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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 $(\tau/\dot{\gamma}^2)_{\text{hist}}$. 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 $(\tau/\dot{\gamma}^2)_{\text{hist}}$ 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.

Regarding the dependence of the critical shear rate on the capillary entrance angle, the verbal interpretation of the results seems to be rather a matter of preference. To me, the explanations of Gieskus[7] and Schümmer[8] are more appealing, though I find them rather compatible with the essence of those suggested by Bagley and Schreiber[9] and Ballenger et al.[10] Figures 1–3 in ref. 5 and figures in ref. 9, according to their legends and the text of the papers, depict photographs of extrudates vs. some of the extrusion data. It is not the first time such phenomena are mentioned in literature either. Figure 9 (ref. 1) depicts *very real* and practically important effects, though differently presented than in references 5 and 9. I am not in a position to resolve this point any further, as I do not see here any conflict of authors' rights.

The note regarding the relaxation process I assume cites some auxiliary facts, and as such it requires no further comments.

Interpretation of the experimental results offered in one of the papers quoted[11] evokes serious reservations. Namely, grains of polymers obtained in emulsion or suspension polymerizations are "coated" with micelles or layers of various surface active agents or protective colloids, or both. Such layers of foreign material may indeed constitute a "barrier" which is difficult to break. The effect of nonsolvents[11] (which could influence the coating layers) on the polymer behavior appears to lend strong support to the suspicion just expressed. It has been decided to omit the reference to the paper,[11] rather than write the above words of doubt, which I have been forced to express now.

My speculative assessment of the reasons and types of melt fracture has been supported with all of the references required by the text or views cited. Perhaps it is necessary to stress once more concisely that according to my views, studies of melt morphology are quite crucial to the further progress in many areas of rheology. Vinogradov[12] with his co-workers published many papers on the wall slip during non-Newtonian flow. One of his most interesting papers[13] appeared when my work[1-3] was in press. A combination of Vinogradov's views with studies of morphology might lead to very exciting solutions.

Last, but not least, I must reemphasize a point about the experimental data concerning capillary dimensions given on p. 154 and included in Figure 1 (ref. 1). The length of the capillary entry was different for a different entry angle in order to preserve the same diameter of the top of the entry cone (equal to the diameter of the rheometer barrel). Such a design has been chosen to avoid the "dead spaces" referred to by Bagley. In case of the flat entry, the "dead spaces" are unavoidable, naturally. The essence and consequence of such a capillary design allowed drawing the stated conclusions regarding short-term history effects.

On the other hand, Bagley's[14] method of extrapolation, using a series of capillaries with identical entries, undoubtedly leads to the mathematical elimination of the entry with all its features, including "dead spaces." The "dead spaces," if present, do not depend on the capillary length, which is the parameter used for extrapolation. However, the "dead spaces" depend on the shear rate,[4,7,8] which is reflected by the variation of the entry correction with shear rate. The last phenomenon is observable, irrespective of the capillary entrance angle.

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Dr. Walczak's response to these comments prompts me to add the following remarks. The third paragraph of his reply needs to be considered in the light of his statement in the introduction of his first paper[1] that no systematic treatment of the effect of mechanical perturbation on polymer melt behavior has been reported in the literature. I feel he is mistaken in this view and wish to reiterate that refs. 5, 7, and 9 make it perfectly clear that shear pretreatment changes a polymer's melt flow characteristics. Die swell (and hence end correction and apparent viscosity) is changed markedly by shearing level as measured by total shear strain and the recovery of properties after shearing is a function of both time and polymer viscosity level (ref. 7, p. 112). Further, contrary to the implication in Dr. Walczak's response, I have not maintained that his shear history parameter was used previously. What I do maintain is that some progress towards a theoretical understanding of Dr. Walczak's results might be achieved by considering his results in terms of earlier work on the effect of mechanical perturbations on viscoelasticity, specifically the use of total shear strain as a variable.

I do not agree with Dr. Walczak's fourth paragraph that the verbal interpretation of the apparent dependence of the critical shear rate is a matter of preference. In my view his Figure 9[1] is wrong. To plot this way distorts the real situation and can lead to incorrect conclusions. I personally made such an error[15] on the basis of plots similar to Dr. Walczak's Figure 9, concluding incorrectly that acceleration effects were important in the entry melt fracture phenomenon. My intention was *not* that attributed to me by Dr. Walczak, namely to avoid a "conflict of authors' rights."

I disagree with paragraph six of Dr. Walczak's response and his interpretation of the Berens and Folt result. I have seen equivalent results in cases where there were no surface active agents or other foreign material present.

Dr. Walczak's paragraph seven misses the point of my comments. I was supporting his position.

I would add to Dr. Walczak's final paragraph the experimental observation that the dead space size depends not only on shear rate but also, above the inlet melt fracture point, on time.[13] As noted by Bagley and Birks,[13] "Since material from the dead space is now surging intermittently through the capillary, the dead space must decrease in size." Eventually, the dead space "has been reduced in size so far that it cannot surge over far enough to reach the capillary and hence the dead space size remains constant."

In summary, I hope this discussion will serve to stimulate publication of more data and information in this scientifically interesting and industrially important rheological area.