Plastic yielding of semicrystalline polymers affected by amorphous phase

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A B S T R A C T

It is shown that plastic yielding of semicrystalline polymers is greatly affected by the state of their amorphous phase. Stress reduction at yield point in crystalline polymers, whose amorphous phase is modified by swelling, has been observed and the mechanism explained. Swelling of amorphous phase with low molecular weight penetrant, which does not affect crystalline phase, causes deformation of lamellae stacks. However, there is no expansion of stacks along lamellae basal planes while stretched chains of amorphous phase generate uniaxial tension transmitted to lamellae surfaces. This additional tensile stress was determined by recording the stress buildup for samples with fixed ends during desorption of penetrant. It appears that measured yield stress plus the stress exerted by swollen amorphous phase amounts exactly to the stress required for plastic deformation of crystals, therefore the yielding is determined by the same crystal plasticity despite different external load. The phenomenon was observed in several systems including polypropylene, polyethylene and polyamide 6 with various penetrants. These observations and explanations seem to pertain to each semicrystalline polymer–penetrant systems.

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1. Introduction

Most of commodity polymers are crystalline materials with unique structure of lamellar crystals arranged parallel in stacks with alternating amorphous layers, both entities having thickness in a nanometer range. Recognition and understanding basic mechanisms of plastic deformation of such materials is essential to fully exploit their potentials. In the case of polymers in glassy state, due to a relatively simple structure of such materials, research conducted in the last three decades allowed to understand a number of aspects accompanying their deformation (Perez, 1998; Srivastava et al., 2010; Haward and Young, 1997). Despite numerous studies being carried out (e.g. Galeski, 2003; Oleinik, 2003; Lin and Argon, 1994b; Haudin, 1982; Farrokh and Khan, 2010; Bowden and Young, 1974; Khan and Farrokh, 2006; Ayoub et al., 2010), the mechanisms of plastic deformation of semicrystalline polymers due to complex, hierarchical architecture of such materials still require more detailed research. The deformation of a semicrystalline polymer is a process where we should take into account the presence of crystalline lamellae as well as amorphous layers lacking order. At temperatures at which amorphous phase exhibits rubber-like properties ($T_d > T_g$), it is in the interlamellar regions that the initial stage of deformation takes place. It follows that stress required to initiate deformation of amorphous phase constitutes from 2% to 10% of the stress needed to activate the mechanisms of crystalline phase deformation (Peterson and Lindenmeyer, 1966). Studies conducted by Bartczak et al. (1992a,b, 1994) also confirmed the observed dependencies. Deformation of amorphous phase is activated relatively easy but it is rapidly exhausted because of different alignment of crystalline lamellae with respect to the deformation direction. Further deformation could be possible by initiation of deformation of lamellar crystals. The character of deformation of polymer crystal, like all other crystals, is plastic.

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Two distinctly different mechanisms have been suggested for yielding of semicrystalline polymers in the past. Historically first concept was initially proposed by Peterson (1966, 1968): an emission of dislocations from the edges of the lamellae across the narrow faces and their travel across crystals via crystallographic slips was the base of the idea that was explored further by Shadrake and Guiu (1976) and more rigorously by Young (1988). Many evidences for correctness of that mechanism were found in the past (Wilhelm et al., 2004; Lin and Argon, 1994a; Seguela, 2007; Kazmierczak et al., 2005; Young, 1974). The model of thermal nucleation of screw dislocations (Peterson, 1966, 1968; Young, 1988, 1974) was demonstrated to account fairly well for the plastic behavior of polyethylene (PE) Crist et al., 1989; Darras and Séguéla, 1993 and polypropylene (PP) Crist et al., 1989 and for the yield stress dependency on the crystal thickness (Seguela, 2002; Brooks and Mukhtar, 2000). Dislocation theory predicts the correct order of magnitude of the yield stress that agrees best for the Burgers vector of dislocations equal to the crystallographic unit cell dimension along macromolecular chains (O'Kane et al., 1995). However, there are experimental evidences that the yield stress of semicrystalline polymers depends not only on crystal thickness but also on the degree of crystallinity (e.g. O'Kane et al., 1995; Kennedy et al., 1994; Ayoub et al., 2011). The yield stress increase has been observed together with the increase in thickness of the sample crystals, however, there are difficulties to maintain the same degree of crystallinity in samples together with varying crystal thickness. In the case of polyethylene such relationship is observed for a certain range of the crystals' thickness, up to 40 nm, while above this level, the increase of crystal thickness is not accompanied by further increase in yield stress (Bartczak et al., 1992a; Argon et al., 2005). The authors of the above mentioned articles explained the observed relationship by the presence of a new, effective source of dislocation, active in thick crystals and at low temperature but inactive in thinner crystals. Electron microscopic investigation of deformed polymers exhibited arrested dislocation lines on side faces of lamellae crystals (Galeski et al., 2010). Olley and Bassett (1994) showed that yielding occurs in thinnest polypropylene lamellae. Those findings support the conclusion that dislocation mechanisms of plastic deformation is the only one that is consistent with crystallographic aspects of the yield and most probably are responsible for setting yield during tensile deformation.

Second mechanism for yielding connected with non-crystallographic changes, related to destroying crystals and resulting in a new crystalline ordering of the material, irrespective of the original structure but characteristic for the temperature of deformation was proposed later (e.g. Flory and Yoon, 1978; Popli and Mandelkern, 1987). It was suggested that during deformation an adiabatic heating occurs (Vincent, 1960; Marshall and Thompson, 1954; Muller, 1949; Hookway, 1958; Maher et al., 1980; Toda, 1933) when accompanied by the applied stress, partial melting and recrystallization takes place. It was also suggested that raising the temperature is not a necessary condition for partial melting and recrystallization (Meinel and Peterlin, 1971; Church et al., 1986). Phillips and Philipot (1986) showed by electron microscopy studies that melting during deformation of polyethylene preferentially occur in the yield zone. Those experiments and considerations did not, however, established at which elongation a partial melting and recrystallization are initiated nor did not predict the correct order of magnitude of the yield stress. The conclusion of those researchers being in favor of melting and recrystallization during deformation was that one cannot assign a unique mechanism to yielding process (Kennedy et al., 1994).

It is commonly believed that the role of the amorphous phase, above the glass transition temperature, in yielding during tensile deformation of semicrystalline polymers is relatively small and is limited to transferring the stress between adjacent crystals (Seguela and Darras, 1994). The role of fraction of tie-molecules spanning adjacent lamellar crystals was emphasized by Nitta and Takayanagi (1999). The term "the tie-molecules fraction" combines all stress transmitting elements such as: tie molecules, entanglements etc. Also in the papers (Bonten and Schmachtenberg, 2001; Humbert et al., 2009) there has been presented the effect of the tie-molecules fraction on the value of yield stress. An increase of the yield stress was observed with the increase in the tie-molecules fraction. In contrary, Men et al. (2003) claimed that tie molecules are of lesser importance with respect to the deformational behavior while the entangled chains in amorphous network play the decisive role.

Since all stress is transferred to crystals via amorphous component it means that amorphous phase is nevertheless crucial for load bearing of a semi-crystalline polymers including yielding. Amorphous phase must then be stressed at yield with a stress similar to plastically deformed crystals. Hence, any modification of the amorphous component should result in changes of the material response to loading. Based on the facts presented above, the plasticity of polymer materials and the structural changes occurring during deformation of such materials are first of all controlled by the properties of the crystalline phase. However, there are no experimentally confirmed simple direct relations. There are several issues that need further exploration: one of the unanswered questions is why the yield stresses differ for materials with nearly identical crystalline structure and do not necessarily correspond to critical resolved shear stresses for polymer crystal plasticity. Annealing causes some limited changes of crystal structure including an increase of their thickness, however, it may cause a significant increase of the yield stress. Average molecular weight and molecular weight distribution of polymers may also drastically change the yield stress (Kennedy et al., 1994). The best known case is polyethylene with bimodal molecular weight distribution for gas pipelines with the yield at 20 MPa while PE of monomodal distribution with nearly identical crystalline structure exhibit 25 or even 30 MPa.

Recently we have designed a type of modification of the amorphous phase of semi-crystalline polymers by infusing low molecular weight penetrant exclusively into amorphous component but neither entering nor affecting crystalline phase (Rozanski and Galeski, 2011). At low concentration a penetrant is filling free volume pores of the amorphous phase while with higher concentration amorphous phase becomes swollen. In this paper we present the results of such experiments and the influence of swelling of amorphous phase on yielding in tensile deformation. The aim of this paper is to explain the mechanisms responsible for changes of the yield stress of semi-crystalline polymers, whose amorphous phase was modified with low molecular weight penetrant, after solidification of the material that is after creating the final crystalline structure. The issue is particularly relevant for polyamide 6, which exhibits a natural tendency to absorb the water in typical use conditions.