Crystalline Morphology of Ultrahigh-molecular-weight Polyethylene Pseudogels

INTRODUCTION

There are numerous reports on the processing of solutions of ultrahigh-molecular-weight polyethylene (UHMWPE) for obtaining high modulus and strength fibers. These processing studies, pioneered by Pennings et al.,[1,2] can be divided into those involving dilute solutions ($\sim\leq 1\%$ w/w concentration) and to those involving more concentrated solutions ($>1\%$ w/w concentration). In the presence of extensional flow fields, the "shish kebab" type of crystals can be grown from the dilute solution and drawn into high-modulus fibrils.[1,2] Likewise, the concentrated solution may result in fibrillar structures when processed under selected processing conditions, and the fibrils are known to have, at least at low deformation ratios, a shish kebab crystalline structure also.[3-5]

As the emphasis in these solution processing studies has been hitherto on the development of ultrahigh modulus and strength fibers, there has been a relatively small effort toward understanding the flow behavior of the concentrated UHMWPE solutions known to exhibit a gellike behavior. As a matter of fact, such concentrated solutions have been always referred to as gels and their processing has been described as gel processing. However, these solution systems are not true gels.[6] Our rheo-optical studies indicate that their gellike behavior is associated with the presence of a crystalline phase discernible up to 140°C and even higher temperatures. The morphology of the crystalline phase varies considerbaly with processing conditions and results in unusual flow properties. In this report we discuss some preliminary results of our rheo-optical studies with the concentrated solutions of ultrahigh-molecular-weight polyethylene.

EXPERIMENTAL

The ultrahigh-molecular-weight PE used in this study was HiFax 1900 (Himont, Inc.) with an average molecular weight of $2\text{–}8 \times 10^6$. The UHMWPE was added to paraffin oil at concentrations from 2 to 5% w/w. To avoid polymer degradation at high temperatures, the polymer was stabilized with approximately 0.5% of BHT antioxidant. The mixture was stirred at 150°C. A solution was obtained that was clear until it was cooled to about 120°C, when it became opaque and transformed into a gellike or a pseudogel. Optical observations were conducted with a Zeiss photomicroscope using polarizing light. Thermal analysis data were obtained with a duPont thermal analyzer (model 1900).

RESULTS AND DISCUSSION

The uniformity of the so-produced pseudogels depends on the preparation conditions. Under nonisothermal conditions, the gellike structure is nonuniform and is comprised of a mixture of single crystals and a fibrillar network in which the fibrils have a shish kebab crystalline morphology. Optical microscopy indicates that the shish kebab fibrils can be a few millimeters or longer in length. This nonuniform structure is shown in Fig. 1.

Under isothermal and quiescent conditions, the pseudogel is more uniform, has a turbid texture, and consists of stacks of single crystals and large spherulitic crystals (diameter ≤ 250 μm). Such a uniform gellike structure is shown in Fig. 2.

The different crystalline morphologies of the UHMWPE pseudogels can also be ascertained by the thermal behavior of the semicrystalline products obtained by extracting the paraffin oil from the pseudogel with a more volatile solvent, such as hexane, and subsequently evaporating out the solvent. The thermal analysis results (Fig. 3) indicate that the semicrystalline

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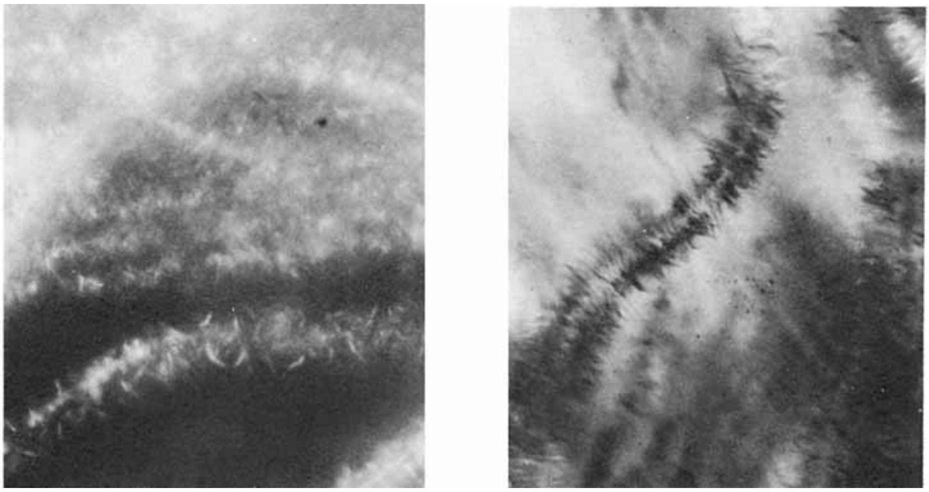

Fig. 1. Optical micrographs of a nonuniform UHMWPE pseudogel obtained under nonisothermal conditions: (a) mixture of single crystals or stacks of single crystals and shish kebab fibrils (210×) and (b) shish kebab fibrils (1260×).

structures obtained from gellike precursors under isothermal and quiescent conditions had a melting temperature at ~129°C, significantly lower than the melting temperature (~137°C) of the semicrystalline structures prepared from gellike precursors under nonisothermal and nonquiescent conditions.

So far, the morphology of the UHMWPE pseudogels has been explored to a small extent. In recent rheo-optical studies, we observed that the crystalline morphology and the degree of the initial crystallinity of the UHMWPE pseudogels, typically 2–10%, change considerably with the processing conditions and significantly affect their flow behavior. For example, when the

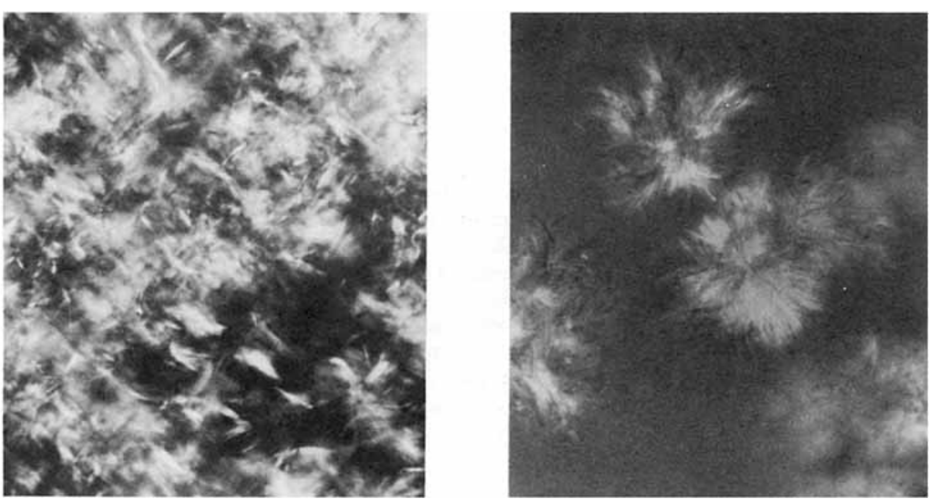

Fig. 2. Optical micrographs of a uniform UHMWPE pseudogel obtained under isothermal and quiescent conditions: (a) single crystals and stacks of single crystals (1120×) and (b) spherulitic crystals (540×).

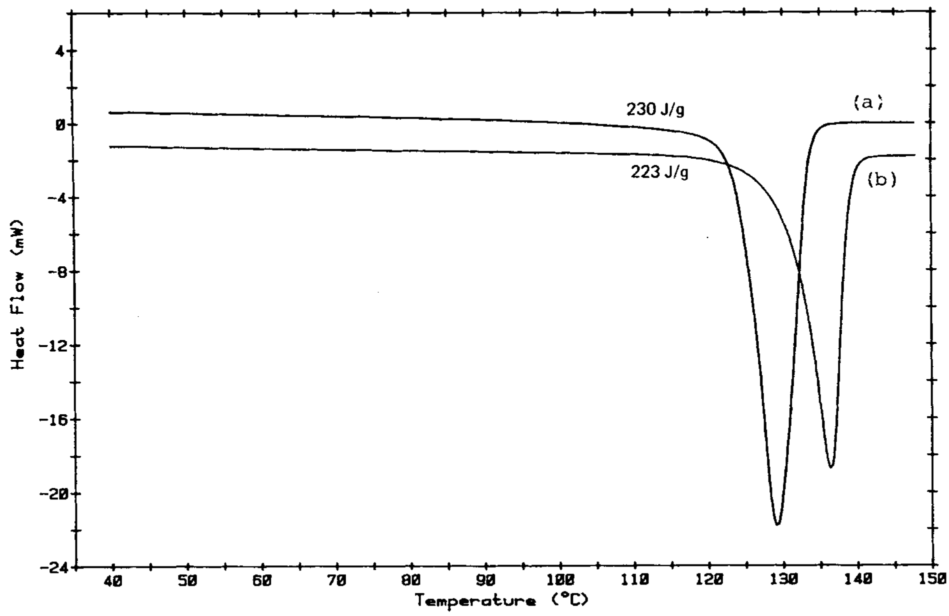

Fig. 3. Different thermal analysis thermographs of the semicrystalline UHMWPE obtained after solvent extraction from pseudogel precursors prepared under (a) isothermal and quiescent conditions and (b) nonisothermal and nonquiescent conditions.

UHMWPE pseudogel is formed under nonquiescent conditions by applying a steady or an oscillatory shear, a fibrillar shish kebab structure is obtained that melts at ~140°C. Some individual crystalline fibrils can be observed in the paraffin solution even at as high as 220°C. Moreover, this fibrillar morphology has been observed to be stable at ambient temperature. This behavior is different for the pseudogels with the spherulitic crystals or the stacks of single crystals, which were observed to melt upon heating at 120–125°C. The degree of crystallinity, although small, appears to play a key role in the formation of the gellike structure. However, unlike the true gels, which have time-independent or equilibrium elastic properties, that is, they will support a static shear stress without undergoing permanent deformation,[7,8] the UHMWPE pseudogels undergo flow even when a small shear stress is applied. These results are documented with studies of the variation of shear modulus with frequency and temperature and are discussed in detail in a separate report.[9]

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