

## Ultimate toughness of amorphous polymers

***Citation for published version (APA):***

Meijer, H. E. H., & Sanden, van der, M. C. M. (1994). Ultimate toughness of amorphous polymers. In *Deformation, yield and fracture of polymers : 9th international conference : 11-14 April, 1994, Cambridge, UK* (pp. 7). The Institute of Materials.

***Document status and date:***

Published: 01/01/1994

***Document Version:***

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

***Please check the document version of this publication:***

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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# ULTIMATE TOUGHNESS OF AMORPHOUS POLYMERS

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As shown by Kramer et al. (1-6), the maximum attainable strain of amorphous polymers can be understood from a molecular (network density) point of view at least on a microscopic level such as the craze extension ratio and the draw ratio in shear deformation zones. In this study it is demonstrated that the maximum network strain can also be reached on a macroscopic level, provided that the material locally is made thin enough e.g. by the incorporation of sub-micron "holes". For the most frequently used thermoplastic polymers, the typical critical material length scale ("the inter hole distance") ranges from 20 to 200 nm. This concept is valid in slow speed and high speed notched tensile testing and also applies on thermosets. Thus, the ultimate toughness of amorphous polymers is reached.

## Introduction

Ultimate properties of polymeric materials (stiffness, strength and toughness) are major topics of research. Nowadays, ultimate stiffness and strength can be directly related to the structure and arrangement of molecular chains and are experimentally confirmed for a selected range of polymers. A thorough understanding of the parameters governing the ultimate macroscopic toughness of amorphous glassy polymers, however, was still lacking.

Toughness is, in a first approximation, proportional to the total energy involved in deformation up to fracture, i.e. the area under the stress-strain curve. Since the stress at which amorphous glassy polymers deform is within the limited range of 50-80 MPa and the strain to break varies in a much wider range (1-150%), the strain to break can be used as a discriminating parameter. On a microscopic level (i.e. inside deformation areas) a satisfying correlation has been established between the local strain and the strain to break based on stretching the molecular network to its full extension (1). The molecular network is characterized by the molecular weight between nodes of enhanced friction, i.e. entanglements for thermoplastic polymers and crosslinks for thermosetting polymers. On a macroscopic scale the strain to break is often two decades below the expected strain to break. This paradox was the issue for our research.

## Experimental results

In this study (7-9), the concept of a *critical thickness* is introduced below which amorphous glassy polymers deform up to their maximum draw ratio (read: toughness) given by their equilibrium polymer-specific molecular network density. A decrease of the sample dimensions in one (thin films) or two (thin ligaments) dimensions results in a sharp increase of the macroscopic strain to break up to a value comparable with the draw ratio ( $\lambda_{\max}$ ) of the molecular network, see Figure 1. For example, the strain to break of polystyrene (PS) can be increased from 1% up to 200% by decreasing the (local) specimen size below 50 nm. The (local) specimen dimensions can be easily controlled via the use of thin films (separated by non-adhering spacers) or by the introduction of (preferably) non-adhering rubbery particles. The average distance between the rubbery particles determines the local thickness in the latter case. Below the critical thickness, all amorphous glassy polymers deform via shear yielding, as demonstrated with tensile dilatometry.

An explanation for the phenomenon of a critical thickness is postulated based on an energy criterion for brittle fracture. If deformation is initiated locally, deformation will continue throughout the complete sample only if catastrophic fracture of fibrillated ligaments is prohibited anywhere in the sample. Decreasing the size of the sample finally results in an equilibrium between the stored elastic energy in the sample (locally around the ligament) and the (brittle fracture) surface energy of the fibrillated sample (the stretched ligament) which is deformed up to  $\lambda_{\max}$ . A further decrease of the ligament thickness prohibits brittle fracture of the fibrillated ligament for the testing conditions applied. Hence, macroscopically ductile deformation behaviour prevails and ultimate toughness is obtained.

The critical thickness ( $ID_c$ ) has been experimentally determined for a wide range of thermoplastic and thermosetting polymers and proves to be highly dependent on the molecular network density showing no differences between the two type of networks, which can be understood from the typical time-scale of the experiments, see Figure 2.  $ID_c$  varies from 0.05  $\mu\text{m}$  for polystyrene (low network density) up to a few micron for relatively densely crosslinked thermosets. This material-dependent critical thickness can be quantitatively understood from the energy-based criterion via the network density dependence of (i) most important: the natural draw ratio ( $\lambda_{\max}$ ) and (ii) the secondary influence of the brittle fracture surface energy.

The influence of extrinsic variables on the absolute value of the critical thickness can be predicted relatively easy via a strain rate and temperature dependence of the yield stress and Young's modulus of the pure polymer.

Any adhesion between the matrix and the dispersed elastomer added to create the desired local thickness in most practical (melt-mixed) systems (lowering of interfacial adhesion), and any subsequent increase in the elastomer cavitation stress, influence the value of the critical thickness in an unfavourable manner: the critical thickness decreases with an increasing degree of adhesion and/or cavitation stress of the elastomer or, alternatively, the brittle-to-tough transition temperature shifts to higher temperatures at a constant ligament thickness, see Figure 3.

## Conclusions

Based on the above findings one of the most ductile amorphous glassy polymers proves to be polystyrene that reveals its ultimate ductility in a non-adhering holey morphology only if the local thickness is below the critical value of 50 nm. Hence, the development of sub-micron foam-like structures based on PS offer a challenging prospect in confirming the findings in this research, see Figure 4. An onset towards the development of these nano-sized structures has been made in our laboratory.

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