FEM Prediction of Dynamic Scratch Resistance of Polymer Coatings

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***Abstract**: Polymer coatings are used in pharmaceutical industry because of their wide functionality. To improve storage stability and performance of pharmaceutical products, the scratch resistance of the coatings must be improved (Gu, 2004). The scratch resistance of a common coating (150 µm HPMC) was predicted by ABAQUS™ simulation. Two models were used. 1) A four-parameter viscoelastic/plastic material model which was implemented using the user-defined material subroutine (UMAT). The material parameters were determined by a Python optimization script so that no extra programs except ABAQUS were needed. The script minimizes the difference between measured and simulated deformation data by changing the material parameters of the model (Ovaert, 2003). The experimental data was obtained from indentation tests made with a Lloyd LRX tester. The presented routine can predict material parameters from any kind of measurement that can be simulated if the theory of material models is known. 2) The predicted material parameters were then input into a separate scratch model that predicts the dynamic scratch resistance. These predictions were verified with experimental data obtained with a scanning white-light interferometer (SWLI) (Kassamakov, 2006). The material parameters (viscoelasticity and plasticity) predicted with the optimization script and validated by the stretching test were determined quantitatively, as were the scratch simulation predictions and the experimentally measured dynamic scratch parameters (groove depth).*

Keywords: FEM, ABAQUS, Experimental Model Verification, Optimization, Plasticity, Polymer, scratch resistance

1. Introduction

Polymer coatings can improve the scratch and mar resistance of materials (Gu, 2004). Such coatings are used in buildings, automobiles and electronics for functional and aesthetic purposes.

The application of coatings to pharmaceutical solids has been practiced for over 150 years. Coating has been used in a variety of pharmaceutical products such as tablets, beads, pellets, granules, capsules, and drug crystals (Lieberman, 1990). It offers many benefits: it improves the aesthetic qualities of the dosage form, provides product identity, masks undesirable taste or odour, facilitates ingestion, improves product stability, and modifies the release characteristics of the drug. In a majority of film-coating formulations, the polymer is the main ingredient. The polymer may originate from cellulose, acrylics, vinyl, and polymer combinations or from hydroxypropyl methylcellulose (HPMC) as in most of the pill coatings.

For aqueous film coatings, such as HPMC, to be successful, the film must be smooth and uniform. When the main function of the film coating is to control the drug release or to protect the drug from humidity, coating defects may reduce the shelf-life of the pharmaceutical product.

Scratch resistance can be interpreted as a material's resistance to scratch deformation. The resistance can be derived from the material response to scratch. Despite improvements in coating technology, problems still exist with long-term performance of polymer coatings exposed to hostile environments such as high acidity, humidity, temperature and other aggressive conditions such as mechanical impacts (Gauthier, 2006).

Contact tests are efficient in ranking materials with respect to their mechanical performance (Ovaert, 2003). While indentation tests provide quantitative information about stiffness and elastic recovery of materials, scratch tests provide information concerning failure mechanisms like initiation of rupture. Scratch tests also differentiate ductile fractures from brittle ones. Most important, though, is the possibility to use scratch tests to estimate shelf life of the pills (Petereit, 1999). Understanding how to engineer the films for improved scratch resistance and hence longer shelf life is therefore important. Moreover, by understanding the scratching event and the effect of material parameters on scratch resistance, one can optimize the coating films for maximum drug shelf-life. This engineering effort must be based on FEM assisted experimental design in order to cope with the otherwise huge experimental matrices.

2. Background

Oliver and Pharr introduced indentation as method to measure the elastic modulus and hardness of materials (Oliver, 1992). According to Oliver and Pharr, the relationship between indentation depth and load force in the unloading curve is (Figure 1):

$$P = \alpha \left(h - h_f \right)^m ,$$

where P is the indenter load, h is the indentation depth, h_f is the final depth of the contact impression after unloading, whereas m is constant which is depend from indenters shape and α is a constant that can be related to elasticity of the film.

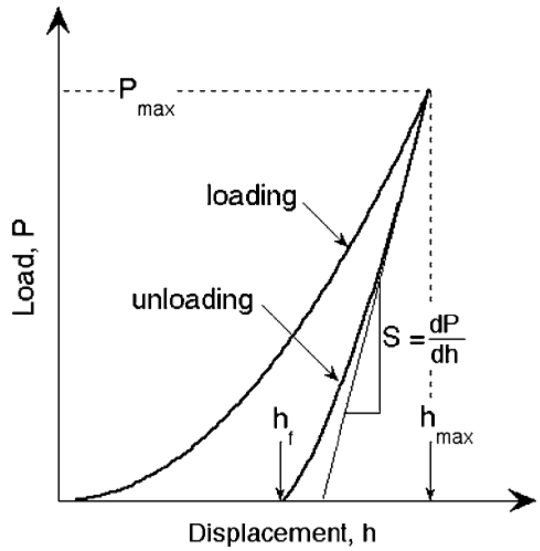

Figure 1. Typical load displacement curve (from (Oliver, 1992))

This relationship has been shown to be inaccurate, and the understanding of the contact mechanics on which the method is based, has mostly been developed by finite element simulations (Oliver, 2004). The problem with the Oliver and Pharr theory is also that it doesn't provide any physical material parameters describing the plasticitity of the material. A remedy to this deficiency is to use the Ramberg-Osgood material model that describes the plastic deformation of many materials. In the Ramberg-Osgood model, strain is defined as a power-law equation from stress:

$$\varepsilon = \frac{\sigma}{E} + \alpha \frac{\sigma_0}{E} \left(\frac{\sigma}{\sigma_0} \right)^n ,$$

where σ is stress, σ_0 is Yield stress, ε is strain, E is the static elastic modulus, α and n are constants. Usually the yield strength is defined as the strength where the yield offset is 0.2% of the strain value. This means that plasticity curve is more than 0.2% off from the linear elasticity. If this fixation is done, α can be also defined:

$$\alpha \frac{\sigma_0}{E} = 0{,}002 ,$$

3. Methods

3.1 Indentation

Material parameters of free films (150 µm thick aqueous HPMC film plasticized with polyethylene glycol, PEG 400, 20% w/w of polymer weight) were studied with indentation. The indentation was carried out with a Lloyd LRX material tester device (Lloyd Instruments Ltd., UK) that featured a 5N force gauge and a spherical steel tip (radius 0.750 mm). Compression forces between 0.5 to 8N were applied orthogonally to the film surface with a speed of 0.1 mm/min to 1mm/min. Indentations were done using a computer-controlled loading routine so that after loading the load was released to see how much the dent recovers due to elastic recovery. A 10 second pause was held after each loading to see whether creep occurred due to the viscoelastic properties of the material. Since no creep was seen in the HPMC films, the viscoelastic properties of the HPMC film were not modelled.

Indentations were simulated with axisymmetric Abaqus/standard simulation. In the simulation a triangular mesh (element type CAX6) was generated by an adaptive meshing procedure. The indentation tip was modelled by a spherical analytic surface and the indentations were done using a constant uniaxial load (Figure 1).

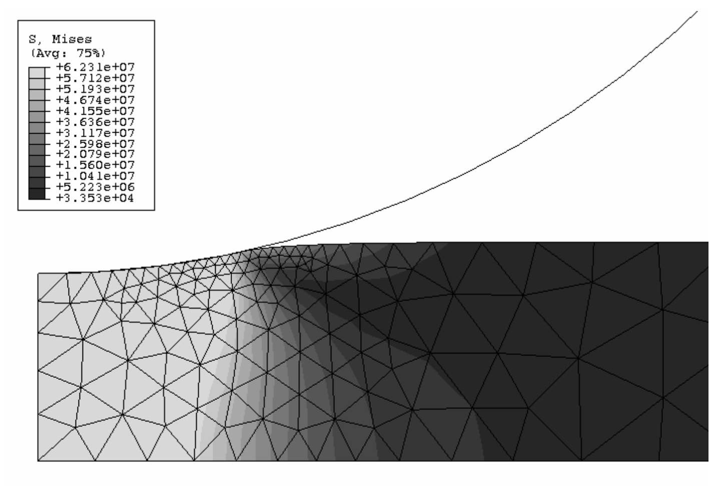

Figure 2: Deformation of 150 µm thick film during indentation with 6N force

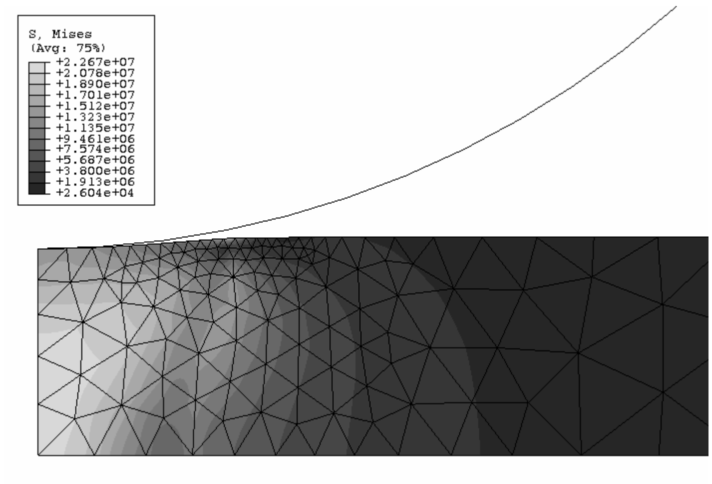

Figure 3: Deformation of 150 µm thick film after indentation with 6N force

3.2 SWLI

Depths of dents and groove profiles were measured with the Lloyd LRX while doing the indentations, and with the Scanning White Light Interferometer (SWLI) after the indentation testing was completed. The SWLI is an optical technique for surface characterization. In SWLI, a light beam passes through an interferometric objective containing a beam splitter that reflects half of the incident beam onto a reference surface and that passes the rest of the beam onto the tested surface. Light reflected from the test surface and from the reference surface combine forming an interferogram, Figure 4. This provides a precise geometrical dimension of the dent or groove.

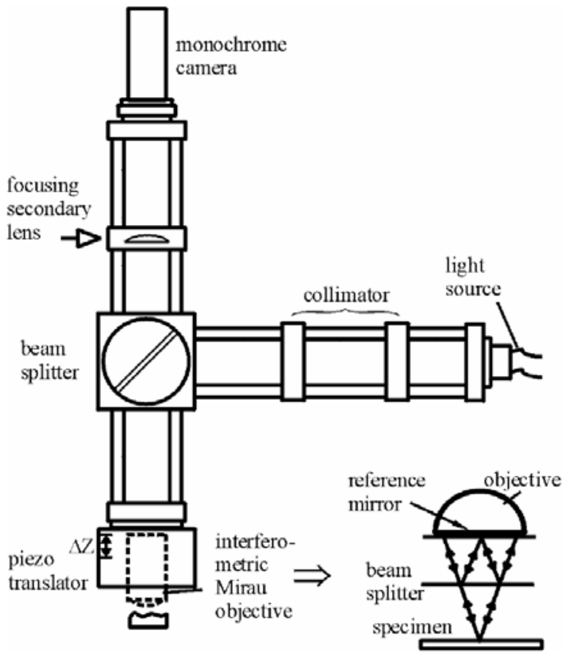

Figure 4. The schematic of SWLI

3.3 Optimization

To get parameters for the Ramberg-Osgood –material model, a Python 2.0 script and Abaqus User material model (UMAT) were written The Python minimization script first read the initial material parameters (Elastic modulus, Yield strength and the power from Ramberg Osgood model) from a text-file, and then launches the ABAQUS 6.6-2 simulation which read the material parameters for the UMAT from the text-file. When the simulation was finished Python used the "abaqus odbreport" –command to get history outputs from the odb-file. These parameters (indentation depths, see Figure 2 and Figure 3) were then compared, point-by-point, with the measured ones. This allowed the Python script to adjust the material parameters to minimize sum of the absolute distance between the measured and the simulated indentation depths. When a minimum (usually defined as relative error less than 5%) between measured and simulated parameters was found, the python script was interrupted. Because the minimization was done with plain Python without Abaqus/CAE libraries (abaqus, visualization), the script can also be used in platforms that doesn't support Abaqus/CAE, such as IBM AIX 5.2 (used by CSC Scientific Computing Ltd.).

3.4 Scratching

Polymer films were also scratched to identify the dynamic nature of the material response. The scratching was done with the same Lloyd LRX as the indentation. The uniaxial indentation force was 3N and the scratches were done with a speed of 36mm/min.

To obtain an analytical tool to analyze the scratching problem, ABAQUS simulations were carried out. Since the viscoelastic properties of the HPMC films were insignificant compared to the elastic film properties, the viscoelasticity of film was not modeled. As a consequence, since the film could be modeled simply focusing on its elastoplastic properties, the ABAQUS simulation could be done using a static time step which reduces computation time. Significant viscoelastic properties could have been implemented in the UMAT material model. This could also have been done with the Abaqus/standard but the time step should have changed to "viscoelastic". The film was meshed with C3D20R and mesh was generated so that its much denser in close to the symmetry axis where the scratch was induced.

4. Results

The film was indented using increasing loads from 2N to 6N. The indentation depth during the load cycle is shown in Figure 5. These results was implemented in the Python minimization script which gave material parameters for the Ramberg-Osgood model E=763MPa, Y_0=60.7MPa, n=1.34. The minimization took about 3 minutes per cycle and about 20 cycles was needed to determine the material parameters. With these parameters the relative difference between depths in measured and simulated indentation test was 3.1%. Error bars in measured depths are because of small fluctuation in Lloyd LRX's output.

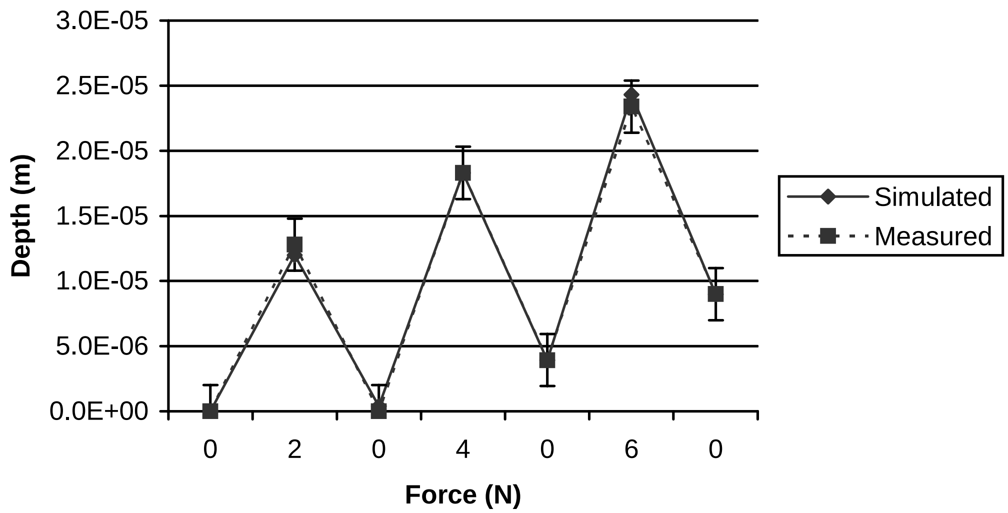

Figure 5. Load cycle of indentation test and FEM simulation of same test.

These predicted material parameters were then used as input parameters in the scratching simulation. When the measured scratch profile was compared with the simulated profile in Figure 6 and Figure 5, one can see that the groove depth and width differs by 25% and that there are "wings" that the simulation does not predict well. The measured wings were 5μm high whereas the simulated scratch exhibited only 1μm high wings. The differences between the simulated and the measured geometries could be addressed with denser mesh or by changing the Poisson's ratio.

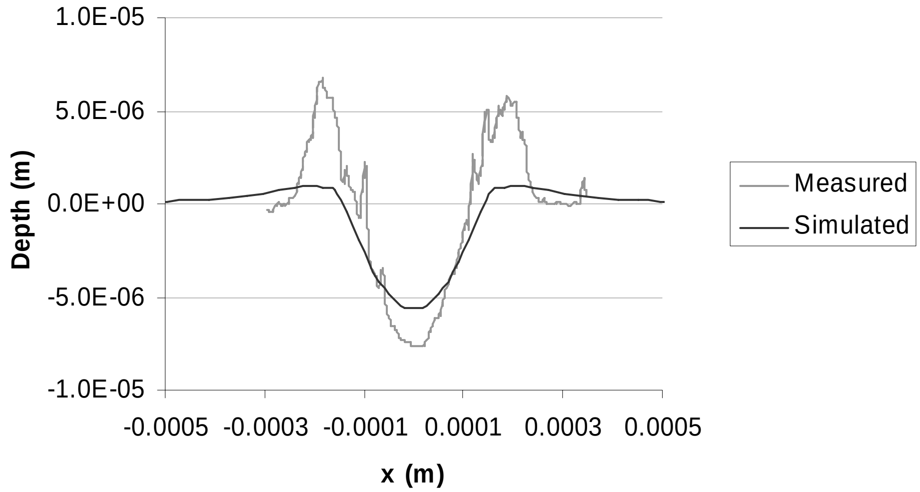

Figure 6. Scratch profile in X-direction (perpendicular to scratch).

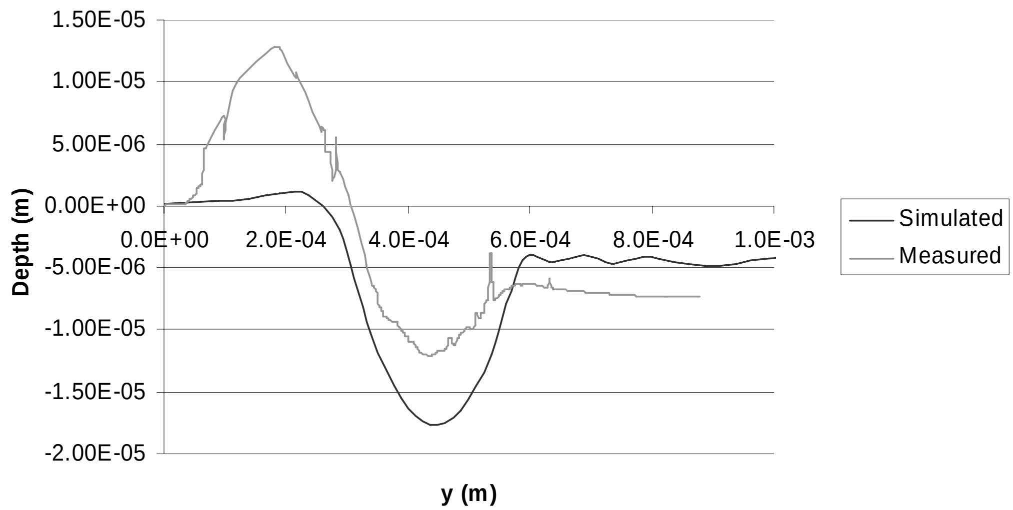

Figure 7: Scratch profile at bottom of the scratch starting point of the scratch in Y-direction (parallel to scratch)

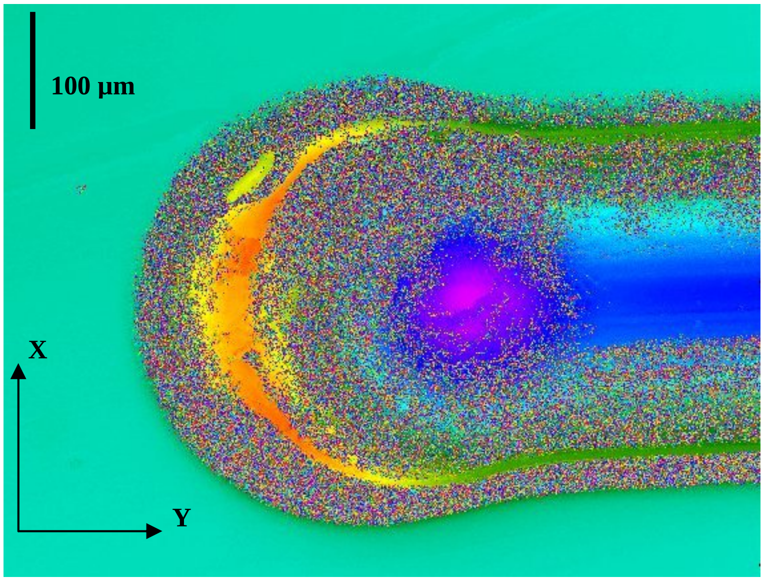

Figure 8. SWLI picture of starting point of the scratch showing coordinates used in figure pictures.

5. Discussion

In this project we could show that ABAQUS used with UMAT and Python can be used with aqueous HPMC films to predict material behaviour and estimate material parameters in situations where analytical response prediction is impossible. Most important part of this project is to understand scratching mechanism and to understand how scratch resistance of pharmaceutical films can be improved. In future we should also try to understand effect of viscoelasticity and friction to scratches.

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