Polymer xxx (2013) 1–14

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Feature article

The physics and micro-mechanics of nano-voids and nano-particles in polymer combinations

Goerg H. Michler [a,*], Hans-Henning Kausch-Blecken von Schmeling [b]

[a] Institute of Physics, Martin Luther University Halle-Wittenberg, 06099 Halle/S., Germany
[b] Institute of Materials, Swiss Federal Institute of Technology Lausanne (EPFL), 1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 20 November 2012
Received in revised form
14 March 2013
Accepted 18 March 2013
Available online xxx

Keywords:
Polymer combinations
Polymer nano-composites
Nano-/micromechanics
Electron microscopy

ABSTRACT

In this article the role of voids or particulate inclusions of different sizes on mechanical properties and particularly on toughness in several polymers is discussed. With decreasing void sizes and intervoid distances, the influence of the interphase material around the voids becomes more important and characteristic changes in the nano- and micro-deformation mechanisms appear. These mechanisms are revealed by several techniques of electron microscopy within rubber modified polymers, nanocomposites and nanofibres respectively. Three nanoscopic toughness enhancing mechanisms are described in detail: thin layer yielding, nanovoid-modulated craze-formation, and the core flattening mechanism. The action of these mechanisms constitutes a distinct advantage of *nano*voids over *micro*voids.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Most load bearing structural materials are heterogeneous on a microscopic scale. Under load, structural irregularities such as voids, variations of local composition or orientation, inclusions, or arbitrary *defects* initiate stress and/or strain concentrations, which modify – and frequently degrade – the mechanical properties. On the other hand, the reinforcing effects of particulate or fibrous components within a binding matrix are known from the very beginning of human civilization. Evidently in such composite solids the geometry and the amount and quality of the interfaces between the matrix and the reinforcing components are of primordial importance – and they are the more notable the larger the surface/volume ratio of the discrete phases. Thus considerable advantages have been obtained from the presence of nanoscopic charges. Principally using the dominantly employed clay-based nano-charges as an example, Paul and Robeson detail in their feature article [1] fundamental considerations concerning nano-reinforced composite technology (exfoliation, morphology, thermo-mechanical behaviour) but also barrier and membrane properties. In this paper particular attention will be given to the micromechanics of such nanocomposites.

The first mathematical analysis of *stress concentrations* caused by the presence of discontinuities in an otherwise homogeneous material and of their effect on mechanical strength was given by the well-known GRIFFITH model. The original elasto-plastic analysis has been well adapted to time-dependent, viscoelastic polymer materials as outlined by Williams in his classic monograph "*Fracture Mechanics of Polymers*" [2]. He takes into account the effect of yielding, microvoiding and crazing on crack initiation, he also points out that the associated fracture toughness values K_{init} are integral quantities which summarize the global response of the material in the crack tip region. In addition it is even necessary to respect well elaborated fracture mechanics standards concerning sample geometry and loading conditions in order to obtain *K*-values which really characterize a material and not simply an experiment [3].

In this paper, however, we are mostly interested in the physical and mechanical phenomena in nanostructured polymers preceding crack initiation such as material property changes related to the *presence of interfaces* and *interfacial layers* around particles, the *formation of voids* triggering fibrillation and crazing and *scaling or confinement effects* deriving from the small sizes of the constituent structural elements. Since the total number of particles or voids in nanocomposites is enormous, even small modifications of their local environment will add up to influencing macroscopic (mechanical) performance. These effects, the resulting micro-mechanical deformation mechanisms and the macroscopic properties of typical nanostructured polymers are discussed in some detail in this work.

* Corresponding author. Tel.: +49 345 5525541; fax: +49 345 5527149.
E-mail addresses: Goerg.michler@physik.uni-halle.de (G.H. Michler), Kausch.cully@bluewin.ch (H.-H.Kausch-B. von Schmeling).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.03.035

Please cite this article in press as: Michler GH, von Schmeling H-HK-B, The physics and micro-mechanics of nano-voids and nano-particles in polymer combinations, Polymer (2013), http://dx.doi.org/10.1016/j.polymer.2013.03.035

We are not concerned, however, with polymer materials which do possess voids specifically created *through processing* (like foams), but will discuss void formation in optimum size and amount *during application*, usually by cavitation or debonding processes during mechanical loading. Some examples of such materials and possible property improvements are presented.

2. Theoretical background

2.1. Void formation

When submitted to (elongational) stresses most polymer materials show a volume dilatation. At small strains the material responds by an *elastic and inelastic intersegmental displacement*. However, at larger strains it becomes energetically more favourable to accommodate volume dilatation by cavitation. The detailed investigations of Béguelin [4] of a glassy thermoplastic polymer, PMMA, have shown that cavitation sets in at 1.5% of uniaxial strain and that rapid sample loading favours cavitation over shear deformation.

An introduction into the effect of stress concentration and cavitation on mechanical properties of nanostructured polymers has been established in Ref. [5] by more than two dozen (mostly European) researchers. Void opening generally weakens the load bearing capability of a polymer specimen; for this reason the phenomenon has been widely studied. One of the most elegant investigations to show the principle governing effect of void formation on stress-strain behaviour is due to Pawlak and Galeski [6,7]. These authors have compared the deformation of semicrystalline polymer samples, such as PP, strained in two rheologically similar ways: by drawing in uniaxial tension and by bi-axial compression in a rectangular channel die. In uniaxial tension voids (between crystal lamellae) are readily formed because disentanglement and/or rupture of tie chain molecules are favoured giving rise to inter-lamellar slip thus preventing notable strain hardening. In bi-axial compression deformation occurs through intra-lamellar slip and molecular orientation thus leading to strain hardening. The appearance and stability of cavitational voids having sizes on the nanoscale level associated with chain scission is discussed by Galeski in Ref. [8]. Plummer [9] had demonstrated through illustrative electron micrographs the important role of entanglements in interlamellar cavitation of semicrystalline polymers. However, in deforming such polymers at elevated temperature cavitation is completely suppressed [8,10].

Haudin, G'Sell et al. have observed by light microscopy the formation of groups of cavities during drawing of polypropylene films [11]. Using small specimens, G'Sell developed a special video-controlled test to exactly measure the dilatation during tension. The original technique [12] has been developed to record the intrinsic plastic behaviour of ductile materials by monitoring the effective stress and effective strain by analysing the sample profile in real time. Later, the developed Video Traction method was also applied to investigate differently shaped samples and relative displacements [13]. Specific studies have been carried out by Segula [14] on the strong positive influence of entanglements and intercrystalline tie molecules on the natural draw ratio and post-yield strain hardening of PE-based materials.

Polymer nanocomposites may show peculiar properties that are not present in micro-composites, not even in analogy. To find the cause of such behaviour, a multiscale approach has been applied in Ref. [15] to come to a deeper understanding of the structure–property relationships in polymer micro- and nanocomposites.

Quite recently two important other monographs on the micromechanics of nano-composites have appeared. Halary, Lauprêtre and Monnerie [16] have analysed in depth the nature of the molecular mechanisms involved in cavitation (e.g. intensity of â-relaxations, rate of disentanglement) and their influence on material toughness. For more than a dozen of the most important families of modified polymers data are given as a function of molecular composition and main geometrical filler particle parameters *size, diameter and distance*. The main focus of Michler and Baltá-Calleja [17] in their equally comprehensive monograph *Nano- and Micromechanics of Polymers* is directed towards an analysis of the morphological changes occurring during loading in a large variety of neat and modified polymer materials and which are at the origin of their improvement of strength and toughness. In particular, nanovoid formation as consequence of disentanglement, particle cavitation, debonding etc. is discussed in connection with theoretical stress analysis for heterogeneous (structured) polymers.

In this section we are particularly interested in the cavitation behaviour of elastomeric nanoparticles. It is generally agreed, that a cavity in a (spherical) elastomeric particle of diameter D is formed if a void *can be nucleated and extended*. For the void to extend it is necessary that the elastic energy U_{elast} liberated by the formation of the cavity is larger than the energy U_{cav} consumed by the creation of the new surface associated with this event. Fond [18] has treated cavitation as tetrahedral tearing under biaxial traction (Fig. 1a and b).

In his model Fond has quantified the elastic energy U_{elast} stored in a particle (which grows with the third power of D) and the energy U_{cav} for the tearing and opening-up of the interior surfaces, which increases with the second power of the void radius r. This condition is more easily fulfilled for particles with larger diameter D. Using the above model Fond points out, that in addition to $U_{elast} > U_{cav}$ another condition must be fulfilled; since cavitation needs to be nucleated in a *small* molecular volume element by chain scission or void formation through disentanglement the *local* strain energy density must be sufficiently large to provide the required potential energy U_{pot} for the elementary event. This second condition is apparently more readily satisfied with *smaller* or *core–shell* particles [19]. In the absence of a thorough theoretical understanding of this phenomenon most work to define the optimum particle structure is done experimentally.

As an example, Fig. 2 shows the cavitation of a 3-layer coreshell particle (hard PMMA core about 180 nm in diameter, soft PBA (polybutylacrylate-co-styrene) rubber shell approx. 40 nm thick and a hard outer shell of PMMA – Fig. 2a). The particles were preformed and posses spherical shape with a narrow size distribution. Under load, the plastic deformation starts in the rubbery PBA shells of the particles. It is easily recognized that many fibrils have formed in the soft PBA rubber shell (Fig. 2a and b) as consequence of multiple cavitation has occurred in the elastomeric shells of all nanoparticles [20,21].

It is also seen in Fig. 2 that the cavitated particles seem to influence each other so that craze-like *deformation bands* are formed (Fig. 2c). The PMMA matrix strands between the cavitated particles

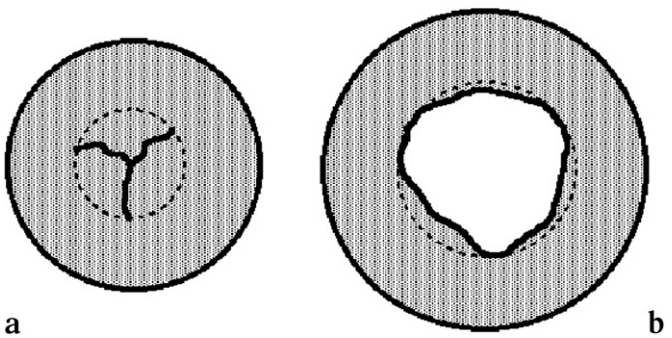

Fig. 1. Cavitation of rubber particles according to the Fond-model demonstrating that the required cavitation energy U_{cav} consists of two terms, a first for the tetrahedral tearing of the nucleus and a second for its viscoelastic deformation up to the opening of the void [18].

Please cite this article in press as: Michler GH, von Schmeling H-HK-B, The physics and micro-mechanics of nano-voids and nano-particles in polymer combinations, Polymer (2013), http://dx.doi.org/10.1016/j.polymer.2013.03.035

Download English Version:

https://daneshyari.com/en/article/5182217

Download Persian Version:

https://daneshyari.com/article/5182217

Daneshyari.com