Formation and properties of polyvinyl butyral-transition metal alkoxides hybrid hollow fibers using air gap spinning

博 士 論 文 内 容 の 要 旨

専攻名 総合創成工学

分野名 繊維先端工学

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１ 論文題目（英文の場合は，和訳を付記すること）

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(エアギャップ紡糸を用いたポリビニルブチラール-遷移金属アルコキシドハイブリッド中空糸の形成と特性)

２ 要 旨（和文 2,000 字程度又は英文 800 語程度にまとめること。）

Organic/inorganic hybrid fibers (OIHFs) of micro-level or nano-level are a class of flexible pseudo-1D materials that have attracted attention for a range of applications due to their unique organic/inorganic species domains and relatively high aspect ratio. OIHFs generate new characteristics of polymers and compounds through the combinations of synergistic interactions between each organic and inorganic entity. These interactions are generally done by chemical bondings like; covalent bonds, ionic bonds, hydrogen bonds, van der Waal's forces, and electrostatic forces which greatly determine the properties of hybrid components. At the same time, hybrid materials always recompense each other’s limitations by introducing new features. During this period, the study of organic-inorganic hybrid materials focused on the following points: firstly, exploration of new preparative methodology for hybrid materials; secondly, new combinations between different materials; thirdly, functionalization of hybrid materials; and fourthly, modification of hybrids for industrial applications. That’s why it has been a growing demand to develop facile methods for producing these OIHFs and materials. Currently, various fabrication procedures like; sol-gel process, liquid phase, wet spinning, electrospinning etc. has been adopted to synthesize homogeneous OIHFs with controlled

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overall structures and properties. The unique behavior of hybrid materials offers promising solutions to some crucial challenges in the field of water treatment, energy applications, biocatalyst carriers, etc. OIHFs are commonly developed from a polymer including cellulose acetate (CA), polyvinyl alcohol (PVA), polyacrylonitrile (PAN), polysulfone (PSF), polyurethane (PU), and conducting polymer fibers, such as polypyrrole (PPy), polyaniline (PANI), and (PEDOT); are bonded with a wide variety of inorganic materials.

Recently, poly(vinyl butyral) (PVB) has gained attention as a base polymer of the hybrid matrix due to its hydrophilicity, efficiency in solvents, and environment-friendly nature. PVB is an excellent organic component for the fabrication of organic/inorganic hybrid materials due to its good compatibility with inorganic compounds.

This thesis reported on the preparation of polyvinyl butyral (PVB)-zirconia hybrid hollow fibers by an air gap (dry-jet wet) spinning. As an organic polymer, three kinds of PVB with different degrees of acetalization were used for the spinning solution with ethanol solvent. A skin-core hybrid structure is developed when the PVB spinning solution went through into the coagulation bath due to strong reactivity between PVB and Zr alkoxide at the interface of the spinning liquid. The formed as-spun hybrid fiber was led by the diffusion of Zr alkoxide to the outer part of the interface, while the unreacted part of PVB remained in the inner part. The fiber contained 20 wt.% PVB with a 2 cm air gap confirms an effective average diameter of about 1016 μm which is strongly influenced by spinning solution viscosity. The variation of maximum Zr content (13.25%~21.07%) confirms the asymmetry of coordinate bonding that occurred in the internal and external surfaces.

Afterward, PVB-Zr alkoxide hybrid fiber is utilized as an enzyme immobilization carrier, especially for β-galactosidase and lipase where both enzymes are physically entrapped-immobilized into the fiber matrix. The enzyme-immobilized PVB-ZrO_2 hybrid fiber displays its constancy in citrate buffer, phosphate buffer, electrolyte solution, and also other organic solvents. To determine the activity of the β-galactosidase enzyme into the fiber network, the measured apparent Michaelis constant K_m and maximum velocity V_{max} were 0.079 mol/l and 4.9 μmol.min-1 respectively; which is better in context to the similar hybrid fiber.

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Furthermore, the activity retained was found to be 90%, after 10 reaction cycles which is vastly greater than other support matrix. Besides, in the scope of ester synthesis, conversion of citronellyl acetate was achieved 52% after 50 hrs by immobilized lipase (IL) in hexane solution.

Lastly, this thesis reported on the development of PVB-amTiO_2 hybrid hollow fibers by the same air gap spinning method described earlier. Unlike PVB-ZrO_2 hybrid fiber, PVB-amTiO_2 hybrid fiber demonstrates a slow reaction between PVB acetyl groups and alkoxides; which results a limp structured fiber. Later on, the developed fiber showed efficiency in the removal of cationic methylene blue (MB) dye from the simulated aqueous solution. Dye removal was mainly led by the adsorption mechanism which shows (68~70%) efficiency. The measured adsorption kinetics was best fitted with the pseudo-second-order model, signifying that adsorption was directed by chemisorption.