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EQUAL-CHANNEL ANGULAR EXTRUSION OF POLYMERS

In the review the possibility of a new method of solid-phase extrusion of polymers, based on a simple shear - equal-channel angular extrusion, have been considered. The data about specific features of realization of this method are reported as well as structure evolution and physical and mechanical properties of the processed polymer materials of different structure: amorphous and semicrystalline polymers, polymer mixtures, filled composites. Structural models of oriented polymers and approaches to modelling of accumulation of plastic deformation in the course of extrusion are discussed.

Keywords: extrusion, polymers, composition materials, plastic deformation.

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РІВНОКАНАЛЬНА КУТОВА ЕКСТРУЗІЯ ПОЛІМЕРІВ

В статті розглянуто можливості нового методу твердофазної екструзії полімерів, який заснований на простому зсуві – рівноканальній кутовій екструзії. Приведені відомості про особливості реалізації цього методу, еволюції структури і фізико-механічних властивостей полімерних матеріалів різної будови після обробки: аморфних і аморфно-кристалічних полімерів, полімерних сумішей, наповнених композитів. Обговорюються структурні моделі орієнтованих полімерів та підходи до моделювання процесу накопичення пластичної деформації при екструзії.

Ключові слова: екструзія, полімери, композиційні матеріали, пластична деформація.

Introduction

Equal-channel angular extrusion (ECAE) is one of effective methods of severe plastic deformation, so it is widely used for obtaining bulk submicro- and nanocrystal metallic billets [1–5]. The method is based on the pressing (extrusion) through oblique channels with the same area of the cross-section. In the contact area between the channels, the material is exposed to severe plastic deformation by simple shear. After numerous ECAE procedure applied to a metal, a systematic increase in the accumulated strain occurs, resulting in successive reduction of the grain size due to formation of a net of low-angle boundaries first, and then high-angle ones. The reduction of the grain size of the processed metals and alloys down to submicron level can enhance substantially their mechanical properties, in particular, to yield strength and tensile strength and to generate ability to superplasticity. A great number of papers including reviews and monographs report the results of experiments and computer simulation of plastic flow of such objects, evolution of their structure and proper- ties under ECAE; different schemes and routes of the process are designed and put into practice that provide a prescribed set of physical and mechanical characteristics.

The works on ECAE of polymers were initiated relatively recently [6]. In this case, as opposite to metals, ECAE is applied in order to form an oriented structure that will promote obtaining articles with higher plastic and strength characteristics. As compared with traditional methods of solid-phase extrusion of polymers (ram and hydrostatic extrusion) resulting in reduction of cross sectional dimensions, ECAE gives a possibility to realize molecular orientation without form change. Besides, new opportunities of structure control are generated, being related to varied geometry of equipment, conditions and routes of deformation.

Now certain experience in ECAE application has been accumulated with respect to structure modification of polymeric materials of different nature: glassy and semicrystalline homo- and co-polymers, filled polymer compositions, too.

However, the results of experimental and theoretical investigations require analysis and generalizations for further development of the method considered. This fact was a reason for writing the present review aimed at fixation of the achieved progress in the study of ECAE features and ECAE effect on the structure and the properties of polymers and polymer composites.

In this technique, a billet is extruded through a die containing two channels, equal in cross-section, intersecting at an angle Φ (Fig. 1a). During the extruding, the billet undergoes severe shear deformation but retains the same cross-sectional geometry so that it is possible to repeat the pressing for a number of passes. Between two adjacent passes, it is possible to rotate the billet around its longitudinal axis, with creating different equal channel angular extrusion (ECAE) routes: route A (the billet orientation remains the same in the course of every pass); route B (the billet is rotated through 90^0); route C (the billet is rotated through 180^0) [1, 3]. Another factor that significantly affects the microstructural evolution is the channel-intersection angle, which determines the shear strain Γ after a single pass [3].

$$\Gamma = 2ctg\left(\frac{\Phi}{2}\right) \quad (1)$$

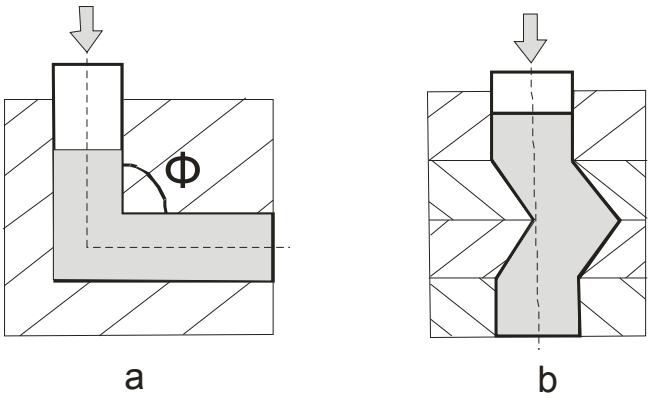

Fig. 1. Schematic representation of equal channel angular extrusion (a) and equal channel multiple – angular extrusion (b)

A smaller Φ will result in higher shear strain after a pass. Usually Φ is equal to 90^0-120^0. If Φ angle is arbitrary, the increment of equivalent plastic strain ε_i caused by shear as a result of one pass through the channels can be calculated as follows

$$\varepsilon_N = N\left[\frac{2ctg(\varphi/2+\psi/2)+\psi\cos ec(\varphi/2+\psi/2)}{\sqrt{3}}\right]. \quad (2)$$

where Ψ is the corner angle.

Structure and properties of extrudates

Semicrystalline polymers. Both ECAE and ECS result in formation of a fibrillar structure in semicrystalline polymers. At the same time, formation of a mono- or bimodal orientation is observed [7–17]. The character of the last parameter and the degree of molecular orientation are determined by the value of Γ, the temperature and the deformation route [18].

ECAE at enhanced temperature provides a substantial improvement of the set of physical and mechanical characteristics. For instance, the extrusion of poly(DL-lactide) at T_e = 75 °C increases T_m and the modulus of flexure E_f, and transforms the brittle character of the fracture into the plastic one [17]. If the non-deformed samples are of E_f = 83 MPa, two passes along A route($\phi=90^0$) make E_f to achieve 179 MPa.

ECAE contributes to better optical properties of semicrystalline polymers. In particular, the light transmission factor in polypropylene (PP) after ECAE is 1,2 times higher than that of the original sample. The parameter increases when the strain degree increases [11]. The observed effect is associated with a decrease in the crystallite size and their orientation.

Amorphous polymers. ECAE forms molecular orientation in amorphous polymers without a loss of transparency [19-22]. Mechanical properties of polymethylmethacrylate after ECAE along A route with heating up to 120 °C demonstrate a small increase in rigidity and strength with high plasticity retained.

EACE effect on the crack resistance and the resistance to impact fracture is very substantial. All the variants of extrusion provide the magnitudes of the fracture toughness and the crack propagation energy to be 2,8 and 4,5 times higher, respectively, as compared to the control samples.

Polymeric composites. In [23], the results about acetal plastic of partially crystallized structure with 13 weight % of glassy fibers were reported. ECAE was demonstrated to decrease the angle of preferable orientation and the length of the fibers as compared to the original material. Besides only the fibers of the critical length or longer were fractured, so this methods could be applied to the production of filamental composites with the controlled fiber length.

ECAE process can produce the immense solid shear force, which is enough to stretch, deform, tear or break both polymer spherulite and filler agglomerated particles. In [24], it was shown by the example of the PP-montmorillonite (MMT) system that the once ECAE process can deform agglomerated MMT particles from a sphere to a rod-like bar with an aspect ratio 5–10. The twice ECAE process further tear or break these rod-like MMT particles into needle-like primary particles even exfoliate a primary particles to silicate nanolayers, which disperse in PP matrix and endow PP great reinforcement.

ECMAE application is also an effective method of structural modification of mixture composites including those with a weak interphase interaction of the components (as PP-high density polypropylene (HDPE) system) [25]. It was found that ECAE determines high strength of cohesion due to increased contact area as a result of dispergation and transformation of the HDPE particle from the sphere to the banded one.

Powder billet. ECAE provides consolidation of the powders of semicrystalline polymers (ultra high weight polyethylene, linear low density polyethylene, HDPE, PP etc.) and production of a monolithic polymeric billet characterized by high density of chain entanglements and crystallites of small size [26]. The succeeding thermal, chemical and radiation treatment contribute to the degree of consolidation due to formation of additional bonds (cross-linking). As a result, a material with enhanced plasticity and strength is obtained. The crystallinity degree and the melting temperature are reduced, as compared to the original polymer.

The mentioned procedure allows production of bulk materials based on renewable natural polymers of high

density, with mechanical properties comparable to those of synthetic polymers [27, 28]. In particular, three-point bending tests showed that the yield strength of wheat starch was 35 MPa, the modulus of elasticity was 923 MPa, and the characteristics of wheat gluten were 28 and 1044 MPa, respectively. At the same time, the use of plasticizers was not necessary, and the problems related to the shrinkage, distortion and bending of the material were absent.

Process modelling. In order to optimize the process conditions, the estimation of the strain achieved in the extruded material is of an utmost importance. Analytical approaches have been developed [29–31] to characterize plastic strain in a sample exposed to ECAE process. However, these models assume that the behavior of the material is rigorously perfectly plastic, i.e. they neglect the elastic deformation component, which may be substantial in the case of polymers. Moreover, the complexity of the ECAE process makes finite element modeling (FEM) essential to understanding the influence of key parameters on the strain homogeneity [32–35].

According to Eq. (2), the value of equivalent plastic strain after ECAE is determined by the angle of channel intersection Φ and the corner angle Ψ. The equation is obtained with supposing that strain is uniformly distributed within the sample. However, the results reported in [32, 33] tell different. There exists a steady flow region, where the plastic strain is almost homogeneous along the longitudinal direction, except the ends of the extrudate [33]. At the same time, a strain gradient along the transversal direction is observed in the steady flow region, and local plastic strain is reduced from the upper surface to the bottom. The last phenomenon is related to the fact that the outside area of the sample is deformed mostly by the bending mechanism, not shear one. The magnitudes of ε are maximums at Φ=90°, but the distribution is more homogeneous at higher Φ. With increase in Φ and Ψ, the equivalent plastic strain is decreased.

The effect of cycling and deformation route on the character of ε distribution was analyzed for routes A and C with using the method of finite elements [32]. It was found that the die with Φ=90° demonstrates a substantially better result, as compared to Φ=120°, 135°. In particular, the value of equivalent plastic strain achieved for one pass at Φ=90° exceeds that after 6 passes at Φ=135. This conclusion contradicts to εi calculations using (2) that yield: εi≈ 1,1 at Φ=90° and 0,4 at Φ=135°. Hence, to accumulate total plastic deformation realized in the course of one pass at Φ=90°, 3 passes through a die with Φ=135° are required. The divergence in estimates can be related to the fact that equation (2) assumes ideal plasticity of material and does not consider the elasticity, hardening and viscosity. The results of [32] as in accordance with experimental data [18], where the best set of elastic and strength characteristics of ECMAE-extruded semicrystalline polymers was observed at higher values of strain intensity determined by the channel intersection angle at the same values of accumulated strain.

It is shown in [32], that an increase in the number of deformation cycles results in reduction of the difference between the variation factors at the minimum and the maximum of Ψ (5° and 64°) for a die with Φ=90°, whereas Φ=120° and 135° were associated with a reverse regularity. The authors of [32] relate this behavior of V in the case of Φ=90° with saturation effect. Other angles are supposed to require more passes before saturation.

According to [32], the choice of the processing route is controlled by the magnitude of Φ. At Φ=90°, route C provides more homogeneous distribution of the equivalent plastic strain than route A. We can expect microstructure and properties of the samples processed by route C to be more homogeneous, too. At the same time, route A is preferable for the dies with higher angles.

The above results are obtained on the assumption that friction between the sample surface and die walls is negligible. In [32, 34], friction between the die and the sample was modeled with using Coulomb friction law, being supposed to be uniform everywhere in the die. It was found that the value of the equivalent plastic strain increases as the friction coefficient f rises. This regularity was found out when testing ECMAE effect on microhardness of semicrystalline polymers:as the friction coefficient increases, microhardness of extrudates is enhanced [35].

Though friction effect on the distribution of the equivalent plastic strain in polymers is insignificant in comparison with metals, being reduced as Φ and Ψ increase, the same is not valid for pressing power. For example, HDPE extrusion at Φ=90° and Φ=135°, when f =0, demonstrated the maximum pressing force F of 4,577 N and 916 N, respectively. At f =0,3, the maximum pressing force was 6,942 N and 1,269 N, respectively [32].

Equal Channel Multi Angular Extrusion (ECMAE). In Fig.1b, the scheme of ECMAE process is presented. Contrary to ECAE, different routes are realized by rotation of the deforming channels through the vertical axis. In the course of extrusion, the billet remains inside the deforming channels, to avoid undesired relaxation processes related to the cooling and the succeeding heating of the deformed samples up to T_e. Besides, the problems associated with the accumulation of plastic strain are solved that are characteristics of ECAE even after the first pass. Moreover, ECMAE allows variation of the shear plane position due to combination of different deformation routes that are impossible in the course of ECAE.

Semicrystalline polymers. ECMAE forms biaxially oriented structures with two types of microfibrils differing in the degree of perfection of crystallites. The first group is characterized by a great number of crystallites with “double” or “triple” folds, i.e. rectified parts of the chains passing two or three lamellae including trans-sections between them. The second type of microfibrils has no crystal formations with rectified sections of macromolecules passing through the neighbor crystallites.

The best set of the mechanical properties is provided by D+C route at the maximum possible shear strain Γ. The realization results in both multiple increase in the microhardness, rigidity and strength, and the plasticity conserved at the level of the original material (Table). The magnitude of the observed effect depends on the chemical composition, morphology and the molecular mass of the polymer. The choice of the optimum thermal and velocity conditions of ECMAE is also very important. The recommended ranges of the temperature and the

velocities of ECMAE are close to those of solid state extrusion with form change.

Table

ECMAE effect on the mechanical properties and the coefficient of thermal expansion in HDPE

Sample (treatment)	Microhardness (MPa)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	α (cross section) $\times 10^6$ °C^{-1}	α (longitudinal section) $\times 10^6$ °C^{-1}
Reference	32	220	20	520	220	210
After ECMAE	202	1400	114	515	-7	-6

Note. $M_w=1\cdot10^6$

ECMAE-modified semicrystalline polymers demonstrate biaxial invar effect within a wide temperature range. It is found as very low coefficients of thermal expansion α measured in the longitudinal and transversal directions that are many times less of the characteristics of the non-deformed polymers and close to the values of α associated with invar alloys (Table).

*Glassy polymers***.** In the case of glassy polymers, the microhardness, the yield strength and the fracture toughness are increased by 1,2–1,5 times. At the same time, an insignificant increment of plasticity and density is registered. The magnitude of the achieved effects is determined by the shear strain Γ and the selected deformation route.

According to the data of the differential scanning calorimetry and the scanning electron microscopy, the main factors controlling the result are: formation of elongated, more energetic G-conformers, improved intermolecular interaction, formation of a network of oriented macromolecules preventing the crack evolution.

Conclusions

1. As opposed to traditional methods of solid-phase modification of polymers based on plastic deformation, equal- channel angular extrusion does not change the form and the size of processed articles but it can provide for substantial improvement of the set of physical and mechanical characteristics due to formation of oriented structure, first of all.

2. To achieve high level of the properties, extrusion must be performed at low pressing speed and at optimum temperatures that are close to the melting temperature (semicrystalline polymers) or to the glass-transition temperature (glassy polymers).

3. The most effective variant of ECAE realization is ECMAE due to possible accumulation of higher plastic strain and change of the deformation route for one cycle of the process.

4. Application of ECAE and its commercial use in the case of polymer materials require further investigations aimed at modelling of the process, ascertainment of structure aspects of simple shear deformation and correlations between strain characteristics, structure elements and properties.

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