In-situ observation and numerical modeling of contact creep and recovery on oriented semi-crystalline polymer surfaces

J. PEPIN[a,b], N.Yi[a,b], A. RUBIN[a], T. ROLAND[a], D. FAVIER[a], C. GAUTHIER[a]

a. UPR22/CNRS, Institut Charles Sadron, Université de Strasbourg, 23 rue du Loess, BP84047, F-67034 Strasbourg Cedex 2, France

b. Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands

julie.pepin@ics-cnrs.unistra.fr

Résumé :

Le but de cette étude est de caractériser l'influence de l'orientation macromoléculaire sur les propriétés de surface de polymères semi-cristallins. Pour ce faire, des expériences de fluage de contact-recouvrance sont réalisées sur du polyéthylène haute densité (HDPE) ainsi que sur du polypropylène isotactique (iPP) avant et après orientation par laminage à chaud grâce à un équipement permettant la vision in-situ de l'aire de contact. L'influence du temps de maintien en fluage et de la déformation initiale imposée sont également étudiés. Les résultats expérimentaux sont comparés aux résultats numériques obtenus par éléments finis.

Abstract :

This work is focused on the influence of macromolecular orientation on the surface properties of semi-crystalline polymers. To that purpose, contact creep and recovery experiments were performed on both oriented and un-oriented high density polyethylene (HDPE) and isotactic polypropylene (iPP) thanks to an original device recently developed in our laboratory giving access to the true contact area during the experiment. The influence of both creep duration and initial imposed strain were also investigated. Numerical modeling was performed using finite element method and the simulations results were compared to the experimental data.

Keywords : indentation, semi-crystalline polymers, viscoelasticity, in-situ creep recovery, anisotropic contact, numerical analysis

1 Introduction

Semi-crystalline polymers are commonly used in industrial sectors where surfaces undergo many damages like scratches or could be submitted to creep during their service life. In order to avoid as much as possible these surface damages, it is necessary to develop mechanical models able to predict such contact mechanical responses. The aim of this work is to study the effect of macromolecular

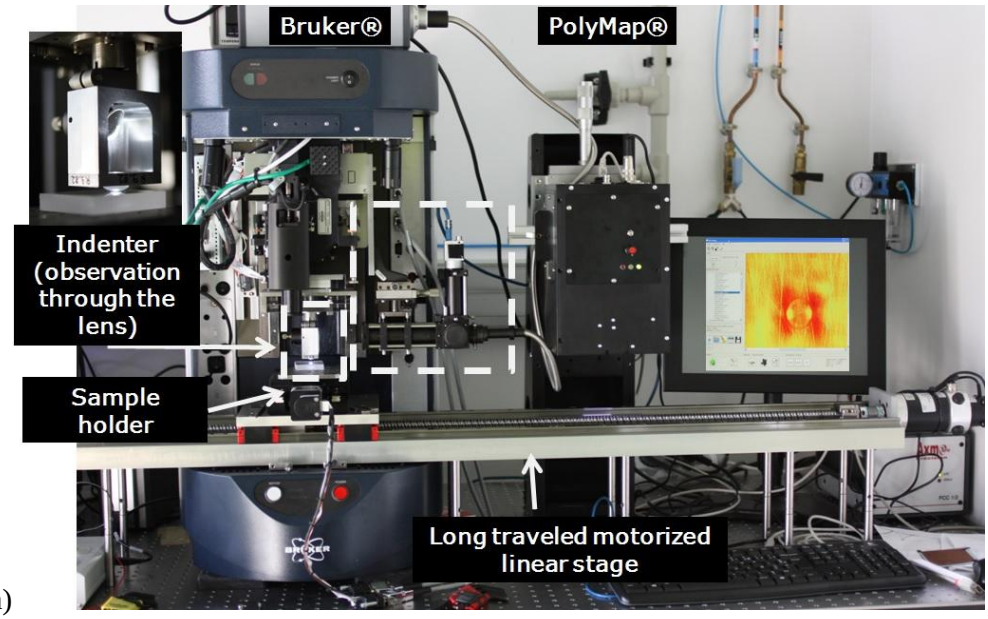
orientation, through stretching in the solid state, on the contact mechanics for semi-crystalline polymer surfaces. Indeed, it was shown by molecular dynamics on HDPE that orientation of macromolecular chains could decrease the coefficient of friction towards the elongation direction [1]. The effects of initial imposed strain levels and creep duration on viscoelastic behavior were also studied. The in-situ observation of the contact makes it possible to no longer be model-dependent by having direct access to the apparent area of contact during the creep phase and to the area of the residual imprint during the recovery phase even at the early stage of this step. To that purpose, two semi-crystalline polymers were chosen: high density polyethylene (HDPE) and isotactic polypropylene (iPP).

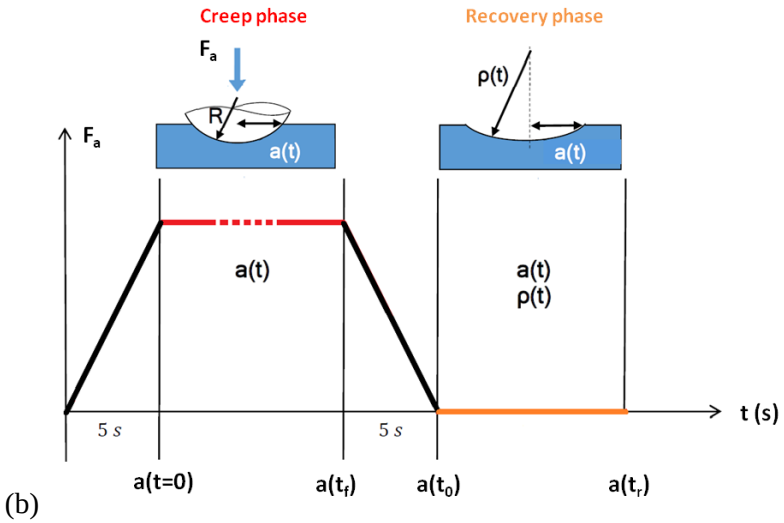
2 Experimental

HDPE pellets were supplied by SABIC. The isotropic samples were obtained by compression-moulding at 180°C and were then deformed by hot two-mill rolling process well above the glass transition temperature at various thickness reduction. The actual reduction ratio (AR) is defined as the ratio of the initial to the final thicknesses. The degree of orientation induced in the material was then characterized by SAXS / WAXS experiments owing to a rotating anode equipment operating at 40 kV and 30 mA (λ=1.5405 Å). The mechanical properties were determined at room temperature by uniaxial tensile tests performed both parallel and perpendicular to the direction of rolling at an initial strain rate of 10^{-3} s^{-1}.

Regarding the surface properties, the experimental procedure could be divided in two steps. Firstly, the contact creep was carried out on a Bruker tribometer which makes it possible to visualize the contact through the spherical indenter by means of a CCD camera. A constant load was applied and the contact area increased with time. Secondly, the indenter was removed and the recovery of the residual imprint was quickly (few seconds after the unloading of the indenter) recorded by an optical deflectometry Holomap® technique developed by CRITT Holo3. The experimental device and the evolution of the applied load during these contact creep and recovery experiments are presented in Figure 1. This experiment gives access to the true contact geometry and provides valuable information about the early stage of viscoelastic recovery.

(a)





(b)

Figure 1: (a) snapshot of the set-up [2] and (b) evolution of the applied load (F_a) during a contact creep and recovery experiment

Experiments were performed with a spherical indenter of radius between R = 9.82 mm and R=51.68 mm for various creep times. These important radius both allow to apply low contact strain and to obtain a good visualization of the contact during creep and recovery phases. In parallel, a numerical finite element study was carried out to determine the contact area and to compare it with the experimental results for both oriented and un-oriented materials.

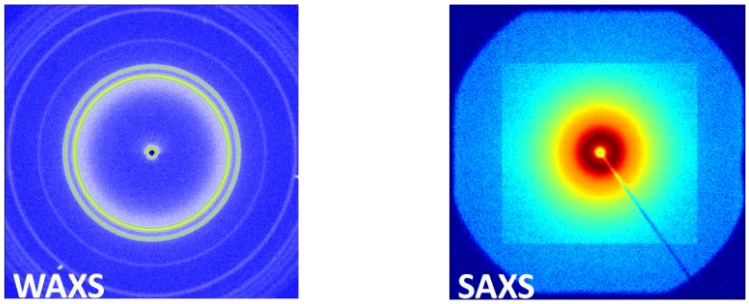
3 Results and Discussion

3.1 Structural characterization

Thermal analysis does not reveal any major changes in crystallinity after the rolling process and the crystal content of both oriented and un-oriented samples is around 68%.

Figure 2 reports the SAXS/WAXS patterns of these two HDPE samples. The structural analysis of the initial sample, presented in Figure 2(a), reveals an isotropic behavior. Combination of XRD and optical microscopy results indicates that this sample displays a spherulitic structure and crystallizes under the orthorhombic lattice with a crystalline lamella thickness of 14 nm. Regarding the rolled sample, the macromolecular chains are preferentially oriented towards the rolling direction as shown by the WAXS pattern in Figure 2(b). The imposed actual reduction ratio during rolling is not enough to induce a fibrillar structure: the oriented sample is made of deformed spherulites with lamellae stacks receding from each other in equatorial region and becoming closer in the polar region due to Poisson effect.

(a) un -oriented HDPE sample



(b) oriented HDPE sample: AR=3.5

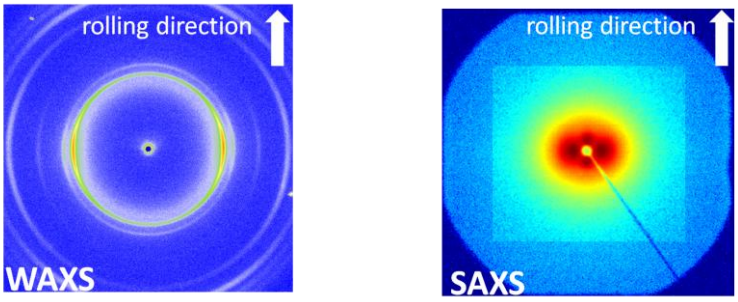


Figure 2: WAXS/SAXS patterns for (a) un-oriented and (b) oriented by hot rolling HDPE samples

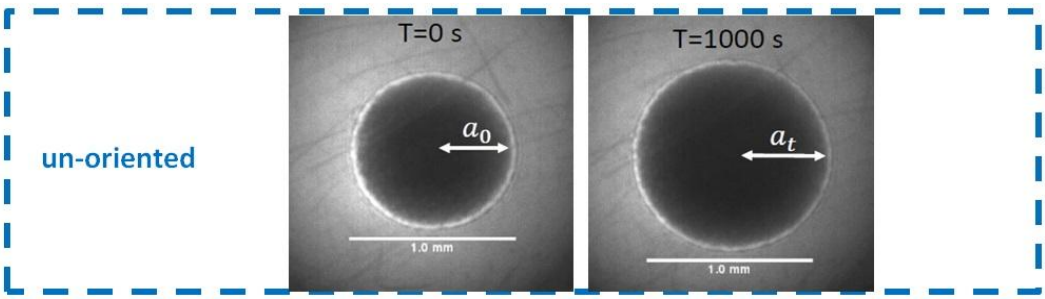
Concerning the mechanical properties evaluated under uniaxial tensile tests, the un-oriented HDPE displays an isotropic behavior with a Young's modulus near 900 MPa. In case of the oriented HDPE sample (AR=3.5), a decrease of this modulus is observed in the direction of rolling with respect to the isotropic sample. This phenomenon was already observed in literature for uniaxial tensile tests performed at room temperature, i.e. above the glass transition temperature of this material [3]. It should be noted that the opposite behavior is observed for a higher elongation rate.

3.2 Contact creep and recovery experiments

Figure 3 (a) displays the evolution of the contact area during the creep phase for un-oriented HDPE surfaces. The contact area is circular for the isotropic material and the comparison of the pictures taken at the beginning and at the end of the creep phase shows that the radius of contact increases with creep time (t_c) due to viscoelasticity. The effects of both initial imposed strain level and creep duration on the viscoelastic behavior were also studied. As regards the first parameter, it was observed that the initial imposed strain has no major influence during the creep phase but that increasing this strain induces an increase of the residual depths at the end of the recovery phase. Concerning the creep duration, it was shown that this parameter has no major effect during the creep step. Nonetheless, as observed for the influence of the initial imposed strain level, residual depths increase with longer creep duration, inducing, in some case, a permanent deformation of the surface.

Focusing on the effect of macromolecular orientation, if the contact creep of the un-oriented surface with a spherical indenter displays a circular contact area; the same experiment performed with oriented semi-crystalline polymers shows an elliptical contact area as illustrated in Figure 3(b). This contact geometry can have several origins: it can result from the differences in mechanical properties observed parallel and perpendicular to the direction of rolling but also from the surface curvature potentially induced during the process.
It could also be note that the ellipticity of the contact increases with t_c as shown in Figure 3(b) by the evolution of the a/b ratio with the creep phase. These results could be explain by the anisotropy of the viscoelastic properties parallel and perpendicular to the rolling direction in case of oriented HDPE.

(a)



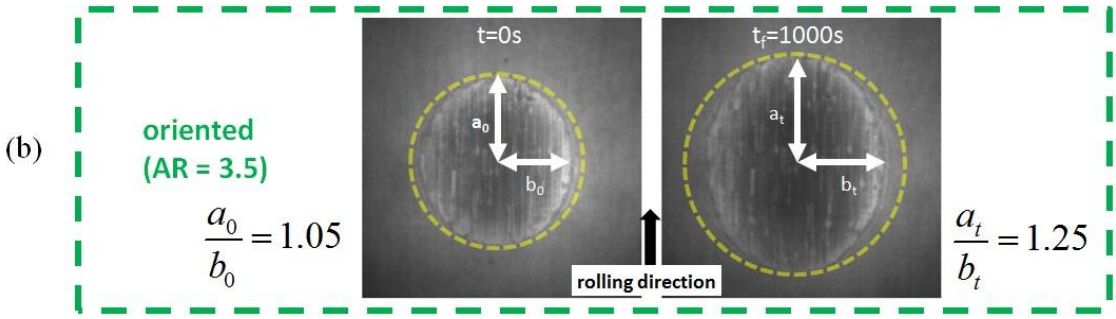


Figure 3: In situ observations of the contact area taken at the beginning and at the end of the creep phase for (a) un-oriented and (b) oriented (AR=3.5) HDPE samples (yellow dotted curves represent a circular contact) for an indenter radius of 25.94 mm and an applied load of 10 N

3.2 Numerical modeling

Numerical modeling of the surface response was performed using MSC MARC® software in order to better understand the in-situ observations of the contact shape during the contact creep and recovery of the residual imprint. The aim is to reproduce, as closely as possible, the contact creep and recovery experiment. To that purpose a 3D numerical model describing the experimental conditions was developed. A constant load is applied on a spherical indenter considered to be infinitely rigid. The mesh is refined on the sample surface and the elements are composed of eight nodes and one Gauss point. This model gives access to the true contact radius during the creep phase. It was verified that the numerical results obtained in static are in good agreement with the Hertz's theory of contact. As regards the contact shape for the oriented sample, the comparison of the experimental and numerical results seems to indicate that the elliptical contact area is rather govern by the anisotropic mechanical properties of the semi-crystalline polymer surface induced during hot rolling as shown in Figure 4.

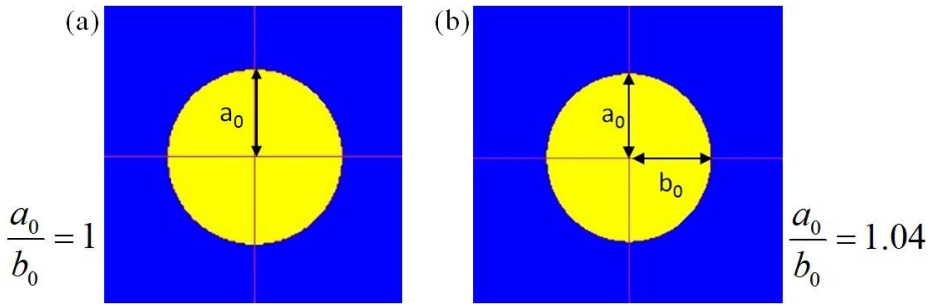


Figure 4: Numerical simulation of the contact area at the beginning of the creep phase for (a) un-oriented and (b) oriented (AR=3.5) HDPE for an indenter radius of 25.94 mm and an applied load of 10 N

In order to take into account the influence of creep duration in the numerical model, it was necessary to determine the viscoelastic properties of the bulk HDPE and relaxations tests were performed at various strains corresponding to 6, 12.5 and 30% of the yield strain (ε_y= 0.08). Poisson coefficient was considered as a constant fixed at 0.42 [4] in such a way that the viscoelastic properties of HDPE could be defined thanks to the time dependance of the deviatoric modulus (G) and the storage modulus (K) following equations (1) [5].

$$G(t) = G_0 + \sum G_i \exp(-t/\tau_i) \quad \text{and} \quad K(t) = K_0 + \sum K_i \exp(-t/\tau_i) \qquad (1)$$

where G_0, K_0, G_i, K_i and τ_i are the identification parameters. i is the number of characteristic relaxation times and is chosen at least equal to the number of time decades explored in the relaxation experiment. To reduce the number of parameters to be identified, the characteristic times are fixed. Figure 5 presents the comparison between the experimental data and the simulated curves from the identified parameters.

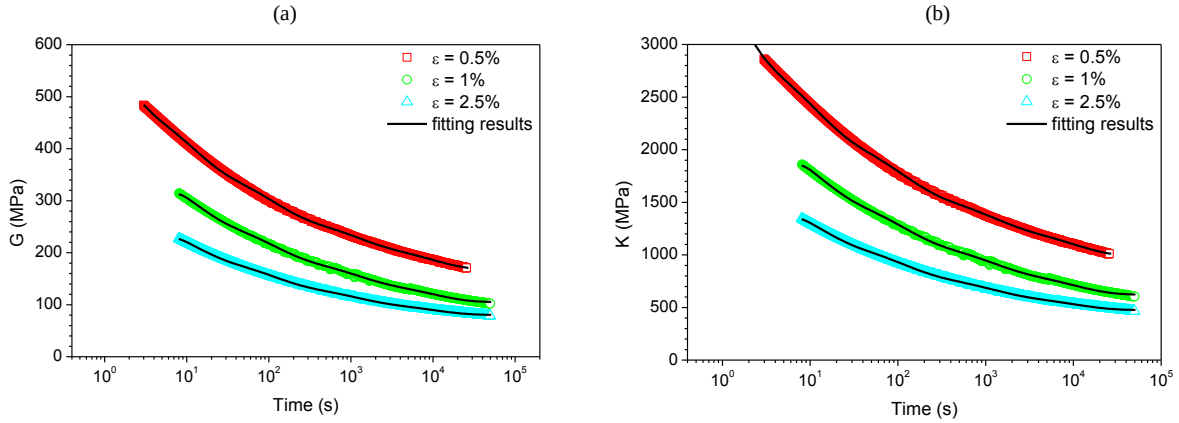


Figure 5: Relaxation tests - Evolution of (a) the deviatoric modulus (G) and (b) the storage modulus (K) as a function of time for several imposed strains

Regarding the viscoelastic properties of the oriented HDPE, nanoindentation experiments are in progress on cryofractured sample along the three directions (rolling, perpendicular and thickness directions). These results will be used in the finite element model in order to determine the evolution of the contact ellipticity during both creep and recovery phases.

4 Conclusions

The anisotropy of the mechanical properties resulting from the orientation of the macromolecular chains in a preferential direction is responsible for the anisotropy of the contact during contact creep and recovery test. The increase in the ellipticity of the contact with the creep time shows that the viscoelastic properties are also modified by the orientation.
Numerical simulations taking into account the viscoelastic properties of HDPE are in progress in order to compare the results with the experimental data.

References

[1] S.J. Heo, I. Jang, P.R. Barry et al, Effect of the sliding orientation on the tribological properties of polyethylene in molecular dynamics simulations, Journal of Applied Physics 103 (2008) 083502
[2] A. Rubin, D. Favier, P. Danieau et al, Direct observation of contact on non transparent viscoelastic polymers surfaces: A new way to study creep and recovery, Progress in Organic Coatings 99 (2016) 134-139
[3] Y. Yang, J. Keum, Z. Zhou et al, Structure and properties of biaxial-oriented crystalline polymers by solid-state crossrolling, Journal of Applied Polymer Science 118 (2010) 659-670
[4] S. Fellahi, B.D. Favis, B. Fisa, Tensile dilatometry of injection-moulded HDPE-PA6 blends, Journal of Materials Science 30 (1995) 5522-5530

[5] : T. Chatel, C. Gauthier, H. Pelletier, V. Le Houérou, D. Favier and R. Schirrer, Creep of the contact with a spherical tip and recovery of the imprint on amorphous polymer surfaces, Journal of Physics D: Applied Physics 44 (2011) 375-403

Acknowledgements

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #783. The authors would like to acknowledge the funding support "MARMA" from Carnot MICA and HOLO3 (Alsace region) company for developing the instrument.