

論文の内容の要旨

BIOMATERIAL SCIENCE 専攻

平成 20 年度博士課程 入学

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論文題目 Preparation and characterization cellulose nanofibers and their polymer composites from Indonesian agricultural wastes (インドネシアの農産廃棄物からのセルロースナノファイバーとそのポリマーコンポジットの調製と性状)

The focus of the study was on the isolation, preparation, and characterization of cellulose nanofibers obtained from some agricultural biomasses, such as oil palm empty-fruit-bunches (OPEFBs), coconut husk, and sugar palm fibers. Furthermore, the study also aimed to use the cellulose nanofibers obtained to develop the high performance nanocomposites which as polymer matrix were a hydrophilic polymer, such as poly(vinyl alcohol) (PVA), a hydrophobic polymer, such as poly(methyl methacrylate) (PMMA), and an elastomer polymer, such as polychloroprene (PCR). In the following, a brief description of some important achievements is given.

1. Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB) (Chapter 2)
Cellulose nanofibers were produced by hydrolyzing oil palm empty-fruit-bunches with sulfuric acid. The effect of hydrolysis time on the structure and properties of the nanofibers was investigated. Fourier transform infrared spectroscopy was employed to evaluate the change of chemical composition. Atomic force microscope images showed that the average thickness of the nanofibers ranged from 1 to 3.5 nm as the hydrolysis time was varied. Longer hydrolysis time produced a higher yield of dispersed nanofibers; whereas the degree of crystallinity and the degree of polymerization decreased with increasing hydrolysis time. The degradation of nanofibers with higher sulfate group content started at a lower temperature.

2. Effect of pre-acid-hydrolysis treatment on morphology and properties of cellulose nanowhiskers from coconut husk (Chapter 3)
Three different pre-acid-hydrolysis treatments were used to treat coconut husk fibers for preparing cellulose nanowhiskers by sulfuric acid hydrolysis. The effects of those treatments on the morphology and properties of the nanowhiskers were investigated. FTIR was employed to evaluate the change of chemical composition due to different pre-acid-hydrolysis treatments. AFM images showed that there was no significant difference of size of nanowhiskers obtained by different pre-acid-hydrolysis treatment, 2-3 nm of average thickness. The thermal decomposition of nanowhiskers shifted to higher temperatures with removal of hemicellulose and lignin.

3. Effect of sulfate group on mechanical and thermal properties of cellulose nanowhiskers from sugar palm fibers (Chapter 4)
In this study, cellulose nanowhiskers from sugar palm fibers were prepared by sulfuric acid hydrolysis. The effect of sulfate group on mechanical and thermal properties of cellulose nanowhiskers was investigated. Nanowhiskers films without and with neutralization were produced using a vacuum filtration technique and the mechanical properties were determined. AFM images showed that the thickness of neutralized and un-neutralized nanowhiskers was similar of each other. The tensile strength and young's modulus of nanowhiskers film with neutralization was higher than that of without neutralization. The degradation of nanowhiskers with sulfate groups started at lower temperature. WAXD analysis showed that there was no significant difference in the degree of crystallinity of neutralized and un-neutralized nanowhiskers. Meanwhile, FTIR and Raman analyses indicated that there was structural change of cellulose after acid hydrolysis.

4. Effect of sonication time on morphology and properties of poly(vinyl alcohol) alone and its cellulose nanocomposites (Chapter 5)

Hydrogen bonding between the cellulose chains in cellulose nanofibers causes agglomeration or entanglement of nanofibers in the polymer matrix. Therefore, to reduce the interaction between hydroxyl groups, the cellulose nanofibers are maintained in the form of suspension in water. Thus the use of cellulose nanofibers for the composites is limited to water soluble polymers.

Poly(vinyl alcohol) (PVA) is a water soluble polymer which its use is widespread in many industrial applications due to its biodegradability, biocompatibility, chemical resistance and excellent physical properties.

Two series of PVA films with and without high dispersed nanofibers were prepared by varying the sonication time. The effect of sonication time on the morphology and properties of the nanocomposite films were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), FTIR and Raman spectroscopy, wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and tensile test. The results showed that there was optimum sonication time whereas the mechanical properties of the nanocomposite films increased. Sonication time within 9 min was able to maintain the crystallinity and thermal stability of PVA nanocomposites. Meanwhile the thermal stability of PVA nanocomposites shifted to lower temperature after 20 min of sonication time.

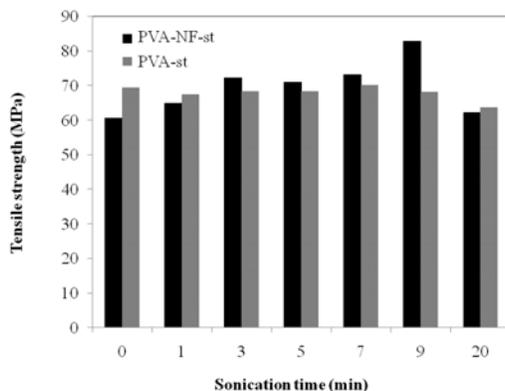


Figure 1. Tensile strength of neat PVA and its nanocomposites with different sonication time.

5. The morphology and properties of Poly(methyl methacrylate) (PMMA) cellulose nanocomposites prepared by immersion precipitation method (Chapter 6)

One major drawback related to the use of cellulose nanofibers for polymer nanocomposites is their inherent difficulty to disperse in non-polar solvent, because of the hydrophilic nature of cellulose. Agglomeration is a common problem when hydrophobic polymers are filled with cellulose nanofibers. This phenomenon causes the worse adhesion between cellulose nanofibers and polymer matrix. Agglomeration usually occurs during the blending. Thus, it is a major challenge how to obtain well cellulose nanofibers dispersion in polymer matrix.

Poly(methyl methacrylate) (PMMA) is a hard glassy amorphous plastic, hydrophobic and low water sorption. In this study we produced PMMA-cellulose nanofibers nanocomposites by immersion precipitation method. In first step, dispersed cellulose nanofibers in N,N-dimethylacetamide (DMAc) were prepared for making it easy to mix with PMMA solution. Thereafter, PMMA-cellulose nanofibers nanocomposites were prepared by immersion precipitation method in non-solvent (water and methanol). With this method the good compatibility and homogenous dispersion of cellulose nanofibers in a polymer matrix could be achieved. The AFM image showed that the average thickness of the nanofibers dispersed in DMAc was around 2 nm and the nanocomposites obtained were translucent. The X-ray analysis showed that neat PMMA and all its nanocomposites had similar patterns, broad non-crystalline peaks. The tensile modulus and strength increased with increasing nanofibers content. Dynamic mechanical analysis (DMA) profiles showed that the presence of cellulose nanofibers affected the storage modulus of PMMA nanocomposites over all the studied temperature range.

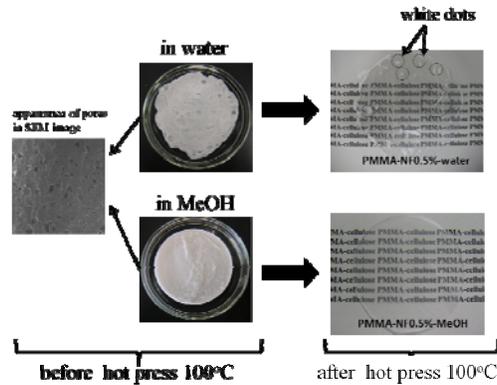


Figure 2. Change of nanocomposite appearance after immersion in non-solvents, before and after hot press 5 MPa at 100°C.

6. Surface acetylation of cellulose nanofibers and its reinforcing function in polychloroprene (PCR) (Chapter 7)

Although some non-polar solvents, such as DMAc, can disperse cellulose nanofibers well, this solvent is very limited in terms of practically, especially for preparing elastomer-cellulose nanocomposite. Therefore, the surface properties of nanocrystals should be modified to improve dispersion and interfacial adhesion in elastomer matrix. Concurrently, during modification the intrinsic structure of the nanofibers, i.e. the original crystalline structure, should not be destroyed. In this work, with the substitution of hydroxyl groups by acetyl groups on the cellulose nanofibers surface, acetylated cellulose nanofibers exhibited improved dispersion in dichloromethane solvent, a decrease in surface polarity. When the acetylated cellulose nanofibers filler was introduced at 3 wt % into the polychloroprene-based polymeric matrix, the tensile strength of the polychloroprene-cellulose nanocomposite was enhanced by 341% and the Young's modulus was 7-fold greater than those of the neat polychloroprene sheet. This was mainly attributed to interfacial adhesion between filler and matrix. In the meantime, the addition of acetylated cellulose nanofibers maintained the thermal property of the nanocomposites close to the neat polychloroprene.

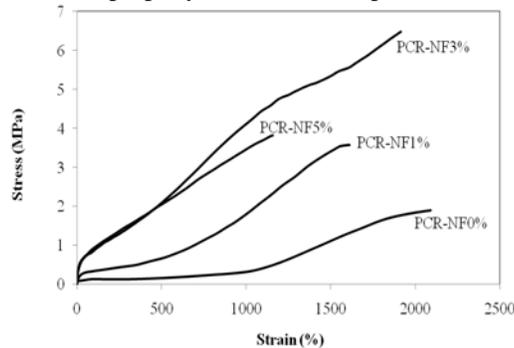


Figure 3. typical stress-strain curves from tensile tests for neat polychloroprene and its nanocomposites