Wrocław, October 31, 2024

mgr inż. Krzysztof Jan Legawiec
Department of Process Engineering and Technology
of Polymer and Carbon Materials

Abstract of Doctoral Dissertation

Cellulose nanostructures as modifiers of interfacial properties in dispersive systems containing fine solid particles

An important group of industrial processing operations consists of those aimed at the separation of solid particles dispersed in a liquid. Examples include coagulation, flocculation, and flotation – key elements of process systems for ore beneficiation and water purification. Control of such processes is achieved by modifying the physicochemical properties of phase boundaries using various chemical substances.

Despite the continuous advancement of knowledge regarding the mechanisms and methods of conducting these processes, new and more complex problems directly related to their efficiency have emerged over the years. One of these problems is the formation of fine solid particles at various stages of processing, whose separation is significantly hindered due to their small sizes. This presents a significant research challenge because only particles within a specific size range can undergo separation processes, particularly flotation. One known solution to this problem is the aggregation of particles using the flocculation process, which is conventionally carried out using ionic flocculants. These substances are most often synthetic in origin, making them resistant to biodegradation and potentially harmful to living organisms. Therefore, in this work, it was decided to design and investigate new reagents capable of aggregating fine solid particles based on the most common biopolymer – cellulose.

The dissertation consists of two parts. In the first part, an evaluation of the existing state of knowledge was conducted in a manner that allows for a critical assessment of the solutions adopted in the research section. Topics related to conducting aggregation processes under industrial conditions were discussed, as well as directions for searching for sustainable alternatives to currently used chemical reagents. Subsequently, a description of methods for the chemical modification of cellulose fibres was presented. In the following chapters, the nature of aggregation processes was characterized, and basic issues related to the thermodynamics of dispersive systems were discussed.

The research part begins with a discussion of the doctoral dissertation objectives, which focus on hypotheses stating that aminated cellulose nanostructures (ANC) increase the removal rate of fine mineral particles from suspensions and that they can positively affect the state of phase boundaries in the gas-solid-liquid system by increasing flotation efficiency.

The first research chapter concerns the development of a method enabling the production of ANC with varying hydrophobicity and degrees of substitution with n-alkyl amines (DS). Cellulose functionalization was carried out in a two-step reaction. The first step involved the regioselective oxidation of cellulose to 2,3-dialdehyde cellulose using sodium periodate. To control the aldehyde content, a mathematical reaction model was created based on a central composite design. The process variables were temperature, the molar ratio of sodium periodate to cellulose, and time. This approach identified reaction parameters that allow obtaining DAC with aldehyde contents of 1.5; 3.0; and 4.5 $mmol \cdot g^{-1}$. The second step involved the reduction of aldehyde groups to corresponding amines of varying aliphatic chain lengths (ethyl-, butyl-, and hexylamines) in the presence of 2-picoline borane. The modified materials were disintegrated to nanometric sizes using a high-pressure homogenizer and characterized using DLS, STEM/TEM, XRD, ^{1}H NMR, FTIR, ELS techniques, and elemental analysis for accurate DS estimation. To demonstrate the ability to modify phase boundaries, not only the water contact angle of films formed from ANC was examined, but also the surface free energy was determined using the van Oss method. The result of these studies was the development of a method enabling the production of ANC with controlled hydrophobicity, ranging from approximately 50° to 100° in water

contact angle, in increments of about 6.6°, and with varying surface electrokinetic potential, depending on DS.

In the second chapter, the impact of the obtained ANC on aggregation processes in a two-phase liquid-solid system was thoroughly investigated. Quartz and pyrite fine particles were used in these studies. The influence of nanostructure concentration, DS, type of substituted amine, and pH of the system on flocculation efficiency was analyzed in detail. These studies were conducted using the SMLS technique, and the morphology of the resulting flocs was observed using an optical microscope. The degree of fine particle removal from solutions was assessed based on transmittance size analysis. The discussion regarding the process mechanism was based on calculations using the extended DLVO theory and electrokinetic potential measurements. As a result, it was determined that the critical factor determining the efficiency of ANC adsorption on mineral surfaces is the system pH, which is related not only to the surface potential of the particles but also to the behaviour of the amine group present in the ANC structure. These studies also showed that as DS increases, attractive interactions between particles are strengthened, which, at an optimally selected concentration, leads to effective suspension flocculation.

The final stage of the dissertation concerned the influence of ANC on the flotation response of selected systems. In the first phase, the foam-forming properties of ANC solutions were examined, proving that these nanomaterials do not act as frothers in the systems. Studies conducted in a Hallimond flotation cell showed that the yield of fine quartz particles could be increased from about 15% to 60% using ANC with high DS at a dosage of 1 mg per gram of mineral. In the case of pyrite, the yield increased from 10% to 80% also after applying nanostructures with high DS, but at a higher dosage of 10 mg per gram of mineral. Studies on the efficiency of forming a solid aggregate with an air bubble were carried out by determining the degree of bubble coverage. The highest values of this parameter, approximately 110°, were recorded in systems containing 2,3-dibutylaminated cellulose nanostructures with the highest DS. The obtained contact angle values were proportional to the flotation yield. Similar trends were observed in the water contact angles of pellets made from flocculant-conditioned flotation feed..

The obtained research results allow for the development of a new understanding of the impact of ANC on phase boundaries and help organize the current, albeit fragmented, knowledge about the mechanisms of the processes occurring on them. They indicate that ANC can find their place as aggregation reagents.