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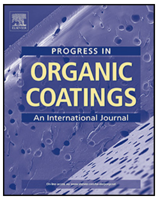

Direct observation of contact on non transparent viscoelastic polymers surfaces: A new way to study creep and recovery

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ABSTRACT

This work presents a new instrumentation dedicated to the study of contact creep and recovery of non transparent polymeric samples. The aim is to be able to analyze viscoelastic properties of polymeric surfaces recording the apparent contact area for the contact creep phase and the residual imprint area for the recovery phase. This gives valuable information not to be model dependant in the analysis compared to classical techniques. Indeed, for the creep phase many methods have been proposed to estimate the contact area, but rarely perform direct vizualisation as we propose. For the recovery phase two main challenges arise: avoid contact probe not to influence on recovery kinetics; get recording at early times to have information before recovery is quite finished. This study focus on indentation problems to prove the concept of viscoelastic analysis directly from experimental data without modeling. But the problematic is more larger than that and widen to more complicated rheological surface studies including indentation and scratching.

1. Introduction

Polymer-based materials (composites, protective coatings...) are often subjected to damages such as scratches during their lifetime. The industrial aim is to limit these surface damages and the scientific main issue is to identify the material parameters that influence such contact mechanical responses. Materials science already showed that polymers have viscoelastic behaviors. It entails that some damaged polymer surfaces can recover their original shape with time due to the polymer mechanical properties, its strain history and the working temperature [1–3]. From a continuum mechanical approach there is not yet complete analytical solutions describing viscoelastic behavior as it is a complex problem but it can be explored from the study of stresses between two bodies in mutual contact.

First, current creep analysis derived from the early work of Hertz who proposed the analytical solution of an elastic contact between an axi-symmetric indenter and a flat surface [4] and from its extension to the linear viscoelastic response in the mid-sixties where Lee & Radok solved the case of a sphere in contact with a plane assuming a monotonic time-dependent condition of Hertz contact [5]. Yang extended this solution to quadratic contacts problems [6]. In parallel several experimental results were used to ensure the validity of these models with set-ups designed so as to load a rigid axi-symmetric indenter on a flat deformable specimen. In such set-ups, the key parameter is the characterization technique. A first one is optical techniques, as for instance photoelastic fringe patterns or optical distortion of a mesh under the contact, which provide the stress distributions under the contact [7,8]. It can be extended to time-dependant measurements as Yoneyama et al. did in the seventies aided by computer image processing on epoxy resin [7]. They evaluated the variation of the principal stress and strain with time. Nonetheless the main drawbacks of this method are that i) automatic detection of the dark fringes is rather tricky; ii) resolution is not so good for low mean contact pressures where pure viscoelasticity occurs; iii) polymer specimen must be photoelastic materials which dismiss opaque polymers (as semi-crystalline's) and iv) this is dedicated to 2D contact problems. The second range of characterization tests, and the major one, consists of depth-sensing techniques: micro- or nano-indentation. It is powerful as instrumentation can now control the load either in micro or nano Newton range and the depth in nanometer resolution. The mechanical properties (Young modulus, hardness...) are extracted from an experimental load-displacement curve using the Oliver & Pharr model [9]. Nonetheless this method is more dedicated to perfect elastic-plastic materials and is not well adapted to

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analyze time-dependant materials. Moreover, for such materials, creep is an undesirable effect of such indentations measurements that needed some peculiar attention to avoid errors on Young's modulus and hardness calculation [10]. The crucial instrumental point is the measurement accuracy that allows to follow the drift in depth for tens of seconds at a constant loading (typically axial resolution < 0.5 nm). Consequently specific protocols of loading/unloading cycles were determined including hold times with Berkovich tip or spherical tip [10–14]. Some partial conclusions can be drawn from these static contact studies: sharp conical indenters or Berkovich tips, which yield the surface, show a load-dependance response (for a loading rate dP/P). On the contrary spherical indenters allow to work within a pure viscoelastic range but for sufficiently large radius (typically 500 μm) the accuracy of applied loads in the range is not enough to get a satisfied response. Moreover in both cases, the apparent contact area and the mechanical properties of the sample are estimated from the shape of the tip. Eventually errors on the apparent contact area estimation combined with uncertainties related to the real tip displacement in the matter entail errors on the mechanical properties calculation. Dynamic depth-sensing has then arisen and has allowed to get rid of the yielding effect of Berkovich tips. With this technique Loubet et al. proposed a model which take into account the possible piling-up or sinking-in of the matter to estimate at best the tip displacement [15,16]. Still, the underlying question is all about the knowledge of the apparent contact area which is over- or under-estimated by one method or the other.

For recovery studies, little experimental research has been undertaken to understand the relaxation of the residual imprints after either an indentation or creep test because of the instrumental difficulty to measure the residual imprint accurately versus the time. The recovery is characterized by two steps: i) an almost instantaneous elastic recovery of the polymer which is quite impossible to measure directly, ii) the time-delayed recovery which could exist even after severe deformation. The collaborative work of Hult and Johansson gave some valuable results on the recovery kinetics of scratch grooves of poly(urethane)-based coatings characterized by AFM and white-light interferometry [17]. There is an obvious lack of experimental data for the recovery study.

In both case, creep and recovery successive phases, an ideal solution is to observe *i*) the contact and *ii*) the residual imprint evolutions during each step of the experiment in order not to be model dependant. For the latter the use of a non-contact technique will also avoid any influence on the recovery kinetics of the residual imprint. Our team has already developed a built-in microscope on a sclerometer dedicated to transparent polymer samples [18] and adapted to contact creep-recovery studies [19]. A CCD camera records through the transparent sample the evolution of the contact during the creep phase and the evolution of interferometric fringes due to the curvature of the residual imprint and a glass blade during the recovery phase. This work was a premiere in creep-recovery analysis as the evolution of representation strain versus time were directly extracted from experimental data and compared in a second step with numerical studies [20]. The team work was then extended to scratch creep-recovery analysis [21]. The major drawbacks are that i) for the recovery phase we only have information on the curvature of the residual imprint (the total depth and elastic deflections of the imprint are missing); ii) opaque materials cannot be studied. Other methods exist for in situ observations of the contact. Pelletier et al. designed another instrumented indentation microscope to follow the contact area during spherical indentation but they did not work yet on pure creep phenomena [22]. Recently Wheeler et al. has also developed an in situ optical oblique observation of scratch but this technique cannot be extended to the study of viscoelastic materials has it gives only lateral information of fracture and severe deformation [23].

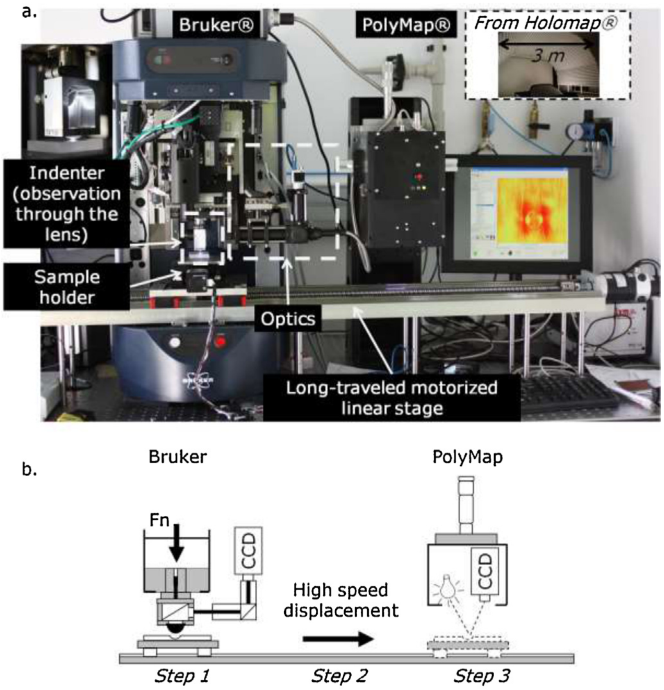

Fig. 1. a) Snapshot of the set-up – b) sketch of the set-up.

This work presents a new method to analyze both contact creep and imprint recovery dedicated to non transparent samples. Pure viscoelastic contacts are obtained by indentation of transparent spherical rigid indenter of millimeter-range radii. The contact can be visualized through the indenter. The time-delayed recovery is measured by deflectometry technique. The main advantages of the latter apparatus are the rapidity and the depth accuracy measurement. Indeed the overall topography of a $10 \times 10\,\mathrm{mm}^2$ is obtained in less than a minute with a depth accuracy over millimeter-range contact less than a micron for this prototype. This new set-up is therefore adapted to a brand type of materials that could not be studied before without any model: opaque glassy materials as semi-crystalline or composites, self-healing materials... It will give experimental datas to finely understand viscoelastic mechanisms.

2. Experimental

The main aim of the designed set-up (Fig. 1a) is to perform creep and recovery experiment without being model dependant. The experiment is controlled by a software completely developed in the lab, which allows three successive steps (Fig. 1b). First an indentation step is performed on the UMT Tribolab® from Bruker. The constant normal load Fn is applied on a transparent rigid indenter of large radius (from 5 to 25 mm) and can vary from 10 N to 500 N. The contact area A is reflected through the indenter on a mirror and captured via a live CCD camera. Usual contact radii can vary from several hundreds of micrometer to millimeter range. It allows to follow the contact radius a(t), the apparent mean contact pressure $p_{\mathrm{mean}} = Fn/A$ and the mean applied strain $\varepsilon(t)$ (proportional to a(t)/R where R is the indenter radius) with creeping time t_c. Then the indenter is removed after a given creeping time and the sample is moved at high speed (500 mm/min) using a long-traveled motorized linear stage under the topographic measurement head PolyMap® (patent pending [24]) from Holo3. The total time between the end of creep and the beginning of recovery is ~10 s. Last the evolution of the topography is recorded in logarithm time. The apparatus developed by Holo3 is based on deflectometry technique: a camera is viewing the object surface's reflection.