MOLECULAR DYNAMICS SIMULATION OF CRAZING IN AMORPHOUS GLASSY POLYMERS

Sudarkodi Venkatesan*[a)] & Sumit Basu
*Department of Mechanical Engineering, Indian Institute of Technology, Kanpur, 208016, India.

Summary Molecular dynamic (MD) simulations of craze nucleation and growth in glassy amorphous polymers were performed using a force field consisting of bond stretching, bending, dihedral and non-bonded contributions. Our MD simulations reveal situations in and mechanisms by which craze fibrils nucleate, grow and fail in these materials. Our simulations bring out the interplay between applied hydrostatic stress and entanglement density fluctuations that govern the morphology of the craze. The competition between disentanglement and scission in causing final failure of the craze fibrils is also explored.

INTRODUCTION

A substantial fraction of failures of polymeric components in service are believed to be due to crazing. Micromechanics of the phenomenon of crazing behaviour in glassy polymers under deformation has been extensively studied by experiments [1] and simulations using a bead spring model [2]. This phenomenon is characterised by formation of a nascent craze which then grows in length at a constant stress and volume fraction. Our molecular simulations are done with detailed force fields [4] and probe the nucleation, growth and failure of crazes. The sample is deformed at a constant speed in the z direction with additional imposed constraints in the x and y directions determining the level of hydrostatic stress in the sample. The MD simulations enable us to trace out the exact sequence of processes by which the fibrils nucleate, grow and finally fail. In particular, we focus on the interplay between the externally applied stress state and the entanglement network. The entanglements are located by deducing the primitive paths of the chains [3] at various stages of the deformation. The relative roles of scission and disentanglement towards final failure are also assessed.

RESULTS AND DISCUSSION

The overall response of the our samples, when deformed at the rate mentioned above, conformed to expectations derived from earlier experimental observations. The stress σ^{33} plotted against elongation λ for the sample is shown in 1(a). The curves in this plot pertain to different levels of imposed hydrostatic stress σ_H. The sample with the highest level of σ_H shows a long stress plateau with no hardening. As the level of σ_H drops, the plateau becomes shorter with hardening setting in at a lower λ. Eventually, the levels of σ_H fall below that required to initiate crazes and the sample deforms in an almost uniaxial manner with no cavitation or fibrillation taking place. This confirms that a critical σ_H is indeed essential for crazes to nucleate and grow. Often, instead of a single dominant fibril, multiple short fibrils with intervening cross-tie fibrils appear sequentially. Each fibril grows for some time maintaining a constant average volume fraction v_f across it.

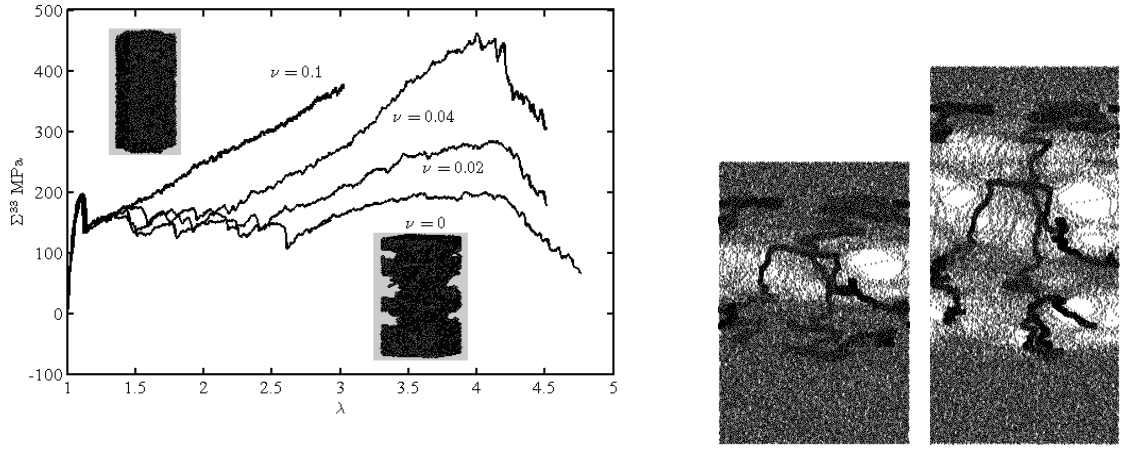
Due to the amorphous nature of the material, fluctuations in density and entanglement density, albeit small, exist all through the sample even in the initial configuration. The van der Waals part of the local hydrostatic stress σ_H^{vdW} is uniform over the sample and increases with deformation in the initial stages. The initial cavity appears suddenly at a region where the entanglement density η (see Fig. 2(a)) is locally low. Cavitation leads to relaxation in the hydrostatic stress and further drop in entanglement density. As shown in Fig. 2(a) and 2(b), with λ, the craze (indicated by a region of low v_f) widens resulting in further disentanglement over the fibril and increase in η above and below it. The development of highly entangled regions in the active zones above and below the fibril not only prevents further growth of the fibril but also lead to development of high enough mean stress σ_H^{vdW} at a location with suitably low η above the active zone, where the cycle of nucleation and growth of a new fibril might replay itself. The beginning of this process of development of a second fibril is seen in Fig. 2(b), just below the first fibril.

Failure of the sample is governed by the either pull-out or scission. Chain scission causes weakening of a well developed fibril. Both chain scission or polydispersity in the sample can provide a supply of short chains that can pull out easily.

SUMMARY AND CONCLUSIONS

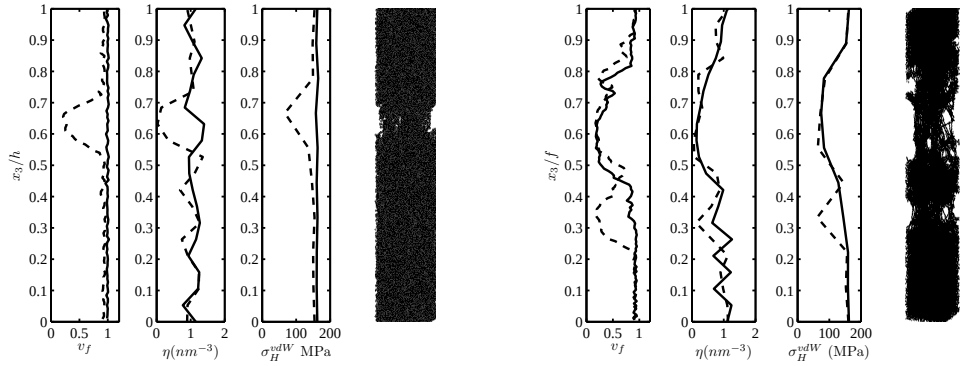
Carefully designed Molecular Dynamics simulations on large glassy macromolecular ensembles have yielded important insights into the mechanics of nucleation, growth and failure of crazes in these materials. Various craze morphologies with and without cross tie fibrils could be generated depending on the level of hydrostatic stress, entanglement density and the presence or absence of short chains. The relative roles of scission and pull-out in causing the final failure of the fibrils has also been elucidated. Our simulations show that both nucleation and growth of a craze depends critically on the entanglement density, while bond strength plays a role in failure.

[a)] Corresponding author. E-mail: sudar@iitk.ac.in



(a) (b) (c)

Figure 1: (a) Overall stress vs stretch plot for a sample at various levels of imposed hydrostatic stress (higher the value of ν, lower is the imposed hydrostatic stress σ_H). Craze morphologies at two strain levels showing (b) the growth of a first craze, followed by (c) nucleation of a second one below it.



(a) (b)

Figure 2: Variation in volume fraction, v_f entanglement density η and non-bonded part of the mean stress σ_H^{vdW} with normalised height for (a) λ=1.1 and 1.2 and (b) 1.4 and 1.6. The configurations at $\lambda = 1.2$ and 1.6 are also shown.

References

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