

Strain rate dependent micro-plasticity of metal-organic framework glasses

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Abstract

The strain rate dependence of micromechanical properties can be key in understanding material-fundamental deformation processes. Moreover, extreme strain rates can also simulate ballistic impact and conditions during drop or crash of devices, which is of special interest in industrial and everyday applications of materials. However, due to the limitations in conventional nanoindentation instrument design where the resonance frequency of the system prevents from high strain rate experiments, this regime remains to date largely unexplored. Recent technological advances in high strain rate micromechanical testing equipment allows us now to test kinetic behavior across up to eight orders of magnitudes of strain rates. Here we exploit this commercially available technique and study the strain rate dependent micromechanical behavior of metal-organic framework (MOF) glasses with the aim to elucidate atomic-scale mechanisms that accommodate plastic strain. To this end, we have performed strain rate dependent uniaxial compression experiments on a_9 ZIF-62 micropillars of 3 μm diameter at strain rates ranging from 10^{-3} s^{-1} up to almost 10^3 s^{-1} . We found that this glass shows substantial plasticity on the micrometer scale. At a quasi-static strain-rate of 10^{-3} s^{-1} , the micro-pillars yielded at approximately 0.32 GPa and subsequently deformed plastically up to 35 % strain. With increasing strain-rate, the yield strength of a_9 ZIF-62 evolved with the strain-rate sensitivity $m = 0.024$ to reach a yield strength of 0.44 GPa at a strain-rate of 510 s^{-1} . Based on this relatively low strain-rate sensitivity and the absence of serrated flow, we conclude that structural densification is the predominant mechanism that accommodates such extensive plasticity.

Introduction

The number of known metal-organic framework (MOF) glasses is constantly growing [1], as is knowledge on both the fundamental behavior[2] and potential applications of these novel amorphous materials.[3] MOF glasses are—similar to their crystalline counterparts—composed of metal ions interconnected by organic linker molecules. While crystalline MOFs thus form three-dimensionally periodic frameworks, MOF glasses consist of continuous random networks. The chemical- and short-range-structural characteristics of MOFs are therefore comparable across the crystalline–amorphous phase boundary. The physical properties of these two states are however strikingly different.[4]

Several ways exist to synthesize MOF glasses from their crystalline MOF precursors, including heating, melt-quenching, mechanical compression, and ball-milling. The family of melt-quenched glasses (*i.e.* formed by cooling of the liquid MOF state) are of particular interest due to the ability to form bulk transparent materials. a_9 ZIF-62, which is formed by the melting of crystalline ZIF-62 (melting temperature $T_m = 370 \text{ }^\circ\text{C} - 440 \text{ }^\circ\text{C}$, ZIF = zeolitic imidazolate framework) and subsequent super-cooling of this melt, is to date the most studied melt-quenched MOF glass.[5] It is composed of Zn nodes and two types of interconnecting organic linker-molecules, imidazolate (Im, $\text{C}_3\text{H}_3\text{N}_2^-$) and benzimidazolate (blm, $\text{C}_7\text{H}_5\text{N}_2^-$). The structure of a_9 ZIF-62 is described by a model with a continuous random network topology analogous to that of amorphous SiO_2 .

Amorphous materials and glasses in general display a diverse range of deformation modes, including shear-banding, homogeneous shear flow, and structural densification.[7] The specific deformation mechanism that ultimately dominates plasticity in such systems depends on a number of factors including axiality of deformation, specimen size, strain rate, and temperature.[8]–[11] Whether MOF glasses display a similar complexity in their mechanical response is, to date, an unanswered question. Furthermore, information on important size-effects during mechanical testing is also lacking. Specifically, the size and the probability of occurrence for preexisting structural flaws, such as micro-cracks and voids, scale with the tested specimen size. Below a certain threshold size, we can consequently probe the fundamental deformation mechanisms and strength only controlled by intrinsic atomic rearrangements. Probing large bulk glass specimens, on the other hand, will inevitably only reflect the strength of the weakest preexisting flaw. The resulting discrepancy between theoretical and practical mechanical behavior in MOF glasses has already been pointed out by To et al. [12], who found diverging results of strength and fracture toughness of a_9 ZIF-62 from beam bending experiments and molecular dynamics simulations, respectively.

Motivated by this lack of knowledge in deformation mechanisms and size effects, we perform a series of strain-rate dependent compression experiments on a_9 ZIF-62 with strain-rates ranging 0.001 s^{-1} up to 510 s^{-1} . This corresponds to durations ranging from approximately 250 s down to 0.5 ms to attain 25% strain. By

covering six orders of magnitude of strain-rates, we probe for the first time potential variations in kinetically controlled deformation-modes of MOF glasses. Because we do this on microscopically small samples, we expect our results to reveal intrinsic material characteristics, including an analysis of the deformation mechanisms responsible for plasticity.

Results and Discussion

The micro-pillar specimens for uniaxial compression testing were focused-ion-beam (FIB) milled on polished surfaces of embedded MOF-glass shards. The micro-pillars are approximately 7 μm in height and 3 μm in diameter, with a taper angle of approximately 5°. The increase in strain rate from 0.001 s^{-1} to 510 s^{-1} for $a_0\text{ZIF-62}$ resulted in a continuous increase of the yield strength. The absolute yield strength values as a function of strain-rate revealed a typical power law relationship. The strain-rate sensitivity m of a material describes this non-linear dependence of stress on the strain rate. It is defined according to $m = d(\ln \sigma)/d(\ln \dot{\epsilon})$, where σ is the yield strength and $\dot{\epsilon}$ is the strain rate. We determined the strain-rate sensitivity m of $a_0\text{ZIF-62}$ as 0.024 ± 0.002 . It is generally difficult to correlate strain-rate sensitivity of glasses with their structural or chemical properties.[13] However, it appears that ZIF glasses display a relatively typical behavior. The relatively low strain rate sensitivity determined here for $a_0\text{ZIF-62}$ compared to other glasses is in line with the trend for highly cross-linked networks and a small packing density of approximately 0.4, which deform mainly through compaction of the free volume.[13], [14] This relationship can be understood qualitatively from the fact that purely displacive densification requires less thermal activation than shear flow, which involves the breaking and reforming of bonds.[15] Further support for a densification dominated plasticity stems from nano-indentation experiments that showed practically no pile-up.[16]

Our finding that the melt-quenched MOF glasses studied here deform predominantly through structural densification without shear banding, partially contradicts the finding of a previous study, which reports shear-band formation in $a_0\text{ZIF-62}$ during nanoindentation[16]. However, this shear-band formation was only detected during the analysis of the residual imprint. They have not manifested themselves – as expected for typical shear-bands – through displacement bursts in the load-displacement curves.[17] The contribution of these shear-bands, as well as that of isochoric shear-flow, to the total plastic deformation was concluded to be minor in view of a predominant densification.

Conclusion

We studied for the first time the mechanical properties of a series of novel MOF glasses by means of strain-rate dependent micro-pillar compression. This technique has several advantages over previously employed nanoindentation, in particular the direct measurement of stress-strain curves thanks to the uniaxial stress field. We thus directly measured the strength and observed ductility, and determined the respective strain-rate sensitivities. These results allowed us to deduce the basic mechanisms that impart ductility to these glasses, at least on the micrometer-scale, which is both of fundamental interest and important for future engineering tasks. Finally, our study prompts for continued investigation in several directions. (1) High strain rate micro-mechanical experiments are now opening up a new and important branch of micromechanical research that will in the near future approach time scales investigated in molecular-dynamics simulations. This is an exciting outlook as experiments will be directly comparable with simulations based on chemical interaction. (2) A broad range of mechanical experiments are now available at the micro- to nanoscale. In some cases, they can be complementary, in other cases, the stress fields created are too different from each other to allow for a direct comparison – especially in complex amorphous systems. This is not to be seen as a contradiction, but rather as a challenge to find more general constitutive relationships. (3) As we perform mechanical experiments on ever smaller length-scales, the response of the materials approaches more and more intrinsic properties. In particular, for network forming glasses, this means that chemical interactions and bonds are the foremost controlling factors. In this sense, the disciplines of solid state mechanics and solid state chemistry thus are no longer separate fields.

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