“Quick-Stabilizing” Acrylic Precursor for Carbon Fibers

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SUMMARY

Copolymers of acrylonitrile and vinyl bromide, with ca 4\% (by weight) of vinyl bromide, are used as precursors for carbon fibers. The precursor fibers can be stabilized in remarkably short time intervals (15 - 20 min), without fiber damage, and result in carbon fibers (at 1400\degree C) of high quality: tensile strength 3,000 MN/m², modulus 290 GN/m², density 1.7 g/cm³. The chemistry behind these findings is discussed.

Polyacrylonitrile, PAN, as well as its copolymers with a few percent of a comonomer ("acrylics"), appear to be the most widely used starting materials for carbon fibers. (For a more recent review see PEEBLES, 1976.) There are two major reasons for that. On one side, stretched fibers from PAN have a high molecular orientation which can, at least in part, be maintained through the pyrolysis process, provided the fibers are continuously held under stress. This is supposed to be responsible for the high tensile strength and modulus. On the other hand, intra- and intermolecular thermal oligomerization of nitrile groups, in air at relatively low temperatures, leads to highly conjugated, crosslinked, oxidized structures, which make the fibers non-flammable and infusible. Such fibers are said to be "stabilized". They can be further heat-treated in an inert atmosphere to form "carbon fibers" (>99% carbon). Heating to 1400 - 1600\degree C leads to high tensile strength carbon fibers; with heat treatment up to 3000\degree C, high modulus carbon fibers ("graphite fibers") are obtained.

The oligomerization of nitrile groups is exothermic (6 - 7 kcal/mol; GRASSIE, 1977). As a consequence, the stabilization of the fibers must generally be carried out slowly, to avoid fiber fusion. Residence times in a stabilization furnace of 1 - 2 hours, with a carefully controlled temperature profile, are usual practice.

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We want to report on acrylic carbon fiber precursors that can be stabilized in as short a time interval as 15 - 20 min, and yet - upon the usual carbonization treatment - resulting in carbon fibers of excellent properties. The technological advantage resides in either smaller stabilization furnaces, or increased throughput.

The precursor fibers are spun from acrylonitrile/vinyl bromide copolymers (AN/VBr), with VBr concentrations in the range of 4 - 6% (by weight). Vinyl bromide features two important properties which are not found together in any other potential comonomer: a very weak bond (C-Br) which is not involved in main chain bonding, and a small molar volume.

In the absence of ionic additives, the oligomerization of CN groups during stabilization is a free radical process. The initiating radicals are formed by thermal bond breaking. In PAN and in most of its copolymers, main chain carbon-carbon bonds are the weakest bonds. In PAN, this bond has a dissociation energy of 71 kcal/mol. (This and the following bond dissociation energies are taken from STEPANYAN et al., 1972, unless otherwise stated.) Apart from radical formation, main chain bond breaking involves molecular fragmentation, and possible formation of low molecular weight fuel.

In AN/VBr copolymers, the C-Br bond is by far the weakest bond, with a dissociation energy of only 61.4 kcal/mol. During stabilization, this bond is the first to break, at a temperature significantly below that required for main chain scission, and without the fragmentation of macromolecules. Hence, the oligomerization of CN groups can start at a lower temperature than with PAN or most of its other copolymers, thus spreading the heat evolution over a greater temperature range, and preventing fiber fusion. Moreover, extensive crosslinking by intermolecular CN oligomerization (cf. HENRICI-OLIVE and OLIVE, 1981), at relatively low temperature, reduces the formation of small fragments in the temperature range of main chain scission.

As mentioned above, PAN fibers have the particular property of high molecular order (for a review see HENRICI-OLIVE and OLIVE, 1979). Vinyl bromide as a comonomer does not essentially reduce this order, due to the small volume of the bromine side chain. Since the carbon fiber tensile properties depend on orientation, the advantage is evident. Intimately related to the high molecular order is a relatively high melting point which helps to prevent fiber fusion, permitting thus stabilization at higher temperatures, as compared to other acrylic precursors. Since higher reaction temperature means increased reaction rate, there is a great potential for short stabilization time.

From the point of view of molecular order and melting point, pure PAN would appear to be the most convenient carbon fiber precursor. However, it has a number of disadvantages: no easily breaking bond; very poor oxygen permeation (SALAME, 1967), taking into account that oxygen is a necessary ingredient in the further course of stabilization (see, e.g., PEEBLES, 1976; COLEMAN and PETCAVICH, 1976); moreover, pure PAN presents difficulties in wet-spinning.