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Homogenized molecular chain plasticity simulation for crystalline polymer using craze evolution model based on chemical kinetics

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ABSTRACT

Most of the polymers used as structural materials are crystalline polymers that are mixtures composed of glassy and crystalline phases. The fracture of ductile polymers occurs on the boundary between the regions with oriented and non-oriented molecular chains after neck propagation. This behavior is caused by the concentration of craze, which is a type of microscopic damage typically observed in polymers. In this paper, by introducing the strain rate and strain dependence of crazing into the activation energy, a craze evolution equation that describes the nucleation and growth of craze is newly proposed on the basis of chemical kinetics. Then, using a multiscale material model that homogenizes the mixed structure of the glassy phase expressed by the molecular chain plasticity model and the crystalline phase represented by the conventional crystal plasticity model in unit cell, a finite element (FE) simulation coupled with the craze evolution equation is carried out for a crystalline polymer subjected to a uniaxial load. We attempt to reproduce the formation and propagation of the high-strain-rate shear band and the craze-concentration region that occur with neck propagation and to directly visualize the orientation of molecular chains inside the macroscopic structure. The relationship between the deformation behaviors of a macroscopic plate and the unit cell is investigated. In addition, the nonlinear strain recovery in the unloading process observed in a stress–strain curve is also represented through the use of an inelastic response law based on the change in the local free volume as a material response law for glassy polymer. Applying a criterion for a fracture prediction obtained from the fibril strength to the numerical results, fracture prediction based on the craze concentration is demonstrated.

1. Introduction

Thermoplastic polymers such as polypropylene (PP) and polyethylene (PE) have many advantages such as a low price, light weight, high ductility and orientation hardening. In particular, composite materials with a polymer matrix are industrially applicable, thus they have been widely used as structural materials in severe mechanical environments with a large strain such as the interior trims of a vehicle during a collision. Therefore, it is highly desirable to develop a material model that can precisely express the mechanical deformation responses and fracture behavior peculiar to polymers. Polymers form different internal structures depending on the cooling rate in the manufacturing process. Generally, polymers tend to form a glassy state at a high cooling rate and a crystalline state at a low cooling rate. Glassy polymers such as polymethyl methacrylate (PMMA) and polycarbonate (PC) have a random coil structure in which molecular chains are irregularly entangled as shown in Fig. 1(a). A crystalline polymer can be regarded as a mixture consisting of glassy phases and lamellar crystalline phases in which molecular chains are regularly folded as shown in Fig. 1 (b). Moreover, a spherulite structure is formed as shown in Fig. 1(c) at a lower cooling rate by the radial growth of a twisted lamellar crystalline phase. However, it is difficult to model a complicated structure such as a spherulite polymer. Most of the crystalline polymers used as structural materials have the mixed structure shown in Fig. 1(b) to reduce the cooling time; thus we focus on the mechanical properties of crystalline polymers with a mixed structure consisting of glassy phases and lamellar crystalline phases.

Polymers above the glass transition temperature have characteristic mechanical properties, i.e., nonlinear viscoelastic behavior before the initial yielding, strain softening after yielding and rehardening after softening, owing to the molecular chain orientation on the stress–strain response as shown in Fig. 2. Corresponding to these mechanical responses, a neck with a high-strain-rate shear band forms and propagates as shown in Fig. 3. When an

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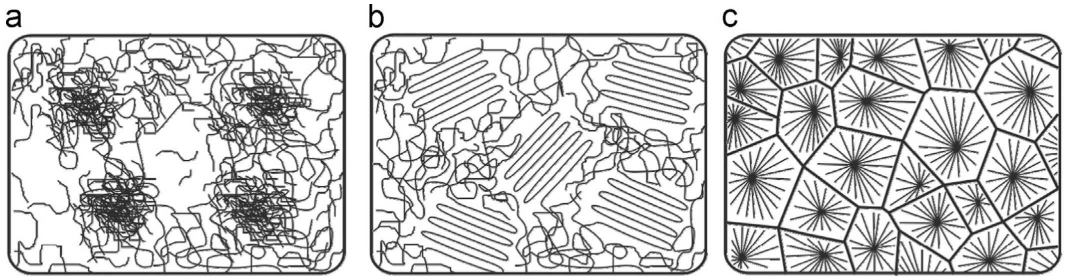

Fig. 1. Internal structures of polymer: (a) general glassy polymer, (b) general crystalline polymer and (c) spherulite polymer.

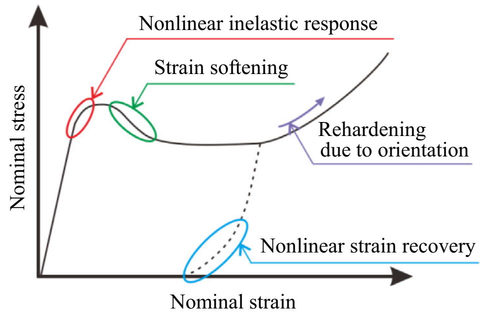

Fig. 2. Stress–strain behavior of polymer.

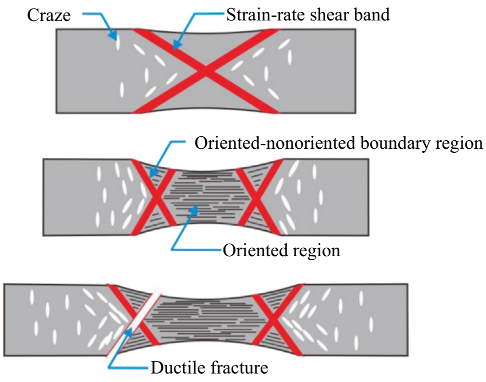

Fig. 3. Ductile fracture mechanism of polymer.

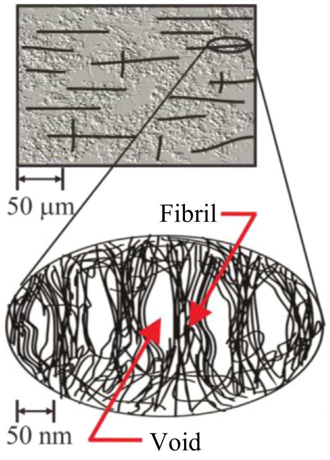

Fig. 4. Internal structure of craze.

inhomogeneous deformation such as a shear band occurs in a structure, the entire region except for the localized strain site automatically undergoes a transition to an unloading state, even in a loading process. It has been experimentally shown that significant nonlinear-strain recovery due to the viscoelastic effect appears in the unloading process of polymers [1], as shown in Fig. 2, unlike in conventional elastic unloading in metals. The fracture of polymers can be classified into brittle fracture and ductile fracture depending on their thermal properties. Brittle fracture is caused at a lower temperature than the glass transition point, whereas ductile fracture occurs above the glass transition point. It is known that brittle fracture occurs at a strain in the vicinity of the elastic strength near the center of a specimen, whereas ductile fracture occurs along the high-strain-rate shear band at the front edge of a propagating neck, i.e. on the boundary between the region with oriented and non-oriented molecular chains after neck propagation. This distinct behavior of ductile fracture stems from the localization of craze, which is typically observed in polymers as shown in Fig. 4. A craze consisting of voids and fibrils, which are aggregates of oriented molecular chains, forms in the glassy phase of a crystalline polymer by tensile loading as shown in Fig. 3. Although the craze sufficiently appears on the entire specimen, it does not cause fracture differently from a conventional crack because the fibrils connecting both sides of the void store stress. When stress exceeding the fibril strength is applied to the region where sufficient craze has accumulated, ductile fracture is caused by the breaking of the fibrils. A schematic diagram of ductile fracture due to craze is shown in Fig. 3. First, craze appears in the entire specimen at the initial hardening stage. Next, on the boundary between the regions with oriented and non-oriented molecular chains, which is near the front edge of the propagating neck, craze concentrates along the high-strain-rate shear band. At this time, the craze does not form in the region of oriented molecular chains owing to the orientation hardening of molecular chains. Moreover, by applying stress greater than the fibril strength, the craze becomes a crack and the specimen fractures at the front edge of the propagating neck. On the other hand, craze becomes longer under low speed deformation [2]. This strain rate dependence of craze growth also results in the propagation of the craze-concentration region.

The mechanical properties of polymers mentioned above have conventionally been discussed in terms of the phenomenological theory of plasticity [3–5]. However, in this theory, it is undesirable that the constitutive equations become complicated when developing a detailed model and to increase material constants, which cannot be identified from experiments. Recently, multiscale models taking account of the knowledge obtained from the materials science to solid mechanics have been actively studied describing the mechanical response of polymers more precisely. The molecular chain network model is a typical example of such attempts. Information on the microscopic yielding of molecular chains was introduced into the plastic constitutive equation of the molecular chain network model by adopting Argon's hardening law [6] for the calculation of the plastic-shear strain rate. Argon regarded the rotation of a kink in a small molecular segment of a molecular chain as an elementary process in the plastic deformation of a