

SOLID-PHASE TECHNOLOGIES OF POLYMER PROCESSING FOR ENGINEERING*

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Abstract: Polymer processing methods by plastic deformation in solid phase are borrowed from solid-phase metal forming technology. All the solid-phase polymer processing methods are based on plastic deformation of a polymer under high hydrostatic pressure.

In terms of research of the general regularities of relaxation behavior and plastic properties of several polymeric systems were obtained the basic requirements for optimal processing conditions and structure of polymeric multicomponent materials having low shear stability, high ductility and high mechanical performance that meet the requirements of technological process thermoplastic pressure in the solid phase. The experimental results are explained in the context of nonequilibrium thermodynamics and physical mesomechanics obtained by thermomechanical analysis spectroscopy (TMS), X-ray diffraction (XRD) analysis, structural, mechanical, diffusion studies, and other physical and chemical methods for studying the processes of solid-phase extrusion and forging products tribotechnical, structural and other functional purpose for mechanical engineering.

Physical and chemical bases of solid-phase technology for processing of polymeric materials are based on the modern physical concepts of the mechanisms of plastic deformation described in several papers [1-6].

In connection with the problem of creating polymer materials that meet the requirements of the processing of thermoplastics by pressure in solid phase, the Research-Educational Center (REC TSTU-ISMAN "Solid-Phase Technology") investigated the structure, relaxation, diffusion and plastic properties of multicomponent polymer construction materials (including polymer alloys and nanocomposites) on the basis of HDPE, UHMWPE, PA, PC, PSU, PTFE, ABS-copolymer for mechanical engineering. As modifying additives were used other polymers such as carbon mono- and many-wall nanotubes (CNTs) produced by "Nano-Tech-Center, Tambov, micro- and nano-products (TiC, TiB₂, etc.) produced by SHS-Technology Institute of Structural Macrokinetics and Materials Science (ISMAN, Chernogolovka).

Experimentally established was the fact that the extreme change of physical and chemical properties of polymer alloys for solid-phase technology is associated with the critical meta-stable condition of the polymeric system in the area of small amounts of other polymer materials. Meta-stable condition for incompatible polymeric systems is associated with the processes of spinodal decomposition of binary polymer system during transition of the structure from single-phase to two-phase condition, which is accompanied by the increase in free volume, loosening of the structure and increase in the mobility of various structural units.

The results obtained experimentally prove the possibility of formation of thermodynamically stable dispersion of polymer systems in the polymer melt as a result of spontaneous dispersion of one component due to instability of the phase boundary and low boundary tension. This state corresponds to the maximum of critical particle size of the polymer additives injected.

The basic requirements for the structure of polymeric alloys with high plasticity is: the incompatibility of the components, which have, however, the thermodynamic affinity of small additions, which guarantees a high degree of dispersion of doping substances and, therefore, highly area of the phase boundary with low boundary tension, providing low shear stability of the system and high mobility of structural elements. The best results are achieved with low concentrations of dopants, i.e., in the critical state of the system, and in the temperature range of pretransition state for the polymeric alloy.

Were conducted the researches on the influence of important technological parameters such as temperature of extrusion T_{extr} , the degree of deformation λ_{extr} and speeds of the appendix of loading V on the process of solid-phase extrusion (SPE). The results allowed to formulate the equation that connects the pressure of SPE P_{comp} and material deformation during the process of solid-phase extrusion $\ln \lambda_{extr}$:

$$P_{\tilde{n}omp} = P_0 \cdot \exp n \cdot \ln \lambda_{extr}, \quad (1)$$

P_0 and n are the coefficients depending on the temperature of SPE, structure of the composite material and geometric parameters of the extrusion zone.

Analytical and experimental dependences between P_{comp} and $\ln \lambda_{extr}$ were obtained in for polymeric composites and alloys based on HDPE, UHMWPE, ABS – copolymer, PSU, PA and PTFE.

Optimal temperature for processing of polymeric materials in solid phase is the temperature of the secondary relaxation transition T_β , the closest to T_g – for glassy polymers. For crystal polymers this optimal temperature is the temperature of prefusion T_l closest to T_{melt} , in this case the following ratio for characteristic temperatures is valid [1]:

$$\frac{\dot{\sigma}_\beta}{\dot{\sigma}_g} = 0,75 \pm 0,15 \text{ or } \frac{\dot{\sigma}_l}{\dot{\sigma}_{melt}} = 0,75 \pm 0,15 \quad (2)$$

Results of thermomechanical spectroscopy (TMS) research [10, 11] of the molecular topological, relaxation and structural characteristics of ABS, UHMWPE, PSU and nanocomposites after SPE at different speed of extrusion showed that the SPE polymer composites results into complete transformation of polymeric structure from isotropic to anisotropic with a radical change of MMP composites, their degree of crystallinity and other quantitative characteristics of the structure.

Researches by method of X-ray diffraction (XRD), ABS, UHMWPE, PSU containing various amounts of TiC, TiB₂ and CNT additives have shown that increasing the amount of additives mainly affect the parameters of the amorphous phase of the composite and to a lesser extent of the crystalline phase, the affect of additives there is observed beginning with 0,5%.

The estimation of physical and mechanical properties of composites based on ABS, HDPE, UHMWPE, PTFE, and PSU under monoaxial tensile and shear stress after SPE in comparison with that of the samples obtained by traditional technology (by melting) shows a sharp increase in the strength characteristics (2÷2,5 time) of the material in a direction perpendicular to the orientation of SPE.

The obtained regularities for structure, properties and optimal conditions for processing of polymers and composites in SPE are confirmed during the study of the forging process [2, 3, 6].

The experimental data on the physical and mechanical properties of polymeric alloys after SPE and forging showed a significant increase in strength characteristics of materials. The maximal strength indices for crystallizable polymeric alloys that were achieved during the plastic deformation of premelting, (where a higher organization level in supramolecular structure is created due to the pretransitional physical and chemical processes in the polymer [1-3], and small-crystallite, movable, mechanically homogeneous structure is formed. For amorphous polymers having virtually disordered supramolecular structures in normal conditions, the highest strength indicators are reached under plastic deformation at lower temperatures, i.e. at high hydrostatic pressure when closing of "pores", "holes" and other structure defects provides the most dense packing of a polymeric material.

The received experimental results are explained in terms of nonequilibrium thermodynamics and the physical mesomechanics [1-9].

Analysis of the experimental data obtained by researching the shrinkage processes of various polymeric systems demonstrated that the level of residual stresses in samples obtained in the optimal temperature of SPE and forging, is more than 2,5 times reduced, and the temperature of the deformation heat resistance of the material is 20-25° higher in comparison with the samples obtained at $T_{comp}=295K$.

For analyzing the regularities of volumetric shrinkage: Y_v at solid forging was used the equation of state for composite materials in the solid phase [1, 10].

$$(P + \pi^{sol}) \left(V - b_0^{sol} \right) = \frac{R(T - T_0^{sol})}{\dot{\epsilon}^{sol}}, \quad (3)$$

and the equation for the volumetric shrinkage (4).

$$Y_v = \frac{V_{comp} - V_{prod}}{V_{comp}} \cdot 100\%, \quad (4)$$

P , V , T - respectively, an external gauge pressure, specific volume, absolute temperature; R - universal gas constant; π^{sol} - internal pressure; M^{sol} - molecular weight region of the chain of composite material in the nonequilibrium region of the polymer; b_0^{sol} , T_0^{sol} - the coordinates of the "pole" of the fan direct dilatometric, and the quantity is Vandervaals-volume of macromolecules, which is always less than b_0^{sol} ; index of "sol" refers to composite materials in the glassy or crystalline states.

The process of solid-phase forging takes place at temperatures close to T_g (T_{comp}). In this case, the equilibrium is established in a closed mold of plunger-type (that fits the parameters P , V and T). Thus the equation (4) is valid:

$$V_{comp} = mV, \quad (5)$$

$$V_{prod} = mV_0,$$

m - mass of the composite material, V_{comp} , V_{prod} , V , and V_0 - volume and specific volume of thermoplastics in terms of punching and under normal conditions ($P=0$ MPa, $T=293$ K). The equation for the volumetric shrinkage can be formulated in the following way:

$$Y_v = 1 - \frac{V_0}{V}, \quad (6)$$

V_0 and V from the equation of state:

$$V_0 = \frac{R(T_r - T_0^{sol})}{\dot{\epsilon}^{sol}(P + \pi)} + b_0^{sol}, \quad (7)$$

$$V = \frac{R(T_r - T_0^{sol})}{\dot{\epsilon}^{sol}(P + \pi)} + b_0^{sol}, \quad (8)$$

T_r - room temperature (293 K), T_{comp} - temperature stamping.

Substituting (6) and (7) in equation (4), we get:

$$Y_v = 1 - \frac{V_0 \dot{\epsilon}^{sol}(P + \pi)}{R(T_{comp} - T_0^{sol}) + \dot{\epsilon}^{sol} b_0^{sol}(P + \pi)}, \quad (9)$$

If the experimental dependence of P-V-T in the solid phase is known, the volume shrinkage can be calculated directly from experimental measurements of the specific volumes of the equation (6).

In case of forging products like bodies of rotation the volume shrinkage is associated with the linear shrinkage of diameter Y_d and height Y_h by the following formula:

$$Y_v = 2Y_d + Y_h. \quad (10)$$

For automatic calculation of the working sizes of industrial equipment for the products represented by bodies of rotation, an information system was developed [10].

Conclusions:

1. Based on the study of general regularities of the formation of molecular relaxation, structural, mechanical and plastic properties of polymer alloys based on HDPE, UHMWPE, ABS, PTFE and PSU were formulated the main requirements to the optimal conditions of processing and the structure of polymeric multicomponent materials with low shear stability, high ductility and high physicochemical indicators that meet the requirements of the technological processing of thermoplastics and composites by pressure in the solid phase for mechanical engineering.

2. The conducted researches of technological process of SPE polymer composite yielded the equation that relates pressure of SPE P_{comp} and the deformation of material during extrusion $\ln \lambda_{KCS}$ as well as analytical expressions for estimating the optimal processing temperature in solid phase for the amorphous - crystalline and glassy polymers and composites.

3. Was proved the possibility of regulating the structure and properties of composite materials by penetration of small additions of polymeric substances, titanium carbide, titanium diboride, and carbon nanomaterial introduction into the polymer matrix. The polymeric composite materials with improved performance were obtained.

4. As a result of analyzing the volume shrinkage during solid forging was developed an engineering method of calculating working dimensions of tooling for polymers using the equation of state for the material in solid phase.

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