学位論文内容の要旨

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学位論文題名

Surface modification of synthetic polymer sheet by direct electrospinning of cellulose acetate

(セルロースアセテートの直接電界紡糸による合成高分子シートの表面改質)

Cellulose is the most abundant component of biomass, and has several advantages over general synthetic polymers and metallic materials: extremely high elastic modulus and low linear expansion coefficient. Natural cellulose has cellulose I polymorph, and regenerated cellulose, e.g. rayon, has cellulose II polymorph. Both crystalline celluloses exhibit a larger specific elastic modulus (Pa/g) than iron. Therefore, surface properties (surface mechanical strength and polarity) of synthetic polymers could be altered and controlled by coating them with cellulose.

An objective of this study is to develop a method to coat the surface of synthetic polymer with fine cellulosic fibers with a micron-scale diameter. To achieve this objective, I made a fabrication strategy as follows. i) Direct dry-electrospinning of cellulose acetate (CA) solution onto a synthetic polymer sheet, ii) fixation of CA to the sheet, iii) saponification of the fixed CA to convert it into regenerated cellulose with cellulose II polymorph. I used two types of CA; one was water-soluble CA (WSCA) with a degree of substitution (DS) of ca. 0.9, and the other was cellulose diacetate (CDA) with a DS of 2.5. CDA is well known as a filter material, but it is dissolved in organic solvents, such acetone and dimethylformamide (DMF). Meanwhile, dry-electrospinning of WSCA may be possible under more environmentally-friendly conditions because it requires no harmful solvent. I used polyurethane sheet with concave-convex surface as a synthetic polymer sample, which was commercially produced as a polishing agent for preparation of hard and compact disks.

So far, nobody has established direct electrospinning of any types of polymer onto non-electro conductive material, such as synthetic polymers. Thereby, I have intensively investigated to develop the direct electrospinning (process-i) and the fixation (process-ii) in the above fabrication process.

Direct dry-electrospinnings of WACA and CDA solutions onto aluminum foil and PU sheet

As a preliminary experiment, direct dry-electrospinning of two types of CA in several aqueous organic solutions onto aluminum foil as a collector material. Consequently, fine electro-spun fibers without any beads were obtained from 11 wt.% of WSCA solution in 40 wt.% aqueous ethanol, and from 9 wt.% of CDA solution in 90 wt.% aqueous acetone.

These spinning dopes were applied to the electrospinning onto PU sheet as the collector material. As expected, no fiber deposited on the sheet because of the electrostatic repulsion between charged fibers and charged collector. The successful fiber deposition was achieved by neutralizing the collector charge with a commercial anti-static agent.

Fixation of deposited fibers and conversion of CA fibers into regenerated cellulose fibers

Disappointingly, the electro-spun fibers deposited on the PU sheet were easily peeled off from the sheet. The fibers were successfully fixed tightly on the sheet by spraying a mixed solvent system of DMF/ethanol (1:1, v/v) solution several times during the electrospinning. Finally, both types of CA were completely converted into regenerated cellulose fibers by saponification with ammonia vapor for 7 days, which was confirmed by FT-IR and X-ray diffraction.

Analyses of surface properties of CA and regenerated cellulose fiber-deposited PU sheet

Surface morphology and mechanical property were evaluated by microscopic observation and tribology test, respectively. SEM and 3-D microscopic observations revealed that the fine fibers were partly fused with PU sheet at the peak of convex. The friction coefficient of the PU sheet dramatically decreased with an increase in the amount of deposited fibers, suggesting that the PU sheet surface became smoother. After saponification, the friction coefficients of the sheets were slightly increased, which might be attributed to the change in the elasticity upon saponification.

In conclusion, I have successfully established a direct electrospinning method of cellulosic solutions onto a non-conductive material, and a fixation method of the resultant fibers. These methods would surely contribute to positive modification of synthetic polymer sheet/film.