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The kinematics and energetics of the anelastic processes of phenylene ring rotation and carbonate group rearrangements in polycarbonate, and the nature of coherent plastic relaxations under imposed conditions of pure shear to large plastic strains in polypropylene have been computationally simulated on computer generated molecular structure models of these polymers in glassy form. In addition, simulations have also been performed on the inelastic dilatational response of polypropylene to probe precursor processes to crazing. Results on these simulations will be presented.

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THE MOLECULAR VIEW OF PLASTIC DEFORMATION AND PRECURSOR PROCESSES OF CRAZING IN GLASSY POLYPROPYLENE AND POLYCARBONATE

A. S. Argon*, M. Hutnik*, P. Mott*, and U. W. Suter**

The kinematics and energetics of the anelastic processes of phenylene ring rotation and carbonate group rearrangements in polycarbonate, and the nature of coherent plastic relaxations under imposed conditions of pure shear to large plastic strains in polypropylene have been computationally simulated on computer generated molecular structure models of these polymers in glassy form. In addition, simulations have also been performed on the inelastic dilatational response of polypropylene to probe precursor processes to crazing. Results on these simulations will be presented.



INTRODUCTION

For too long both the kinematics and the rate mechanism of plastic flow of amorphous solids have remained unclear. Based on the important recent advances made in the mechanisms of plastic flow of atomic glasses (1), and the availability of methods to obtain accurate three dimensional molecular structural models of glassy polymers such as polypropylene (PP) (2), and polycarbonate of bisphenol-A (PC) (3), it is now possible to simulate plastic deformation in the computer. Here we will present a summary of some of this computer simulation research applied to PP and PC.

DESCRIPTION OF METHOD

The principal ingredient of the simulation is the prescription of the atomic interactions. These are given as a system of force fields that include among intramolecular interactions the torsional bond potentials between neighboring atoms on the backbone of the chain molecule, coulombic interactions between atomic groups, and non-bonded intermolecular interactions by means of Lennard-Jones potentials. In addition to these, the bonds between backbone atoms and their angular arrangements are considered rigid in comparison with the above stated interactions.

The details of how acceptable 3-D molecular structures of the appropriate density, subject to periodic boundary conditions are obtained by static energy minimization techniques in the computer, without any arbitrary assumptions are described in refs. (2,3). These references also describe the level of excellent agreement between the simulation model and experiments that has been obtained for x-ray structure factor, cohesive energy density, and

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small strain elastic constants. Here we will discuss only some results on several modes of inelastic response of PC and PP to internally or externally imposed moderate to large-strain deformations of the structure of both shear and dilatational type.

RESULTS

Anelastic response in PC

In PC anelastic mechanical and dielectric relaxations have often been attributed to the rotations of the phenylene ring and/or the conformational rearrangements of the carbonate groups to imposed cyclic strain fields or electrical fields (4). Since such alterations have been studied separately also by NMR (5), they have been simulated by us in detail. The simulation was performed on two separate glassy configurations where a specific phenylene ring was given small increments of rotation about the main ring axis, at constant volume of the overall cell, followed by fixing the torsion angle between either the ring and the adjacent carbonate group (Type A) or that between the ring and the isopropylidene group (Type B) on the other side, and minimizing the energy of the entire configuration of all atoms in the cell. The procedure was repeated for all rings in two entire configurations. The imposed rotations were reversible up to a certain total angle of rotation, but beyond this, they underwent an irreversible rotational relaxation into a new lowest energy state. Two separate modes of relaxation response were obtained. When the torsion angle of Type A was fixed the eventual irreversible alteration was a rotation of the ring, while when the torsion angle of Type B was fixed the response was either the rotation of the ring or a conformational rearrangement in the neighboring carbonate group. The peak barrier energies for the system just prior to the irreversible relaxation were widely distributed. These distributions are shown in Fig. 1 for the ring rotation. The distribution for the carbonate group rearrangement is very similar to that shown in Fig. 1. The average energy barrier for the ring rotation at $\Delta E_r = 10.4 \pm 6.7$ kcal/mole and that for the carbonate group rearrangements at $\Delta E_c = 10.1 \pm 6.5$ kcal/mole compare quite favorably with the NMR measurements of 11.0 kcal/mole (5), and are both more than a factor 3 higher than the corresponding intra-molecular energy barriers for these alterations in the isolated molecule.

Large Strain Plastic Response in PP

Plastic flow in PP at 233 K under conditions of pure shear at constant volume was simulated by imposing small extensional displacements of 2×10^{-3} of the edge length along one principal direction of the tetragonal simulation cell, and corresponding compressional increments of -2×10^{-3} along another principal direction of the cell, while holding the cell thickness constant, followed by complete re-minimization of energy of the cell. The process was repeated monotonically 100 times to accumulate a total Mises equivalent strain of 0.2 in 9 separate configurations. As described in detail elsewhere (6), for each distortional increment atomic site strain increment tensors were calculated. Of these strain increment tensors the first and second invariants (dilatation and deviatoric strain) were of particular interest. In parallel to the computation of the local atom site invariants of strain increment, atomic site stress tensors were also calculated by the method of Theodorou and Suter (2). Volume averages of these stress tensors were then obtained for the entire cell for each state of distortion and were averaged out over the 9 configurations. Again, the two invariants, i.e., the negative pressure and the Mises equivalent tensile stress were of particular interest.

The resulting configuration average stress, strain curve of the pure shear simulation is shown in Fig. 2, together with the change of pressure on the system. The curve shows that the initial response of the structure is linear paralleling the known elastic behavior shown

by the dotted straight line. Departure from linear behavior occurs at a strain of about 0.04 or a tensile stress of about 110 MPa. This is taken as the macroscopic yield stress of the PP. The plastic behavior shows considerable strain hardening. The stress strain curve is very jerky, even in the initial linear and apparently elastic range. In the 9 individual configurations the jerks occur as sharp stress drops between stretches of linear and reversible elastic loading behavior having slopes close to the elastic modulus. Many of the vertical drops are individual and far-reaching plastic relaxation events of irreversible nature have been studied extensively by stereo imaging to detect the presence of any recurring simple local kinematical rearrangements. No such satisfying identifications could be made. The single most profound observation that could be made about the plastic relaxations was that they were, always covering the entire simulation cell of roughly $6 \times 10^{-21} \text{ cm}^3$, and that they amounted to relatively small overall average transformation shear strains. The cumulative distribution and the frequency distribution of the transformation shear strains of these sudden plastics relaxations are shown in Fig. 3. The average value of those transformation shear strains is 0.037 with a coefficient of variation of nearly unity. These are nearly a factor of 20 smaller than the usually assumed levels of transformation shear strains occurring in individual plastic relaxations, but are remarkably of nearly identical magnitude as the transformation shear strains obtained in plastic flow simulations of atomic glasses. Since strain rate change experiments during plastic flow of glassy polymers give the activation volume of the unit event, which is the product of the actual volume and the transformation shear strain, it is possible now to estimate the actual volume over which a coherent plastic relaxation event occurs. Using the extensive strain rate change measurements of Argon and Bessonov (7) on glassy polymers and assuming that the average level of plastic shear strain in all of these polymers is similar to that obtained for PP, the actual sizes of the volume elements of the transforming regions have been calculated for all the polymers measured by Argon and Bessonov. These are listed in Table 1. Examination of their magnitudes show that the volume elements over which coherent plastic relaxations occur are very large indeed. This is a direct consequence of the rigidity of the backbone bonds and the inflexibility of the bond angles requiring that the shear strains be made up only by a series of torsion angle changes along the backbone of the molecule. Figure 2 shows also that as the plastic shear deformations develops the pressure on the cell increases monotonically. This is a direct consequence of the dilatant nature of plastic flow in amorphous media. (See also Ref. 1).

Table I Calculated Volumes Ω of Unit Plastic Events from Results of Argon and Bessonov (7) (for $\Delta\gamma^* = 0.037$)

	PS	PMMA	PPO	PET	PC	Kapton
$\Delta v^*, (\text{\AA}^3)$	1142	1510	2464	3985	4262	9157
$\Omega, (\text{\AA}^3)$	3.09×10^4	4.08×10^4	6.66×10^4	1.08×10^5	1.15×10^5	2.47×10^5
$d, (\text{\AA})$	38.9	42.7	50.3	59.1	60.3	77.9
$\Delta v^* = kT(\partial \ln \dot{\gamma} / \partial \sigma); \Omega = \Delta v^* / \Delta \gamma^*; d = (6\Omega/\pi)^{1/3}$						

In addition to the plastic shear response of PP at constant volume the dilatational response was also simulated to probe for pre-cursor processes to craze initiation. These results cannot be presented here because of space limitations but will be discussed during oral presentation at the conference.

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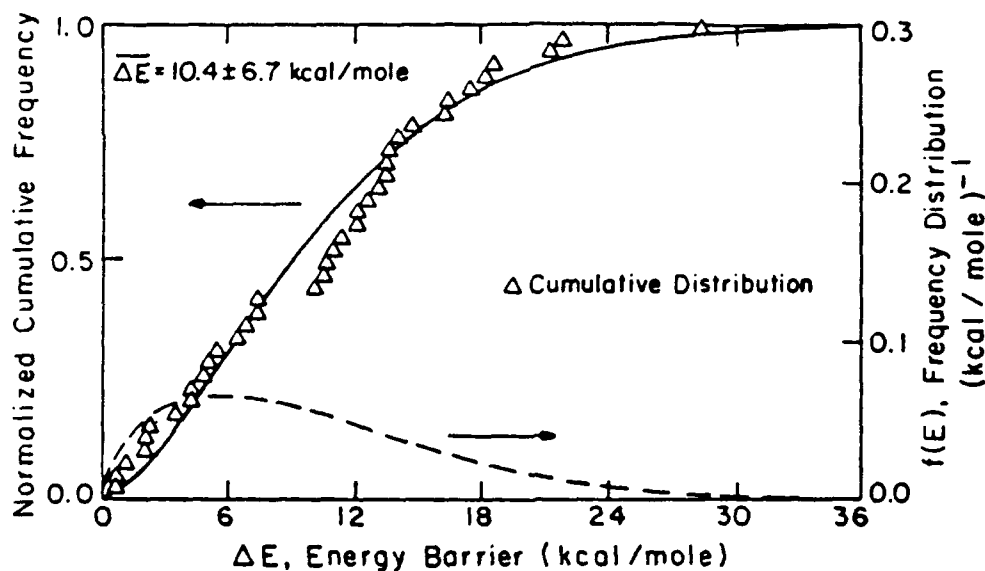


Figure 1: Distributions of free energy barriers to ring rotations in PC

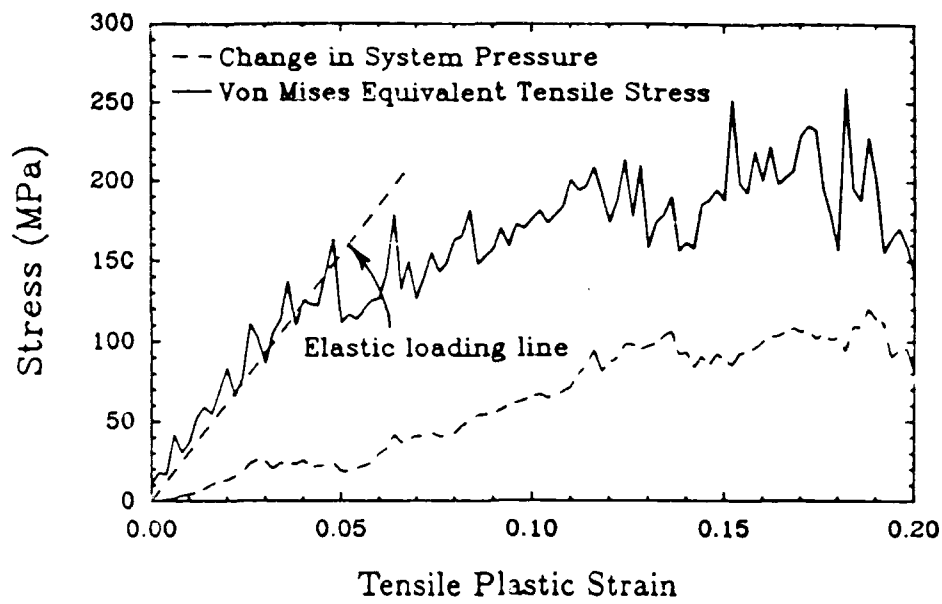


Figure 2: Equivalent stress strain curve of PP, and the corresponding build-up of pressure at 233 K

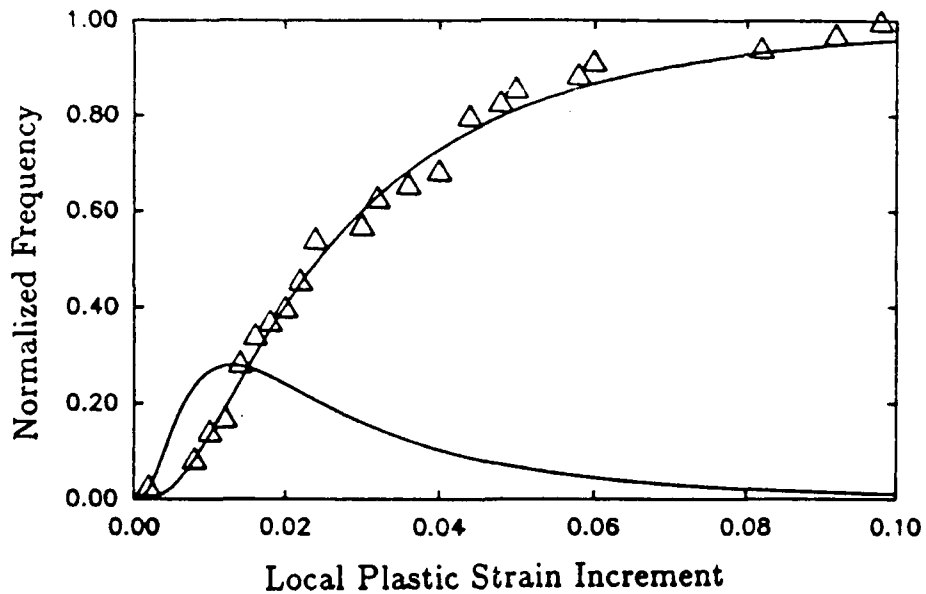


Figure 3: Distribution of transformation shear strains in unit plastic events in PP at 233 K