicate the analysis of the experimental results. In the few nanoindentation studies on polymers presented in the literature, the authors use the method of Oliver and Pharr [1] on polymers and agree on the other hand that the test must be used with caution, keeping the maximum load constant for some time before unloading (creep) [2, 4] and a quick unloading in order to avoid the development of a 'nose' [2-3], the discharge is taken purely elastic in their model. This modification was done in order to study the visco-plastic behavior of the polymers where conventional nanoindentation method was based on the assumption that polymer behave in an elastic-plastic manner [5].

Instrumented indentation could be a useful tool for the mechanical characterization of the surface of nanoscale polymers. Nanoindentation is a powerful tool for this purpose, but the technique currently has certain limitations when applied to the characterization of polymers. Indeed, it is well known that the same approach used to characterize metals, does not make it possible to correctly measure the mechanical properties of polymers [6, 7, 8]. The reasons are usually found in the viscoelastic nature of the polymers that modifies the contact area. The influence of the discharge curve does not allow its adaptation according to common procedures [1].

The purpose of this article is to study the mechanical properties of polypropylene resin, by means of investigational testing and numerical simulation of the indentation test. This one is conventionally used to study the elastic and elasto-plastic behavior of the metals, making it possible to give the elastic contact and to compare it with that calculated by the new experimental procedure proposed in this work. This characterization requires a thorough knowledge of the indentation test that is commonly used to determine surface mechanical properties. The major difficulty of this type of material, which has a viscoplastic mechanical behavior, is to interpret the experimental results of indentation in order to bring out Young's modulus values, from the registered load-depth curves (F-h). The development of numerical tools makes it possible to simulate the indentation test and to better understand the indentation. The simulation makes it possible in particular to determine certain mechanical properties of the materials.

2) EXPERIMENTAL

The indentation tests were carried out on cylindrical polypropylene (PP) polypropylene samples having a diameter d equal to 3 cm and a height h equal to 5 mm. The samples were polished to 1 μm before indentation. Indentation tests were performed at room temperature using a Nanoindenter NHT^3 (Anton Paar, Austria) with a Berkovich tip. The nanoindenter has a maximum load of 500 mN. In the load programs used, the load was first increased to a selected value at a constant load rate. This is followed by a load maintenance period followed by subsequent unloading at a constant rate (zeroed). The applied load is 50 μN, while the charging speed is 100 μN/min and the discharge rate is between 1 and 400 μN/min.

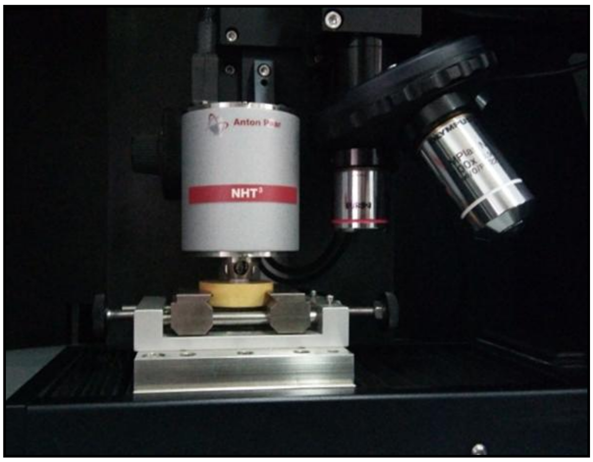


Figure 1. Nanoindentation Tester (NHT³)

At the place of indentation, the surface will deform in a manner that reflects the mechanical properties of the indented material. The elastic modulus and the hardness can be calculated according to the maximum load and the maximum penetration. The method we will use is that of Olivier and Pharr, this method shows that the indentation curves are rarely linear even at the initial stage of unload. They propose then to adjust the unloading curve by a law of type power

$$F = F_{max} \left(\frac{h - h_p}{h_m - h_p}\right)^m$$

where F is the load ; F_{max} is the maximum force applied ; h is the depth of indentation ; h_p is the depth of indentation unloading; h_m is the maximum depth indentation at F_{max} ; m is a constant determined by means of a least squares method and is a function of the geometry of the indenter.

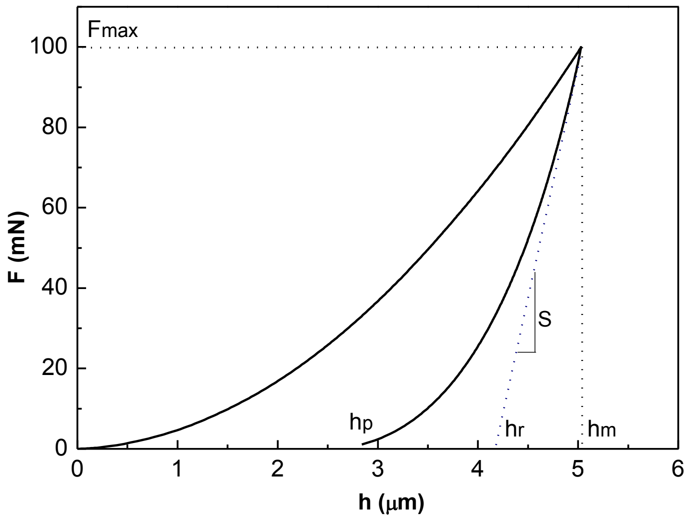


Figure 2. Typical load/unload curve resulting from indentation, analysis of the test and obtaining a stiffness and depth of contact.

The contact stiffness S is given by the tangent of the unloading curve at the point of maximum load

$$S = \left(\frac{dF}{dh}\right)_{max} = mF_m(h_m - h_r)^{-1}$$

the extension of this tangent gives the depth h_r :

$h_r = h_m - \frac{F_m}{S}$

the contact depth h_c is then determined by :

$$h_c = h_m - \varepsilon(h_m - h_r)$$

where ε depends on the exponent m.

the H_{IT} hardness is identified from the maximum load, F_m, of the projected contact area A_p to the contact depth h_c, A_p is a function of the contact depth h_c, and is determined by calibration of the tip of the indenter.

$$H_{IT} = \frac{F_m}{A_p(h_c)}$$

the reduced module, E_r is given by

$$E_r = \frac{\sqrt{\pi}S}{2\beta\sqrt{A_p(h_c)}}$$

where β is the form shape of the indenter tip. for the Berkovich indenter, β = 1.034. This modulus E_r includes the elastic modulus of the specimen *PP* and the diamond indenter (E_p and E_i, respectively) and the corresponding values of Poisson's ration (ν_p and ν_i, respectively):

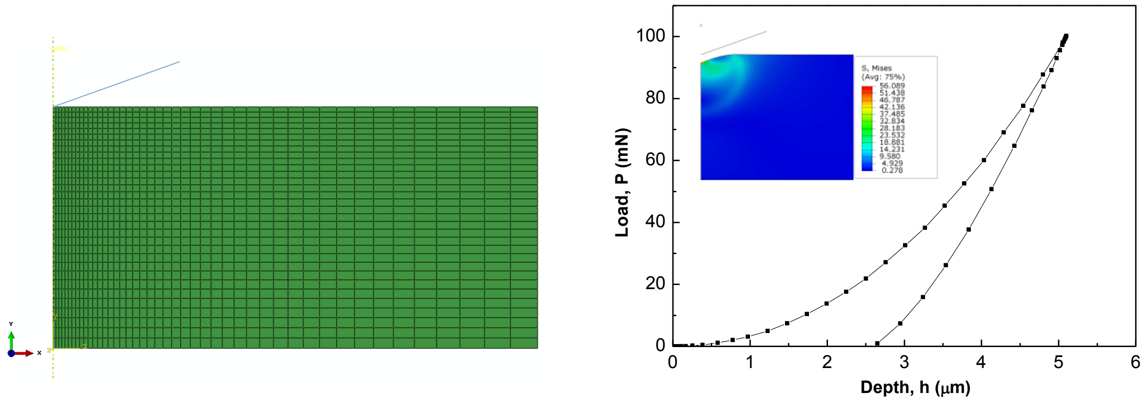
:

$$\frac{1}{E_r} = \frac{1-\nu_p^2}{E_{IT}} + \frac{1-\nu_i^2}{E_i}$$

where E_i and ν_i are, respectively, the elastic modulus and Poisson's ratio of the indenter and ν_{pp} is the Poisson's ratio of the sample. In our study: for the diamond indenter, the known parameters are E_i=1140 GPa and ν_i =0.07 and for the polypropylene ν_p =0.40.

3) NUMERICAL SIMULATIONS OF THE NANOINDENTATION TEST

The numerical simulation of the nanoindentation test is carried out using the finite element code Abaqus, was used in this study to give the purely elastic response of the polymer without the effect of viscosity. A 2D axisymmetric model was implemented using conical indenter with half-included angle of 70.3°. The friction between the indenter and the polymer surface has been neglected. The indenter tip radius R=0.2 µm was modeled to approximate the experimental conditions. A loading profile at 100 mN load was simulated. An elastoplastic constitutive law has been adopted for polypropylene. The elastic parameters used were determined from the experimental results of the tensile tests. The Poisson's ratio was set at 0.4. The test simulated is conducted under displacement imposed. The optimal mesh identified for this problem is shown in figure 3a. The figure 3b presents, for its part, the resulting force-displacement curve of the numerical analysis.



(a). (b)

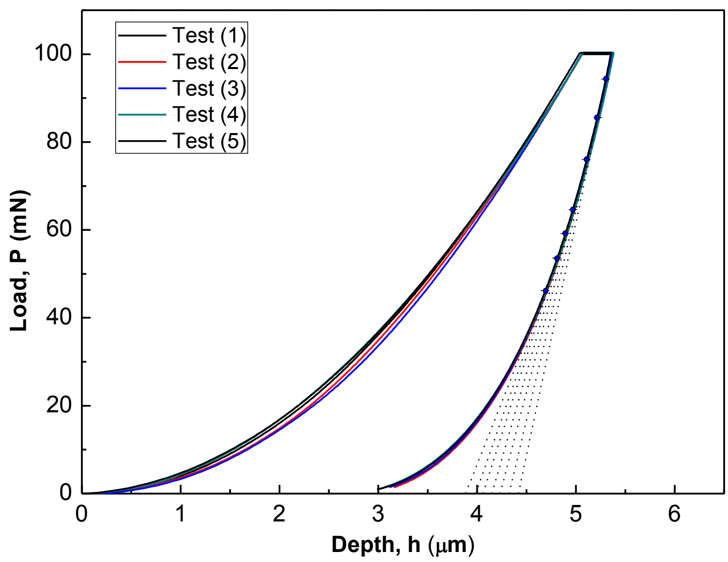
Figure 3. (a) Mesh of the nanoindentation test and (b) force-depth curve obtained on elastoplastic material.

4) CONCLUSION AND DISCUSSION OF RESULTS

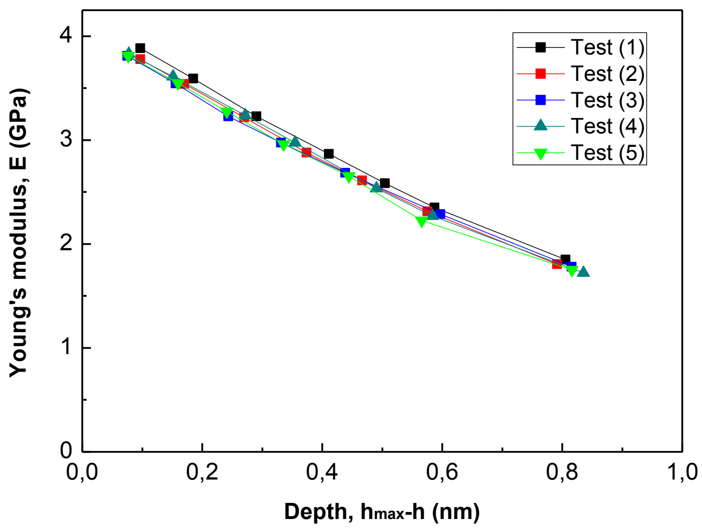
The nanoindentation tests results are shown in figure 4 for the polypropylene matrix. The curves show good reproducibility of the test. The appearance of a creep bearing during the maintenance of the maximum load (P_{max} = 100mN) is characteristic of materials whose mechanical behavior depends on time. The tangent of the numerical unloading curve at the maximum load (Figure 3b) is parallel to that of the experimental unloading curve which corresponds to the contact stiffness S_7. This point corresponds to the value from which we can obtain a purely elastic module of polypropylene.

The test results give higher Young's modulus values than the tensile test. However, these values were determined assuming Oliver and Pharr's approach applied to our samples. Gold, this approach only really applies to elastic materials.

Current methods do not allow to correctly estimate the Young's modulus to correct this anomaly. Indeed, the tests showed the viscoplastic behavior of the tested polypropylene. In addition, to avoid any influence of the bead and the viscosity on the measurements, the depression of the indenter corresponds to a displacement return of approximately 661.2 nm.



(a)



(b)

Figure 4. The graphic illustration of data analysis of unload curves with several slopes (S_1, S_2, S_3, S_4, S_5, S_6 and S_7), (a) load-unload curves obtained from the nanoindentation test on the polypropylene and (b) (E_1, E_2, E_3, E_4, E_5, E_6 and E_7) calculated modulus of slopes.

Accordingly, the measurement of the elastic properties of the polymers is strongly influenced by the viscous behavior of the material. This data analysis procedure given in Figure 4, shows us that it is possible to correct this anomaly. In this case, we obtain modulus of elasticity values calculated at about 46% of the force on the unloading curve, close to those determined by the tensile test (E_t = 1.86GPa).

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