Review

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Solid-state extrusion of polymers using simple shear deformation

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Abstract: The review considers the possibilities of new methods of solid-state extrusion of polymers based on the use of deformation schemes that include simple shear - equal-channel angular extrusion, equal-channel multi-angle extrusion and combined extrusion. Information on the evolution of the physico-mechanical properties of glassy, semi-crystalline polymers, polymer blends and composites is given.

Keywords: combined extrusion; equal channel angle extrusion; equal channel multi-angle extrusion; physical and mechanical properties; severe plastic deformation.

1 Introduction

Solid-state extrusion is one of the effective methods for the formation of orientational order in polymers. It makes it possible to process polymeric materials with different chemical structures and morphologies, to obtain bulk products with different shapes and cross-sectional sizes, to carry out drawing of brittle films in the coextrusion variant, to combine in one process the operations of monolithization of a powder preform and its orientation drawing, to change the parameters over a wide range, technological process and automate it [1, 2]. Simultaneous exposure to high pressure and shear deformation provides favorable conditions for shaping, and the presence of a plasticizing effect due to hydrostatic pressure makes it possible to deform materials with a low level of plasticity.

Traditional solid-state extrusion methods based on the shaping of a polymer preform are well studied and successfully used to solve various technical problems [1], but their possibilities have already been practically exhausted. In this regard, it is topical to develop new approaches that make it possible to implement oriented states in polymeric materials as a result of SSE, while maintaining the shape and size of workpieces unchanged. They consist in the use of deformation schemes including simple shear (equal-channel angular and equal-channel multi-angle extrusion [ECAE and ECMA]) [3], as well as the combination of these schemes with SSE through a conical die [4]. It should be noted that such methods are widely known in the case of processing metals and alloys and are called methods of severe plastic deformation (SPD). Severe deformation is called because in one cycle of the process, an equivalent plastic deformation of the order of 2.0 [5] accumulates in the material.

A feature of SPD methods is the possibility of changing deformation routes (the position of the simple shear plane and the direction of simple shear) providing various options for the spatial development of deformation and the formation of oriented textures [6, 7].

In the present work, a brief review of publications on this subject, devoted to the modification of various polymeric materials (glassy and semi-crystalline, polymer blends and composites) by SPD, is carried out.

2 Glassy polymers

The SPD process forms the molecular orientation in glassy polymers (poly (methyl methacrylate), polycarbonate) without losing their transparency [8–14]. Compared with the original material, they exhibit an increase in stiffness, strength and, at the same time, high plasticity values. This solid state extrusion method also improves the quasi-static crack resistance and impact strength of these materials.

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As for other characteristics, the situation here is more complicated and apparently requires additional studies on a larger number of materials.

3 Semi-crystalline polymers

The use of SPD for processing semi-crystalline polymers increases their density, stiffness and strength, while maintaining a high level of plastic characteristics, while ensuring low anisotropy of hardness and yield strength. SPD also has a positive effect on the optical properties of semi-crystalline polymers [15–29]. In particular, using polypropylene (PP) as an example, it was shown in [22] that the light transmission coefficient after SPD increases in comparison with the initial sample and increases with increasing degree of deformation. A similar phenomenon was noted after rolling PP [30]. It is explained by the fact that the incident light is scattered by scattering centers (spherulites, crystallites, boundaries between the crystalline and amorphous phases), which are characterized by different refractive indices. The destruction of spherulites during SPD increases the transmission coefficient due to a decrease in the size of crystallites and their orientation.

4 Polymer blends

The use of SPD is also effective for the structural modification of polymer blends, including those with weak interfacial interaction of the components due to their thermodynamic incompatibility. In particular, this was shown in [31] using the example of a polypropylene-high-density polyethylene (PP-HDPE) system with different content of components. It is known that the addition of HDPE to PP initially leads to an increase in the impact strength of the blend compared to pure PP, and then to its decrease with a further increase in the proportion of HDPE. This is due to the fact that the introduction of HDPE promotes the formation of more perfect PP spherulites, which improve the impact strength of PP/HDPE. At the same time, an excess of HDPE can provide phase separation with PP, leading to a decrease in the impact strength of the mixture. For the polymer matrices selected in the work, the best result is achieved for a blend of PP/HDPE with 10% HDPE. The SPD process causes the HDPE to be dispersed in the PP. The shape of HDPE particles also changes from spherical to striped, which significantly increases the contact area between HDPE and PP. As a result, the bond strength between HDPE and PP is increased. In this case, the orientation of HDPE in PP causes the appearance of impact strength anisotropy: for specimens cut along the orientation direction, it is higher than for specimens cut along the extrusion direction. This behaviour is explained by the authors by the fact that macromolecules oriented at a certain angle to the direction of crack propagation prevent its development, causing a deviation from the direction of the impact load and dissipation of the acting stresses. The greatest resistance to crack propagation occurs when the direction of its propagation is perpendicular to the direction of orientation of macromolecules.

5 Polymer composites

SPD can influence the characteristics of fiber composites by giving the filler fibers a specific orientation [32–40]. Studies [35] performed on polyacetate glass-reinforced plastic containing 13 wt% fibers about 110 μm long and 14.5 ± 3.5 μm in diameter showed that SPD promotes the formation of a narrower fiber length distribution due to the destruction of longer fibers. In the case of inorganic fillers (nanoclays, carbon nanofibers and carbon nanoplates), SPD leads to efficient delamination and dispersion of the filler over the volume of the polymer matrix. As a result, the crack resistance of composites improves and their strength increases.

6 Polymer powders

SPD is effective as a process for the consolidation of powders of semi-crystalline polymers (ultra-high-molecular-weight polyethylene, low density polyethylene, high density polyethylene, polypropylene, etc.) [41]. For such polymers, SPD ensures the production of a monolithic polymer preform with a high density of chain links and small crystallites. Thermal, chemical and radiation treatments after SPD contribute to an increase in the degree of consolidation due to the creation of additional ligaments (crosslinks). There is a greater efficiency of the SPD process in the formation of auto-crosslinks in extrudates compared to such consolidation methods as compression molding, hot isostatic pressing and ram extrusion. As a result of SPD consolidation, a material with increased strength and plasticity is obtained, but with a reduced degree of crystallinity and melting temperature compared to the original polymer.

The efficiency of SPD consolidation can also be improved by using disentangled polymer powders. In [42] differently entangled polypropylene powders were sintered, without melting, applying severe plastic deformation. It was shown that the consolidation of disentangled powder is drastically better than entangled polypropylene powder. The better consolidation of disentangled polypropylene powder was probably due to the repetition of longer slacks between entanglement knots and also due to sideway motions of their loops.

Studies performed on wheat starch, wheat gluten and cellulose also indicate the promise of using the SPD-consolidation method for the structural modification of renewable natural polymers. It was shown in [43–47] that such processing makes it possible to create bulk materials based on natural polymers with high density and mechanical properties comparable to those of synthetic polymers. In particular, when tested for three-point bending, the tensile strength of starch exceeded 35 MPa, the elastic modulus - 923 MPa, gluten - 28 and 1044 MPa, respectively. It should be noted that traditional approaches to the creation of thermoplastics based on natural polymers are unsuitable, since their glass transition and melting temperatures exceed the thermal decomposition temperature. Plasticizers can be used to lower the processing temperatures needed to create crosslinks. However, plasticization leads to a significant decrease in the strength of the material and causes a number of problems in its application associated with shrinkage, warping, folding, etc.

7 Combined extrusion

It is known that a combination of various methods of solid-state orientation, for example, solid-state extrusion and orientation stretching, promotes the formation of an increased level of properties in polymers, which is often unattainable in a single-stage process. In [48, 49], the possibilities of combined solid-state extrusion schemes, including extrusion through a conical die (EC) and SPD in various sequences, are considered. Polyamide-6 served as the object of research. It has been established that the most effective is the processing according to the EC-SPD scheme, when the highest values of stiffness, hardness and strength are achieved at high values of the fracture strain. In this case, a state with minimum strength anisotropy is realized.

8 Conclusions

Solid-state extrusion based on simple shear schemes is an effective method for altering the physical and mechanical properties of polymer materials with various architectures. The creation of oriented order, enhancement of interfacial interaction, improvement of the degree of dispersion of the minor polymer phase or filler, exfoliation in the case of multilayer fillers are the main processes accompanying solid-state extrusion based on simple shear schemes. The use of combined deformation schemes, including EC and SPD, makes it possible to increase the resource of achieved properties in comparison with single-stage solid-state extrusion processes. Further research is needed to introduce solid-state extrusion based on simple shear schemes into industry for efficient commercial use. For materials design and process optimization, computer simulations using physically based constitutive models will be indispensable.

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