**Comments on "Influence of Shearing History on the Properties of Polymer Melts. I"**

Z. WALCZAK *J. Appl. Polym. Sci.*, **17**, 153, 1973

The recent interesting and important papers by Walczak[1-3] emphasize the significance of shear history effects on polymer melt rheology and on the final physical properties of the processed polymer. Walczak proposed a new "shear history" parameter, defined as the ratio of shear stress at the wall to the square of the shear rate, as a convenient approach to describe shear history effects which eliminates the necessity of handling the data for each capillary length separately.

At least two other approaches describing these effects should perhaps be mentioned. Arai and Aoyama have eliminated die geometry effects in a most interesting way by correlating die swell phenomena with an "elastic shear stress at the wall."[4] Bagley, Storey, and West, by analysis of data similar to that of Walczak's Figure 10 concluded that total shear strain imposed on the melt was the critical variable.[5] As Walczak rightly remarks the effect is of considerable importance in practice and I would note that the term "shear refining" has been applied to the process.[6] The most obvious effect occurs when infinite shear strain has been imposed on the melt. This occurs, for example, when the melt flows past an obstruction such as a "Spider." The melt is actually cut, resulting in a "weld line" which is a common physical weakness often easily observable in extruded tubular film.[7]

Another point worthy of comment concerns Figures 8 and 9 in Walczak's paper[1] showing a variation of critical shear rate for melt fracture as a function of die entry geometry. Bagley and Schreiber contend that this effect is only apparent, not real.[7,8] As they note: "With steeply tapered dies much higher values of shearing stress and shear rate can be achieved without apparent filament distortion. This is not due to any dependence of the critical shearing stress for melt fracture on entry angle. Rather, as the included entry angle decreases, the strain inhomogeneity introduced into the filament per fracture is decreased. At the same time the frequency of fractures increases, making the heterogeneities smaller and more evenly distributed." The effect of shear history on filament die swell, apparent distortion, and gloss are indicated in Figures 2 and 3 of reference (5).

Walczak comments that in his samples "the effects of shearing 'survived' all of the opportunities for relaxation." Certainly the recovery of "melt structure" can be a slow process but it does occur,[9] at rates which depend on the molecular weight level of the polymer.

This relates also to the self-cure of weld lines which can be rapid in relatively fluid resins and to the behavior, noted by Walczak, that "the virgin sample behaves differently from the pelletized sample." This is particularly strong in polyvinyl-chloride (PVC) resins is noted by Berens and Folt,[10] who observed that even quite severe melt treatment can be surprisingly ineffective in eliminating grain boundaries between granules of PVC.

On p. 164 of Walczak's paper, some views on the origin of extrudate effects are summarized. The importance of recognizing the varied origins of these defects and of distinguishing among the different types of defects cannot be overemphasized, as has been noted by Bartos and Holomek,[11] Virogradov,[12] and others.[7]

Finally, Walczak notes that the corrected shear stress in capillary flow is not, experimentally, independent of die entry geometry, and that the effect is different in different polymers. The effect is undoubtedly related to the magnitude of the "dead-space"[13] formed by the flowing polymer in the viscometer reservoir prior to entry into a flat-entry die. This "dead-space" can be large or small,[13,14] depending on the particular polymer being studied. If the dead-space is large, so that the natural lead-in funnel is long and narrow, then the dependence of "corrected" shear stress on included entry angle should be relatively weak except for very steeply tapered dies.

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## Response to Comments on "Influence of Shearing History on the Properties of Polymer Melts. I."

A number of remarks concerning one[1] of the series of my papers[1-3] has been expressed by Bagley. It has been suggested that perhaps I should have mentioned some additional references.

I do extend my sincere apologies to Dr. Bagley and all of the other authors possibly involved, as well as to those readers who may have similar feelings. Nevertheless, after carefully studying the comments, I concluded that only a misunderstanding of some of the details of my papers may be the grounds for Dr. Bagley's comments. If many more readers have been led to a similar misunderstanding, I do accept the blame for expressing my views without the proper clarity. An attempt to provide an additional clarification follows.

The magnitude of the die-swell data presented in Figure 10[1] is neither correlated with anything fundamental nor singular in nature, nor is it intended to discuss in any way the approaches suggested by Arai and Aoyama[4] or Bagley, Storey, and West.[5] The figure shows very simply that a die swell, at a given shear rate and capillary aspect ratio, may change very markedly, for what usually would be considered as "the same polymer," after a shear pretreatment. It is indeed quite reasonable to approach the phenomenon of die-swell decay with increasing capillary aspect ratio as a "short-term shear history" effect. In consequence, one might expect that the long-lasting shear effects might be described using the same parameter, be it the "total shear strain imposed on the melt,"[5] "elastic shear stress at the wall,"[4] or any other parameter. Unfortunately, none of the suggested parameters gave as general a description of the changes in polymer behavior as $(\tau/\dot{\gamma}^2)_{hist}$. To the best of my knowledge, none of the authors[4,5] ever published a work on the long-lasting shearing history, as understood in the papers in question,[1-3] nor did they use $(\tau/\dot{\gamma}^2)_{hist}$ in the sense and meaning suggested.[1-3] If it would be indeed necessary to mention the above-cited approaches,[4,5] then, in truth, a score of other works ought to be discussed too;[6] and the references given[6] mention only a small fraction of the whole, randomly selected without any prejudice. On the other hand, it is rather difficult for an author to describe all of the attempts which did not lead to a positive solution. In this author's opinion, such a discussion would unnecessarily prolong the paper by several pages.