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Dry Path to High-Performance Threads from Ultra-High Molecular Weight Polyethylene

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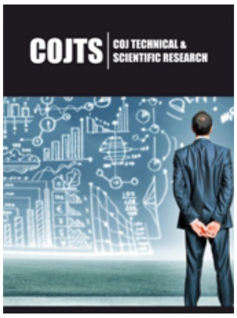

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UHMWPE is a unique polymeric material due to its high chemical resistance, high wear resistance, low coefficient of friction, high impact strength, as well as the possibility of obtaining high performance fibers which are used, in particular, in bulletproof vests. Due to the high viscosity of the UHMWPE melt, it cannot be processed by traditional methods. The non-traditional routes to high performance fibers and the details of processing are discussed. At present, super strong (σ =3.6-3.9 GPa) and high modulus (E=109-132 GPa) UHMWPE fibers are produced all over the world via gel technology developed at the end of the last century [1]. However, this method is expensive and environmentally unsafe, since it requires the recovery of a large amount of solvent. P. Smith, one of the inventors of gel technology [1], proposed an alternative route to obtain high-performance fibers [2]. He discovered that high performance UHMWPE films can be obtained directly from a nascent never processed "virgin" polymer synthesized at -40 °C on glass supported vanadium trichloride-aluminium triethyl catalyst followed orientation hardening. The σ values appear to be only slightly below (~15%) those of gel-spun filaments of similar molecular weight [2-4]. This work triggered a great deal of activity in academia and industry to find suitable commercial catalyst systems and synthesis conditions that would provide high compactability and drawability of the nascent polymer. However, it turned out that not all reactor PE powders are suitable for dry processing into high-performance fibers. Their suitability for dry processing is usually discussed in terms of the topological constraints (entanglements). The latter are localized in the disordered regions and limit the drawability in the solid state [5,6]. It has been established that a low density of entanglements can only be achieved by carrying out the synthesis at a temperature not exceeding 30°C÷40°C, at which the polymerization rate is close to the crystallization rate of the growing chain. The low entanglement density is also facilitated by the use of new generation catalysts, such as homogeneous single-site catalysts based on cationic complexes of metallocenes and methylaluminoxane (MAO) or modified Ziegler/Natta catalysts ($MgCl_2$ supported $TiCl_4$ catalyst systems with catalyst sites with different reactivity) [7-9]. But not everything is so simple. The reactor powder particles have a very complex hierarchical morphology depending on the catalyst system used. The entanglements, which are actually segments of molecules in different conformations passing from one crystalline region to another, can be localized in disorder regions between different morphological units (lamellae, fibrils, shish-kebabs). This cannot but affect the nascent polymer processing. The results of the investigation of reactor powder morphology with the help of all the comprehensive techniques are given in a collection book as well as the data about change of the morphology in the thermal and mechanical fields [10]. In addition, UHMWPE reactor powders may have various crystalline structures. The presence of a metastable monoclinic phase in the nascent UHMWPE along with the usual orthorhombic one and its localization in the various morphological units was found in the study of single particles using bright synchrotron radiation [11] and micro focus technique [12]. All of this controls the next steps of transformation reactor particles into high performance material: compaction\sintering and orientation drawing. To create a good monolithic preform, for subsequent orientation drawing, it is necessary to “heal” the boundaries between the nascent particles, for which they are sintered at an elevated temperature under pressure at a temperature below the melting temperature (Tm) of the polymer, since heating the powder is above the Tm of the polymer leads to the loss of the ability of the powder to achieve large orientation elongations and, accordingly, high mechanical characteristics. Then one should find a proper regime for orientation drawing. A scientifically-based approach to this problem one can find in [13]. The leading company Tejin-Aramid, using the dry processing method of UHMWPE reactor powder produces Endumax films with high modulus E= 170 GPa but with σ = 2.2 Gpa, which is lower than that of gel-spun fibers. At the same time the lab-scale film-filaments demonstrate mechanical characteristics even slightly exceed those of gel fibers [14-17], though they still are lower than the theoretical estimates of these values.

Conclusion

Thus, not all potential possibilities of the solution-free method have been exhausted and one has to continue searching for the new catalyst systems to improve the particle morphology provided high compactability and drawability, and continue to search for the optimal sintering conditions to produce high quality preform for orientation hardening.

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