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Polymer 41 (2000) 3837–3840

polymer

Thermal shrinkage of polymer mixtures obtained by solid-state extrusion

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Received 3 March 1999; received in revised form 21 May 1999; accepted 30 July 1999

Abstract

The peculiarities of the process of thermal shrinkage of polymer-mixture specimens obtained by plunger extrusion of powder billet have been studied. Shrinkage has been found to be accompanied by the increase of extrudate volume, which is connected with the formation of discontinuities at the interface. The proposed model explains material loosening under shrinkage. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer mixtures; Thermal shrinkage; Relative volume

1. Introduction

At present solid-state extrusion is one of the widely used methods of polymer modification. When a monolith or powder sample is simultaneously influenced by high pressure and shear deformation it becomes possible not only to achieve the improvement of strain–strength characteristics of the processed material [1,2], but to realize qualitatively new properties such as negative Poisson's ratio [3,4] or the effect of thermal shrinkage [5,6]. The latter has been investigated in many works with homopolymers as examples. Thermal shrinkage characteristics of the polymer mixture block samples have not been practically studied. At the same time these systems possess high potentialities for the physical-and-mechanical properties of the articles to be controlled by variation of chemical composition. This paper deals with the peculiarities of thermal shrinkage of thermodynamically incompatible crystallizing and amorphous polymer mixtures.

2. Experimental

The systems such as the isotactic polypropylene–low-density polyethylene (PP–LDPE), the isotactic polypropylene–ultra-high-molecular polyethylene (PP–UHMPE), the polyvinylchloride–ultra-high-molecular polyethylene (PVC–UHMPE) and for comparison the UHMWP have been investigated. In the initial state the components of mixtures were powders with particles of 10–50 μm in diameter. The specimens were obtained according to the scheme: the dry mixing of powders with a necessary ratio—the room temperature compaction of cylindrical billets, 12 mm in diameter—the extrusion of preheated compacted billets. The latter was done by the method of plunger extrusion [2,7] using a high-pressure container with the diameter of operating channel being 12 mm. The temperature of the billet, container and deforming die was kept constant and equal to $(0.95-1)T_m$ (the melting temperature, K) of high-fusible polymer component. The extrusion ratio λ was changed by using dies of different diameters and calculated by the formula $\lambda = d_b^2/d_d^2$, where d_b, d_d are diameters of the billet and die orifice. Extrudates with $\lambda = 1.8$, 2, 3, 4 and 6 were investigated. The thermal shrinkage was measured under the room temperature conditions in specimens with the initial diameter 6–8 mm and 20 mm long after their heating and holding at each temperature of testing for 15 min. The change of linear dimensions of the extrudates $S = ((l_0 - l)/l_0)100\%$ and their cross-section areas $\psi = ((d^2 - d_0^2)/d^2)100\%$, where l_0 and d_0 are the length and diameter of the initial specimen, respectively, l and d are the length and diameter of the specimen after heating and holding at a preset temperature have been determined. The relative change of volume $(\Delta V/V) = ((V - V_0)/V)100\%$, where V_0 and V are volumes of the extrudate in the initial state and after heating and holding at a preset temperature, was found by the data of measuring the sample dimensions.

The strain–strength characteristics were measured at the compression of cylindrical specimens of 8 mm diameter and 16 mm long under the room-temperature conditions. The density was determined by hydrostatic weighing.

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PII: S0032-3861(99)00553-4

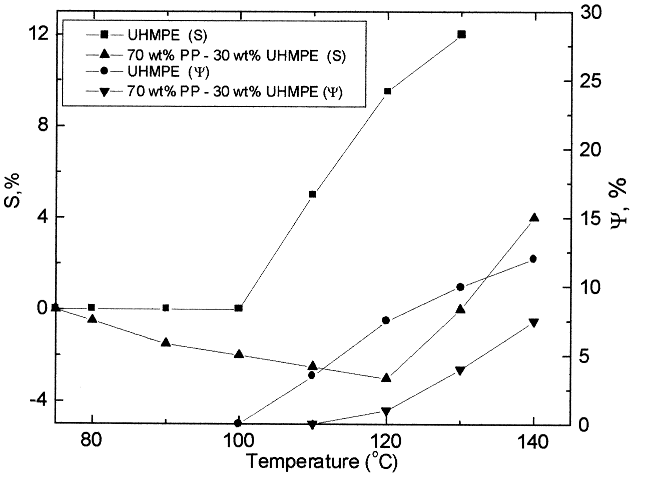

Fig. 1. Temperature dependences of the parameters of UHMPE extrudates and 70 wt% PP–30 wt% UHMPE mixture shrinkage $\lambda = 2$.

Investigations of structure and microphotography were done by using the reflected-light microscopy. The structure was detected by the etching of the specimen polished surfaces. Sections were performed in planes parallel and normal to the extrusion axis.

3. Results and discussion

Fig. 1 shows the dependence of parameters of the UHMPE extrudate shrinkage on the temperature of heating. They reveal the traditional behavior of homopolymers [6]: when $T > 100$°C is achieved, which is close to the temperature of UHMPE melting (extrusion), it equals 130°C, the diameter of specimens increases with the simultaneous decrease of their length, i.e. the initial forms (dimensions) restore. Moreover, the volume does not change. At polymer mixtures the relaxation processes start at lower temperatures (80–110°) as compared to the temperature of their extrusion (160°C). With the increase of the temperature of heating in all the investigated systems, the same as in UHMPE, a monotonous increase of ψ occurs which is accompanied by an unusual change of S (Fig. 1). At the beginning the length of the sample increases and at achieving the temperature close to T_m of one of the components it starts decreasing sharply. Calculations of $\Delta V/V$ show that changes in ψ and S are accompanied by increase of the volume (Fig. 2). The degree of this increase depends on the composition of the mixture, ratio of the components and value of the extrusion ratio.

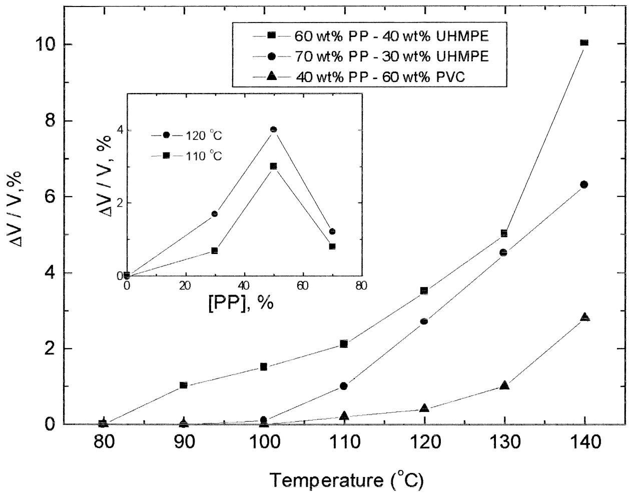

Fig. 2. Dependences of the relative change of volume of the extrudates of different mixtures on heating temperature. In the insert—dependences of $\Delta V/V$ on PP concentration in mixture PP–UHMPE $\lambda = 2$.

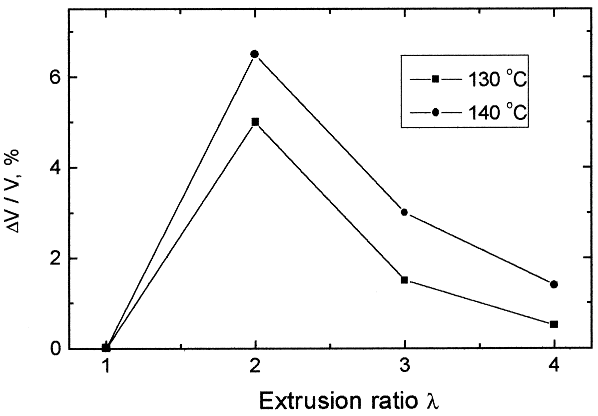

Fig. 3. Dependences of the relative change of volume of 70 wt% PP–30 wt% LDPE mixture extrudates on the extrusion ratio.

In the insert of Fig. 2 there are dependences of $\Delta V/V$ on PP concentration in mixture PP–UHMPE constructed from the $\Delta V/V(T)$ dependences by the secant method. A similar character of the concentration dependences of volume relative change is also observed in other polymer systems at the temperatures of heating at which the relaxation of shape occurs. The peak of $\Delta V/V$ maximum is in the range of concentrations corresponding to the content of components equal by mass and approximately equal by volume.

The $\Delta V/V(\lambda)$ dependences of Fig. 3 are also obtained from the $\Delta V/V(T)$ dependences by the secant method. They make it possible to find the optimal value of the extrusion ratio at which the maximal effect in the increase of volume namely $\lambda \approx 2$, is attained. At $\lambda < 2$ the scheme of processing mixtures used does not allow one to obtain specimens possessing stable characteristics, and at $\lambda = 3$ and $\lambda = 4$ the $\Delta V/V$ values are essentially lower than at $\lambda = 2$. Values of density for the polymer mixture extrudates are lower as compared to that of block specimens they are composed of or the density of similar specimens obtained by the method of hot pressing. Thus, in the case of the 70 wt% PP–30 wt% LDPE system at $\lambda = 2$ the density of extrudates equals 0.87 g/cm^3, whereas that of the hot-pressed specimens is 0.91 g/cm^3. When extrudates are heated to the temperature $T = T_m$ of the low-fusible component

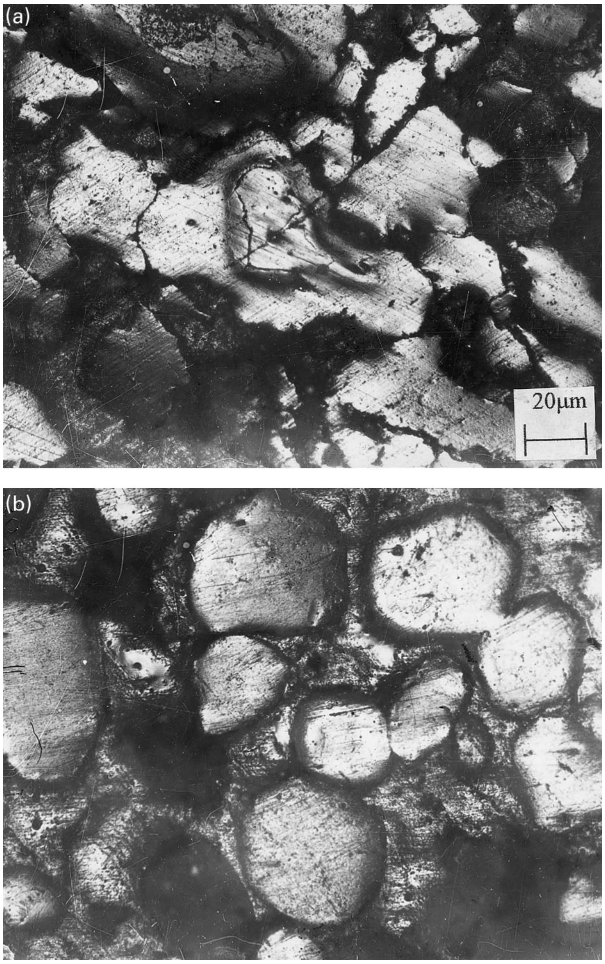

Fig. 4. Morphology of 60 wt% PP–40 wt% UHMPE mixture extrudates: $a - \lambda = 2$, $b - \lambda = 4$.

there occurs the decrease of the density in correlation with $\Delta V/V$ change.

The strain–strength properties of the extruded mixtures are comparatively high. Thus, for the 60 wt% PP–30 wt% UHMPE system, at $\lambda = 2$, the elasticity modulus $E =$ 220 MPa, the breaking stress $\sigma_b = 14$ MPa, the breaking strain $\epsilon_b = 27\%$ With the growth of the extrusion ratio the values of E and σ increase.

The study of the microstructure done with the 60 wt% PP–40 wt% UHMPE shows that at $\lambda = 2$ the extrudates have the two-phase structure with clear enough phase separation. The microstructure represents the PP particles irregular in shape and 100–600 μm in size and surrounded by the polyethylene phase (Fig. 4a). The microstructure character revealed in the plane parallel to and normal to the extrusion axis is the same. An increase of the extrusion ratio to $\lambda = 4$ causes the change of the PP particle shape. In both the investigated planes they are of the round form with smooth boundaries (Fig. 4b). The particle size is in the same range: 100–600 μm. At $\lambda = 6$ the extrudates acquire a spiral-like form, there appear cracks showing that for the system under investigation the limiting extrusion ratio has been reached. In this case the yield strength becomes close to the ultimate strength, and any local non-uniformity of the flow results in extrudate failure [8]. The microstructure of extrudates with $\lambda = 6$ does not qualitatively differ from that of the specimens obtained under the extrusion with $\lambda = 4$, however, the maximal size of the PP particles decreases to 450 μm.

Analysis of the obtained results shows that the oriented state of the polymer chains is typical of all the investigated specimens. It occurs during the heating of extrudates through the restoration of the initial form of the billet. As seen from Fig. 1, the kinetics of the form restoration process in homopolymer and polymer mixtures is essentially different. This difference can be related to the presence of interfaces in the two-phase mixtures.

When the oriented polymer specimens are heated, there occurs the contraction of elongated macromolecules or of their parts under the influence of the entropy factors, transformation of the framework (in the case of semi-crystalline polymers) and disorientation of amorphous-phase conformations [9]. Differences in structure, strain–strength properties, temperatures of melting for the components of mixtures result in the fact that the degree of the specimen orientation under extrusion and, thus, the value and the character of the microstress distribution in each of the phases will differ too. It may be supposed that in the processes of thermal shrinkage the relaxation of those stresses causes the appearance of discontinuities at the interfaces, and, as a result, the volume of the specimens increases. The value of volume increment is determined by both the differences in properties of polymer components and the extent of the interface boundaries.

Presence of the $\Delta V/V$ maximum in the region of equal concentrations of the components (Fig. 2), i.e. in the region of the maximal extent of the boundaries, shows that the above suppositions are valid. At considerable values of λ the internal stresses relax during the extrusion, so with the growth of λ there is a decrease of $\Delta V/V$ (Fig. 3). The anomalous effect of the increase in the length of the extruded specimen after heating needs explanation.

To our mind, the mentioned effect is connected with peculiarities of relaxation of the internal microstresses present in the specimen after the extrusion. We show this by using a simple model of the two-phase composite based on the self-consistent field approach developed in Ref. [10]. Earlier it has been pointed out that the extruded two-phase composite possesses a structure of the matrix-inclusion type, where the polyethylene phase is the matrix and the PP particles are the inclusions. That is why in the following we call the polyethylene phase the matrix and PP the inclusion.

According to Ref. [10], the axial inner stresses appearing in the composite due to the differences between the plastic deformation magnitude of its components could be estimated

$$\sigma_l^i = \Sigma_l + M(E_l - e_l^i), \tag{1}$$

where $\sum_l$ and E_l are the stress tensor axial components and the plastic strain of the whole composite correspondingly; σ_l^i, e_l^i are the i-phase stress and strain tensors axial components and M is the effective elasticity modulus of the composite.

Since the composite does not experience the outer stress influence, Σ_l is equal to 0. The magnitude of E is found through averaging of e^i, i.e.

$$\mathrm{E} = \frac{1}{N}\sum_{i=1}^{N} e^i, \tag{2}$$

where N is the quantity of phases (in our case $N = 2$).

According to Eq. (2), E_l could be found under the formula

$$\mathrm{E}_l = e_l^{\mathrm{M}}(1-\delta) + e_l^{\mathrm{I}}\cdot\delta, \tag{3}$$

where e_l^{M} and e_l^{I} are the plastic deformation of matrix and the plastic deformation of inclusions correspondingly and δ the relative volume part of the inclusions. From the relations (1) and (3), considering that $\Sigma_i = 0$, we have:

$$\sigma_l^{\mathrm{M}} = -M\cdot\delta(e_l^{\mathrm{M}} - e_l^{\mathrm{I}}) \tag{4}$$

$$\sigma_l^{\mathrm{I}} = M(1-\delta)(e_l^{\mathrm{M}} - e_l^{\mathrm{I}}) \tag{5}$$

Since $e_l^{\mathrm{M}} > e_l^{\mathrm{I}}$, it follows that the billet matrix is compressed after the extrusion), and ($e_l^{\mathrm{M}} < 0$), the inclusions are extended ($e_l^{\mathrm{I}} > 0$). At the heating of extruded billets the inner stresses cause the fracture of the links between the composite parts. Consequently, the irreversible deformations of both matrix and inclusions are realized: the matrix elongates (because it had been initially compressed before the heating) and the inclusions are shortened. All this leads to the creation of discontinuities at the borders of the its components.

The magnitude of deformations ε_l^i that are caused by the effect mentioned above and that are connected with the creation of discontinuities could be estimated by

$$\varepsilon_l^i = -\frac{\sigma_l^i}{M} \tag{6}$$

If we substitute expressions (4) and (5) into (6), we obtain

$$\varepsilon_l^{\mathrm{M}} = \delta(e_l^{\mathrm{M}} - e_l^{\mathrm{I}}) \tag{7}$$

$$\varepsilon_l^{\mathrm{I}} = -(1-\delta)(e_{\mathrm{m}}^{M} - e_l^{\mathrm{I}}) \tag{8}$$

Complete deformation of the composite ε_l can be estimated by the formula similar to Eq. (3) where $\varepsilon_l^{\mathrm{M}}$ and $\varepsilon_l^{\mathrm{I}}$ from Eqs. (7) and (8) should be substituted instead of e_l^{M} and e_l^{I}:

$$\varepsilon_l = \delta(1-\delta)(e_l^{\mathrm{M}} - e_l^{\mathrm{I}})^2 \tag{9}$$

From Eq. (9) it follows that $\varepsilon_l > 0$ and the maximum of ε_l is reached at $\delta = 0.5$. This is in correspondence with the experiment.

So, the proposed model shows that maximal stretching of the specimen after heating should be observed in the case when the volume fraction of inclusions is equal to 0.5. As was stated above, this conclusion is in compliance with the experiment.

4. Conclusion

For polymer mixtures obtained by plunger extrusion of powder billet the anomalous thermal shrinkage effect has been found which appears as the simultaneous irreversible increase of extrudate diameter and length under heating. The increase of volume in this case is connected with the formation of microdiscontinuities at the interfaces. A mathematical model of the two-phase composite extrusion has been proposed which explains the change of dimensions of the specimens under heating.

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