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ABSTRACT

The implementation of nano-sized TiO₂ dispersions for mass coloration of polyimide fibers is considered in the paper. Titanium dioxide (TiO₂) is not classified as hazardous according to United Nations (UN) Globally Harmonized System of Classification and Labeling of Chemicals (GHS). The stability of TiO₂ dispersions in dimethylformamide (DMF) medium in presence of different surfactants as well as the viscosity of poly(amic) acid spinning solutions was investigated. It was illustrated that nano fraction of mineral pigment increase the stability of spinning medium. Moreover, the introduction of 4,5% TiO₂ in poly(amic) acid stabilized with 0,24% of surfactant (leukanol) caused the increasing of thermal stability on 10°C in comparison with non-colored fibers. Proposed method enables to get light colours and improve the thermal stability of polyimide fiber. The application of TiO₂ in the mass coloration of fibers does not cause dangerous effect on consumer because the pigment is tightly connected with polymer inside fiber structure.

KEYWORDS


INTRODUCTION

High performance fibers (including the polyimide fibers) are generally characterized by remarkably high unit tensile strength and modulus as well as resistance to heat, flame, and chemical agents that normally degrade conventional fibers. The aromatic polyimides are well known in films, enamels as well as in fibers due to their excellent resistance to high temperatures. Aromatic polyimide fibers have a very high level of thermal and dimensional stability and property retention at high temperatures, as well as a good, all-round level of other fiber properties (Herman, 2007).

These fibers are difficult to dye using classical methods (in a special solution containing dyes) due to their chemical structure and absence of sufficient amount of active groups on surface for binding dyes. Coloration of fiber-forming polyheteroarylenes from their synthesis to the textile production with using known methods (Cates & Fitzgerald, 1987; Hamid, 1993; Hamid & Va, 1992; Hartzler, 1991; Johnson, 1988; Kobayashi et al., 1995; Nicolai & Nechwatal, 1994; Riggins & Hansen, 1994; Riggins & Hauser, 1990) in processes of their realization in the industry lead to decrease in level of
mechanical and thermal characteristics and also don’t allow to receive various colors. The proposed in the study method of coloring was aimed to overcome these disadvantages (keeping safe the mechanical and thermal characteristics of fibers).

The diversity of dyeing methods is described in the Handbook of Textile and Industrial Dyeing (Clark, 2011). The mass coloration was employed in the study. It is an increasingly important alternative to classical methods of dyeing textiles using water-soluble or dispersed dyes applied from as aqueous bath. Mass coloration (or spin coloration, solution dyeing, and dope dyeing) yields colored fibers by introduction of the coloring material during formation of fiber forming polymer. The color is thus dispersed within the filament rather than absorbed on its surface (Holme, 2000). Mass coloration has low energy costs, no effluent or water costs, no dyehouse (dyebath) investments, reduced labor costs. It supports the large batches of uniform shade and makes the higher fastness properties possible.

The polyimide fibers have a yellow-brown original color. The aim of study was to obtain the light colors of fibers. For this purpose, the white pigment TiO$_2$ in organic solution was applied. Titanium dioxide (TiO$_2$) is a white solid inorganic substance not classified as a hazardous according to United Nations (UN) Globally Harmonized System of Classification and Labeling of Chemicals (GHS). TiO$_2$ is the ninth most common element in the earth’s crust. TiO$_2$ is typically thought of as being chemically inert. Since the introduction of TiO$_2$ as a commercial product in 1923, there have been no identified health concerns associated with its exposure among consumers or general population. These facts are supported by the results from four large epidemiology studies involving more than 20,000 workers in the titanium dioxide manufacturing industry in North America and Europe which indicate no association with an increased risk of cancer or with any other adverse lung effects (Boffetta et al., 2001; Boffetta et al., 2004; Chen & Fayerweather, 1988; Fryzek et al., 2003; Garabrant et al., 1987; Ramanakumar et al., 2008). These studies did not specifically differentiate between the ultrafine and pigmentary TiO$_2$.

The introduction (bringing in) of TiO$_2$ directly into the spinning solution can cause the reduction of physical properties of fiber as well as reduction of productivity of process because the extrusion nozzles can be blocked. To solve this problem, the stability of spinning solution was investigated depending on concentrations of TiO$_2$ and surfactants. Sedimentation analysis as well as atomic force microscopy was applied to obtain the dispersion with nano-fraction of TiO$_2$. The effect of pigment and surfactants on thermal properties of polyimide fibers was explored and the optimal concentrations proposed.

In other words, first of all, the stability of TiO$_2$ dispersions in dimethylformamide (DMF) medium in presence of different surfactants was investigated. The selection of the best surfactants was made. The sedimentation method was applied to find optimal concentrations of surfactants and TiO$_2$ in DMF.

Secondly, the study of viscosity of solution of poly(amic) acid spinning solutions were measured and the obtained results illustrated the increasing the stability in presence of nano fraction of mineral pigment.

Thirdly, the best time of sedimentation (20min) for selected optimal solutions contained 72% nano sized particles was determined using the atomic force microscopy (AFM).

Finally, the thermal stability of colored fibers was explored using thermogravimetric analysis (TGA). Introduction of 4,5% TiO$_2$ in poly(amic) acid stabilized with 0,24% of surfactant (leukanol) caused the increasing of thermal stability on 10°C in comparison with non-colored fibers.

Application of TiO$_2$ for the mass coloration is safe for final product as titanium dioxide at high temperature condition of fiber manufacture tightly connected with polymer inside fiber structure.

**MATERIALS AND METHODS**

**Titanium Dioxide (TiO$_2$)**

TiO$_2$ particles naturally crystallize in three forms: rutile, anatase, and brookite. Both rutile and anatase have a tetragonal ditetragonal dipyramidal crystal system but have different space group lattices. Brookite has orthorhombic crystal system. The titanium atoms are grey and the oxygen atoms are red.
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