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Direct Observation on the Surface Fracture of Ultrathin Film Double-Network Hydrogels

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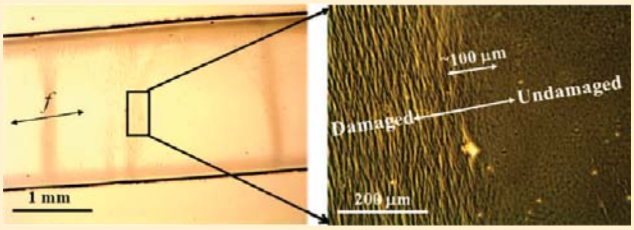
ABSTRACT: Double-network (DN) hydrogels have attracted much attention in the soft matter community due to their excellent mechanical performance and unique fracture mechanism. On the basis of ultrathin film technique and optical microscope, we here report a method which is quite effective for accessing the fractured microstructure of DN hydrogels formed during the tensile and tearing process. During tensile deformation, fracture of the first network occurs even before yielding occurs. Concomitant with the yielding, wrinkle-like structure, which is due to the fracture of the first network, is clearly observed for the first time. This wrinkle-like structure disappears upon further deformation to strain-hardening region because of the further fracture of the first network. Similar microstructures are observed at the crack tip for samples experienced the tearing test. This work provides direct proofs for the assumption concerning the occurrence of local yielding and the formation of a huge damage zone at the crack tip during the crack propagation process of DN hydrogels.



INTRODUCTION

The double-network (DN) technique has been developed by our group with an emphasis on addressing the poor mechanical properties of polymer hydrogels since 2003.[1] DN gels, composed of a rigid and brittle first network and a soft and ductile second network, show not only a high fracture stress and strain but also a high toughness with a fracture energy (G) of 10^2-10^3 J/m^2, which is 10−1000 times larger than that of the individual single-network hydrogels.[2−4] Owing to the tough feature, extensive studies have been focused on the toughening mechanism of this soft and water containing wet material.[3−12] Investigations on the tensile test have revealed the necking phenomena and the large hysteresis of the DN gels, implying that the DN gels could accumulate the internal damage before its macroscopic fracture through the connection of the soft second network to the fragments of the brittle first network.[5,9] As a result, softening of the gels occurs concomitantly with large energy dissipation. This dissipation in the energy is considered to be active at the crack tip and contributes dominantly to the high tearing energy.[5,6,8] Phenomenological models concerning the formation of the softened (damaged) zone at the crack tip vicinity and its role to the propagation of the crack tip have been proposed.[6,8] According to these models, the softened damage zone was estimated in an order of hundreds of micrometers. This softening of the fractured surface has been clarified by the micromechanical measurement using AFM.[11] Furthermore, direct visualization of the crack tip using 3D violet laser scanning microscopy confirmed the existence of the damage zone of several hundred micrometers, which seems to be several times wider than the model prediction.[12] However, those previously developed methods give no detailed information on the characteristic structure distribution of the damage zone. Main blocks to the issues arise from the high water content and the large thickness of the bulk DN gels, which lead to an average overlay of the characteristic structure along the observed direction. Consequently, magnification and resolution on the characteristic structure were very limited.

More recently, we have successfully created the ultrathin film DN (UTDN) gels of 100 μm in thickness by coupling the salt-controlled swelling process and the polymer chain prereinforced technique.[13] These UTDN gels show very high toughness which is comparable with that of the bulk DN gels. Yielding and necking behavior have also been observed in these gels during the tensile process. These results indicate that the DN technique was effective even at the micrometer scale by means of a similar toughening mechanism. This permits us to further study about the fracture structure of the DN gels using the UTDN gels, which takes great advantage of removing the thickness and water interference suffered by the bulk DN gels. In this work, we report the visualization of the characteristic fracture structure of the UTDN gels induced by tensile and/or tearing process and discuss the correlation of these two processes.

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