

Modelling of Elastic Modulus and Molecular Structure Interrelationship for an Oriented Crystalline Polymer

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Introduction

Macroscopic properties amorphous-crystalline polymers are complexly and the fundamentals of stress and strain distribution in the heterogeneous solid are still of essential interest [1-5]. The structural features lead to the irregular wide distribution of local loads, especially for the flexible-chain polymers since the value of the elasticity modulus of the macromolecular sections with coiled rotary isomers in the polymers is low. The purpose of the present study is to suggest the molecular model of the stretching of molecular chains in a loaded oriented linear amorphously-crystalline polymer, to estimate connection of polymer elastic modulus experimental values and the amorphous sections molecular (conformation) structure.

Structure model

Let us consider two-phase model of an oriented flexible-chain crystalline polymer type of linear polyethylene microfibrils of which consist of interchanging crystalline and amorphous regions. The longitudinal length (period) is the sum of the lengths of amorphous and crystalline regions $L = L_k + L_a$.

Elastic modulus and molecular structure of interconnecting amorphous sections

After some initial stress the deformation of a flexible-chain crystalline polymer is rotary isomeric and the macromolecule segments of the polymer are primarily in straightened conformation state [6]. To this portion of the deformation curve corresponds the low value of the elasticity modulus. If the conformation straightening of some part of strained passing chains has taken place, further stretching of the polymer leads to the considerable increasing of the elasticity modulus.

Let us suppose that in some cross-section of a polymer sample the relative middle number of interconnecting sections being in straightened *trans*-conformation state is n_i and the relative number of the sections including coiled isomers is n_j . The lengths and the elasticity modulus of the two groups of passing chains are E_i , and E_j . We shall believe that in some section of the sample the amorphous regions and longitudinal periods have the same length and the elastic deformation of the highly oriented polymer is primarily defined by stretching of the amorphous sections being inside fibril

Since straightened sections can be considerably loaded then one should take into account the stretching of the chains in the crystalline regions. So the deformation is the sum of the amorphous section lengthening and of the value of the pulling out of polymer crystallites of the strained

chain in *trans*-conformation structures out of both of sides of the amorphous section, e.g. $\Delta L_a = \Delta L_i + 2x_i$

For average load on the sample in Hookean approximation we can write -

$$\sigma = E \frac{\Delta L}{L} = n_i E_i \frac{\Delta L_i}{L_i} + n_j E_j \frac{\Delta L_j}{L_j} = n_i E_i \frac{\Delta L - 2x_i}{L_i} + n_j E_j \frac{\Delta L_j}{L_j},$$

where ΔL_i and ΔL_j -lengthening of the straightened interconnecting amorphous sections and the sections with coiled rotary isomers correspondingly, L_i and L_j - correspondingly lengths of interconnecting amorphous sections in straighten and with coiled rotary isomers, and E is elastic modulus experimental value in tension of the polymer sample.

In continual approximation with the use of Frenkel-Kontorova's dislocation model and expressions for the pulling out value of interconnecting chain out of crystalline region one can find relationship between molecular structural parameters for the passing chains and elasticity modulus of the polymer sample-

$$E = E_t n_i \frac{L}{L_i} \left(1 - \frac{2a}{\pi} \frac{1}{\frac{L_i}{E_t} \sqrt{2kU_0} + \frac{2a}{\pi}} \right) + n_j E_j \frac{L}{L_j},$$

where a - is the period of the crystal lattice, ΔU_0 - is the height of intermolecular interaction barrier, x_i is the displacement of the molecular group from the crystalline lattice site. The value of the elasticity constant k has been calculated with the use of the elasticity constant values for the valence angle and covalence bound taken from literature.

Conclusion

Having defined the sizes and the distribution of supermolecular elements (e.g. of crystalline and amorphous regions) and of interconnecting amorphous sections over lengths and conformation structure, having measured the deformation curve and having calculated with help of the curve the elasticity modulus one could find the local load on the chains (or sections). On experimental value of elastic modulus can be to elevated the content of the interconnecting amorphous molecular chains in straightening conformation states.

References

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