

PLASTIC FLOW IN SOLID POLYMERS

E.F. Oleinik, S.N. Rudnev, O.B. Salamatina

N.N.Semenov Institute of Chemical Physics Russian Academy of Sciences, Moscow, Russia

efoleinik@chph.ras.ru

A review of the most important features of molecular level plasticity processes in bulk isotropic macromolecular solids is presented. Development and new findings in the field which had appeared during last 10 years are emphasized. Polymers of different structure: lamellar crystals, glasses, semi-crystalline materials with rubbery and glassy amorphous phase and glassy polymer materials containing LC phase in their disordered structure are considered. Physically different deformation processes: linear elastic, delayed elastic (anelastic), plastic and plastic flow are analyzed and compared with same processes in non-polymeric materials. Today, the clearest picture of polymer plasticity exists for polymer crystals. Classical slip of dislocations in crystallographic directions is responsible for such behavior. Existence of dislocations and their glide is proved by electron microscopy techniques. Chain nature of macromolecules limits some processes in crystals. The limitations are: glide of dislocations is possible only in directions parallel to chain main axes and deformation of chain crystals is, therefore, kinematically deficient; nucleation of dislocations occurs only at a lamella surface and some others. Glassy polymers undergo two different deformation mechanisms above and below $T_{\text{def}} \approx < 0.7 T_g$. The low temperature mechanism is guided by an appearance in a bulk of glass local "undeveloped" shear events. Nucleation of them controls kinetics of macroscopic deformation process. Dislocations in glassy polymers can't slip in a disordered structure, even if they exist. Therefore they can't develop plastic mass transfer. Plastic deformation mechanisms in polymer glasses are seriously different compared to crystals and rubbers. It appears now that chain glasses much stronger resist to plastic deformation than chain folded crystals, PE for example. Glassy polymers underwent plastic flow at $T_{\text{def}} > 0.7 T_g$ through mechanism of diffusional plasticity. The "forced elasticity" process may only exist in polymer glasses at high T_{def} regime. Introduction of LC phase in glassy macromolecular material (main chain aromatic co-polyesters) decreases its total resistivity to plastic behavior. Linear polyethylene demonstrates interesting room temperature deformation behavior. Deformation work and heat of the material are mainly produced by plastic processes in crystallites. The amorphous phase of PE produces a little heat and takes small amount of deformation work due to entropic character of its deformation. However, the energy of deformation is stored by both, crystalline and amorphous phases. At total strains $\varepsilon_{\text{def}} > 30\%$, the amorphous phase carry even more energy than crystalline phase. The specific deformation energy stored in deformed PE crystals is twice lower than in glassy polymers. Strong deformation constrains operates in PE. Plastically deformed crystallites do not permit to the soft amorphous chains to change their shapes and lengths to values corresponding to acting force. Such constrains stop relaxation of amorphous material even after sample complete unloading. Chains in the amorphous phase are strongly stretched in the plastically deformed and unloaded material. Plasticity of semi-crystalline polymers with glassy amorphous phase proceeds differently. Both, crystalline and amorphous phases are involved in plastic deformation as solids. Glassy phase resistivity to plastic deformation is higher than the crystalline phase and therefore controls thermodynamics and kinetics of plastic process of the material as whole. Possible ways of modification of plasticity in solid polymers are discussed. This work is financially supported by the Russian Foundation for Basic Research (project09-03-00048, the Chemistry and Material Science Division RAS (Program 3 and the Presidium of RAS (Program 27).