

## THE INFLUENCE OF DEFORMATION TEMPERATURE UNDER UNIAXIAL STRETCHING ON THE PARAMETERS OF HEAT SHRINKAGE OF HIGH DENSITY POLYETHYLENE

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**Abstract**—The influence of deformation temperature under uniaxial stretching on the nature of shrinkage stress and the change in linear dimensions of PE oriented samples during subsequent heating has been studied. It has been shown that thermal expansion of the material takes place in the initial stages of heating under orientation above the temperature of PE melting. Subsequent increase in temperature to that of PE melting causes the development of shrinkage stress and sample shrinkage. On orientation below the melting temperature, the heat expansion can be completely balanced, whereas sample shrinkage develops in the early stages of heating; high values of shrinkage stress are observed.

### INTRODUCTION

At present heat-shrinkable polymeric materials have been widely applied in various fields of engineering [1, 2]. These materials are capable of recovering their original dimensions and their shape under heating, exhibiting some shrinkage stress. The parameters of heat shrinkage (the degree of shrinkage,  $S$ , shrinkage stress,  $\sigma_s$ , the temperature range of shrinkage, etc.) depend on the orientation conditions during the production of heat-shrinkable polymeric materials, usually chosen empirically. The production of materials with preset parameters of heat shrinkage is of importance for their diverse application.

In most cases heat-shrinkable polymeric materials should have relatively high shrinkage stress of about 2 MPa and more at a degree of shrinkage of no more than 50%. For some special heat-shrinkable polymeric articles, the heat shrinkage is often performed in isometric heating environment, when the material dimensions undergo negligible changes or remain almost the same, and the shrinkage stress is needed for pressing loads, sealing etc. Further, the polymeric materials produced by conventional processing methods are somewhat subject to orientation and have a shrinking capacity. During usage these materials may exhibit internal stresses responsible for deterioration of their operating characteristics and serviceability. Therefore, studies on the effect of orientation on the properties of heat-shrinkable materials obtained are of great practical significance.

### EXPERIMENTAL

In our experiments we have used high-density polyethylene (HDPE) bands, 1 mm thick, prepared by extrusion and then irradiated in an electron accelerator. Gel-fraction measured by the method of extraction in a boiling xylol was 60%. Melting temperature,  $T_m$ , was 125°, and the degree of crystallinity was 57%. Before studying, the samples were annealed at 140° for an hour and then cooled slowly. The

isotropy of stresses during stretching of annealed samples in mutually perpendicular directions indicates relief of internal stresses under given conditions.

Strain dependences of stresses at various temperatures were measured by an Instron instrument at a constant rate of stretching of 50 mm/min on HDPE samples. The samples were in the shape of two-sided spade, 15 mm long and 5 mm thick in its working section, cut from the original annealed strips.

The uniaxial oriented stretching to the desired elongation  $\epsilon$  was performed on the  $100 \times 10 \times 1$  mm samples in the temperature range 50–135°. The samples were fixed in the clamps of a tearing machine and held in a thermostated bath at the orientation temperature,  $T_{or}$ , for 5 min with subsequent stretching. The samples were then cooled in a water bath at 15°.

Temperature dependences of internal stresses of HDPE oriented samples were obtained by isometric heating at a heating rate of 4° min<sup>-1</sup>. The technique involves the oriented sample being fixed in the stationary clamps of a tearing machine and being heated at a constant rate. At elevated temperature, the sample should either expand according to its coefficient of linear heat expansion or shrink if it is shrinkable. Since during measurement the specimen dimensions are constant, the recorded arising stress would differ in sign during expansion and shrinkage. Positive values are assigned to the shrinkage stress and negative values to expansion.

Temperature dependence of the change in sample linear dimensions  $S = (l - l_0/l_0) \cdot 100\%$ , where  $l_0$  and  $l$  are the dimensions of the initial sample and that heated to temperature  $T$ , respectively, has been determined dilatometrically by an UIP-70M instrument at a heating rate of 5° min<sup>-1</sup>.

### RESULTS AND DISCUSSION

Strain dependences of HDPE initial specimens at 50–135° are shown in Fig. 1. One can see that, at the increased temperature of stretching, the changes are typical for PE strain: the elasticity modulus decreases in the initial stages of strain, as well as the limit of forced elasticity falls and the elongation at rupture

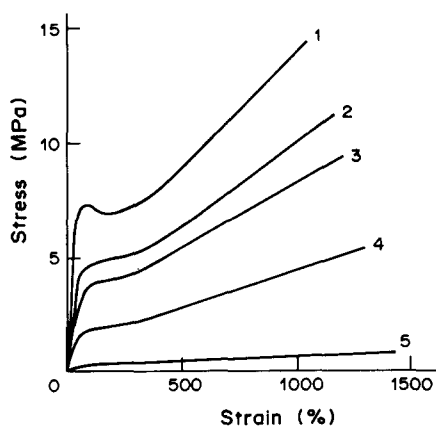


Fig. 1. The dependences of stress on strain of initial HDPE at various temperatures: (1) 50°; (2) 70°; (3) 80°; (4) 100°; (5) 135°.

increases. These dependences permit determination of the strain working domain under orientation in order to obtain heat-shrinkable materials. The strain domain under study includes the elongations corresponding to the reversible changes in the polymer structure. On studying the effect of the orientation temperature on the heat-shrinkage parameters, we have chosen the value of elongation  $\epsilon = 30\%$ , since  $\sim 30\%$  degree of shrinkage is of interest in terms of production of heat-shrinkable materials for rust protection of pipelines, reservoirs, etc. Consider the character of changes in stresses (Fig. 2) and in linear dimensions (Fig. 3) of HDPE oriented samples on heating from 20° to 150°. Orientation above  $T_m$  of the HDPE crystalline phase is referred to as high-temperature orientation. Change in stresses of the samples obtained by high-temperature orientation is of extremal nature. In this case the extremum is in the region of the stress negative values reaching about 0.3 MPa. At first with increasing temperature, the negative stresses increase owing to the thermal expansion of the material (Fig. 3) in this temperature range. The fall in the absolute values of stresses to zero is

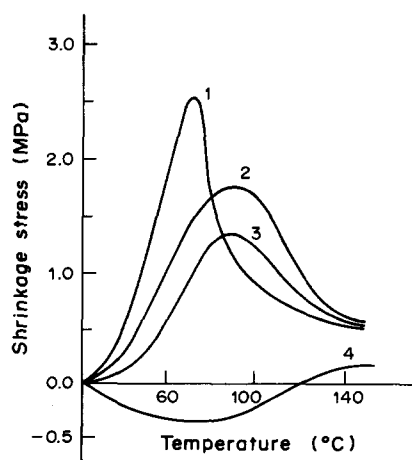


Fig. 2. Temperature dependences of shrinkage stress of HDPE samples oriented at various temperatures: (1) 50°; (2) 70°; (3) 80°; (4) 135°.

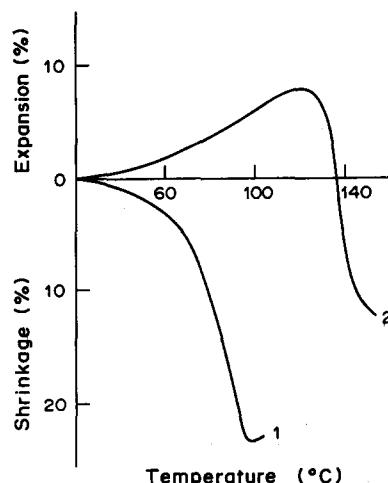


Fig. 3. Temperature dependences of linear dimensions of HDPE samples oriented at various temperatures: (1) 70°; (2) 135°.

observed at temperatures close to  $T_m$  due to the material softening under isometric conditions. At temperatures above  $T_m$ , the proper shrinkage stresses develop, the sample dimensions decreasing (Fig. 3). Finally, with further increasing temperature the dependence assumes practically adiothermal nature, whereas the change in sizes reaches equilibrium values corresponding to a given temperature  $T_i$ .

Stresses in the specimens obtained by low-temperature orientation also undergo considerable changes but shrinkage stress only is observed. Three typical regions can be resolved for the temperature dependence of shrinkage stress. At first, shrinkage stress increases, whereas the values  $\sigma$ , close to those of strain stress observed under orientation are attained at the extremum. Subsequent rise in temperature causes fall in shrinkage stress and finally, at a temperature above 140°, the dependences acquire practically adiothermal character. The decreased dimensions of the samples obtained by low-temperature orientation are observed in the early stages of heating, the thermal expansion of the material as well as the thermal stress of expansion being balanced. Complete shrinkage is attained at the temperature corresponding to  $\sigma$ , maximum.

Analysis of the temperature dependences of shrinkage stress and the change in the sample linear dimensions on heating has shown that, depending on the orientation temperature, substantial differences are observed in the behaviour of an oriented sample. The samples prepared by high-temperature orientation behave on heating to the melting temperature in the same way as "conventional" polymer samples, i.e. they exhibit increased linear dimensions and considerable thermal stress, the proper shrinkage properties being realized only above  $T_m$ . In the samples obtained by low-temperature orientation, the processes caused by the material heat expansion are balanced, the shrinkage stress developing in two temperature ranges: below  $T_m$  with the high extremal values of  $\sigma$ , and above  $T_m$  with the constant values of  $\sigma$ , as under the high-temperature orientation. The lower orientation temperature leads to the higher

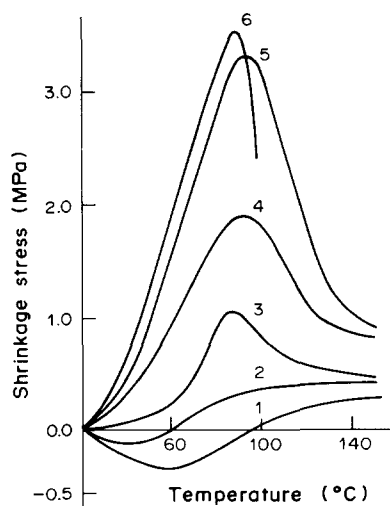


Fig. 4. Temperature dependences of shrinkage stress of crosslinked (1-5) and non-crosslinked (6) HDPE stretched at 70° to various elongations: (1) 5%; (2) 9%; (3) 12%, (4) 25%; (5) 45%; (6) 30%.

maximum values of  $\sigma_s$  and shifts the temperature range of shrinkage stress and relaxation of sample dimensions towards lower temperatures.

Figure 4 shows the temperature dependences of the internal stresses of HDPE samples stretched to various elongations  $\epsilon$  at 70°. The samples with a low value exhibit the sign-alternating character of the change in the internal stresses. In the initial stages of heating, the stress of heat expansion is recorded; they reach some extremum and then approach zero. On further heating, the internal stresses change the sign, i.e. shrinkage stress is observed in the sample, and it increases to a constant value as the temperature increases. Similar changes in the internal stresses were also observed for quite high values of  $\epsilon$  in the HDPE samples exposed to orientation stretching above  $T_m$  of the material (Fig. 2). Increase in elongations to  $\epsilon = 10\%$  in the strain region is responsible for the smaller temperature range of heat expansion stress and the decreased inversion temperature (the temperature at which the internal stresses change the sign).

In the region of strain exceeding  $\epsilon = 10\%$ , the heat expansion is fully balanced by the shrinkage stress observed at the early stages of heating. The higher is  $\epsilon$ , the greater are the values of shrinkage stress  $\sigma_s$  at every given temperature during heating. The temperature dependence of  $\sigma_s$  is of extremal nature and takes the form of a smeared peak. At temperatures above  $T_m$ ,  $\sigma_s$  values reach some constant values of  $\sigma_{res}$ . Generally the higher  $\epsilon$  causes the increase in  $\sigma_s$  and  $\sigma_{res}$  maxima.

The dependences presented assume the existence of two different processes in a crosslinked HDPE during stretching and shrinkage. The specific feature of the first one lies in that the shrinkage stress determined by isometric heating method is observed in the temperature range exceeding  $T_m$  and reaches some constant value of  $\sigma_{res}$  on further increasing temperature. Supposedly, this process is mostly determined by deformation of the network of chemical bonds due to

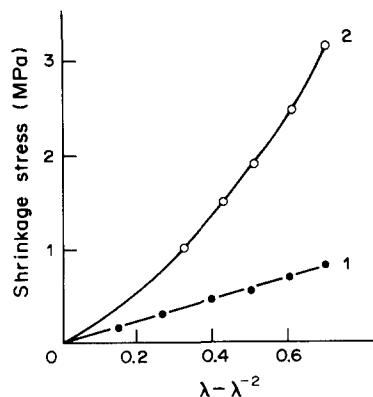


Fig. 5. Strain dependence of residual (1) and maximum (2) shrinkage stress on the coordinates of the equation of the high-elasticity theory for crosslinked HDPE.

the uniaxial stretching and can occur under isometric conditions only on melting of the HDPE crystalline phase. The shrinkage stress associated with this mechanism reaches relatively low values at all studied  $\epsilon$  and  $T_{or}$ . It is known that the strain dependence of stress for an ideal three-dimensional network is described by the basic relation of the high-elasticity theory [3]. In our case the shrinkage stress is supposedly determined by the strain of a chemical bond network at temperatures exceeding  $T_m$ , when the HDPE crystalline phase has melted. Therefore, it was of interest to discover whether the high-elasticity equation is applicable to the data obtained by the isometric heating method. Figure 5 shows that the strain dependence of  $\sigma_{res}$  shrinkage stress is linear on the coordinates of the high-elasticity theory of an ideal three-dimensional network. The molecular weight of the chain between the network points,  $M_c$ , calculated from the slope of a straight line in Fig. 5, reaches nearly 3000, which is close to  $M_c$  values for polyethylene with about 60% gel-fraction [4].

The second mechanism, with contribution increasing with higher  $\epsilon$  and lower  $T_{or}$ , is observed in a low-temperature range of heating. The nature of this mechanism is due to polymer structural rearrangement during stretching. It should be noted that, even under isometric heating, the process is of relaxation character. The role of the chemical bond network is negligible. In fact, the temperature dependence of shrinkage stress in a non-crosslinked HDPE sample is the same as in a crosslinked HDPE. But at about 100° a sample is disrupted by the action of the shrinkage stress exceeding the rupture stress of the material at a given temperature (Fig. 4, curve 6). Hence, this is the network of chemical bonds which is responsible for the shrinkage stress at high temperatures. At the same time, the strain dependence of  $\sigma_s$  maxima (Fig. 5, curve 2) falls off from linear, indicating the difference in the mechanisms of strain and, consequently, of shrinkage.

## CONCLUSIONS

Thus, orientation of partially crystalline polymers at temperatures above and below  $T_m$  of a crystalline phase is responsible for great differences in the char-

acter of shrinkage phenomena. Unlike the high-temperature orientation, the low-temperature process permits production of polymeric heat-shrinkable materials characterized by a balanced heat expansion and high values of shrinkage stress. In this case the three-dimensional network of chemical bonds does not affect the development of a shrinkage process which is complete on heating to the melting temperature.

## REFERENCES

1. M. L. Fridman. *Tekhnologia pererabotki kristallicheskih poliolefinov*. M.: Khimiya (1977).
2. E. E. Finkel and R. P. Braginski. *Nagrevostoykiye provoda i kabeli s radiatsionno-modifitsirovannoy izolyatsiyey*. M.: Energiya (1975).
3. D. V. Van Crevelen. *Svoystva i khimicheskoye stroeniye polimerov*. M.: Khimiya s. 159.
4. V. K. Knyazev and N. A. Sidorov. *Obluchenny polietilen v tekhnike*. M.: Khimiya, s. 178 (1974).