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Thermosensitive flocculation of aqueous suspension using a UCST polymer

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In this work the thermosensitive aggregation and breakage of a model TiO_2 suspension in water in the presence of poly(acrylic acid) – a polymer characterized by Upper Critical Solution Temperature (USCT) behavior, is presented. Contrary to the Lower Critical Solution Temperature (LCST) polymer flocculation, in this case the suspension is stable at higher temperatures and the particles aggregate upon cooling. In the experiments the suspension was destabilized in a baffled mixing tank equipped with a mechanical stirrer and thermostating jacket. Due to the extremely high sensitivity of the system to the change of any of the process parameters the aggregation process was investigated via digital analysis of the microscopic photographs. The UCST thermo-sensitive flocculation in an aqueous environment was found to be reversible and as such suitable to be used in processing run under a cyclic regime.

Keywords: aggregation, thermosensitive polymers, poly(acrylic acid), Lower Critical Solution Temperature (LCST), Upper Critical Solution Temperature (UCST)

INTRODUCTION

Nowadays extensive research is dedicated to the novel approaches to aggregation phenomenon [1]. For example, *N*-isopropylacrylamide is known for its Lower Critical Solution Temperature (LCST), *i.e.* the polymer is hydrophilic below LCST and becomes hydrophobic above this temperature, this process is reversible and can be run repeatedly [2]. When derivatives of such polymers are used as flocculants the temperature greatly influences the particle size distribution [3 − 5] or sediment volume [6, 7]. Moreover, they can be used simultaneously in flotation due to their hydrophobic nature [8, 9]. Thermosensitive aggregation has two significant advantages over the conventional process. First, it can be triggered and reversed on demand and therefore the aggregation and breakage phenomena may be repeated in a cyclic manner. Second, thermo-sensitive polymers can be tailor made to show affinity to chosen substances, thus stimuli-controlled processes may be realized in a new way.

In general Upper Critical Solution Temperature (UCST) polymers have attracted only a small fraction of the attention devoted to their LCST counterparts, most likely because the UCST transition is usually less drastic (the UCST is a wider range of temperature than the sharp LCST of PNIPAM) and very strongly dependent on the solution pH and salinity in the suspending media [10]. To the best of our knowledge there have been no reports of UCST flocculation of solid dispersions in water, even though the most popular UCST polymer – poly(acrylic acid) (PAA) is easily available commercially. In this paper the results of flocculation of a model TiO_2 aqueous suspension with a UCST polymer are presented. To the best of our knowledge UCST flocculation of water-dispersed solid suspensions has not been studied up to the present.

EXPERIMENTAL

A model suspension of TiO_2 particles (Avantor Performance Materials Poland S.A.) in reverse osmosis water was used. The solid particles in the form of white powder were weighted on an analytical balance and transferred to a small beaker. Subsequently a dense sludge was created by the addition of a small portion of RO water. Poly(acrylic acid) was used as the flocculating agent. It was received in the form of 25% w/w water solution (Avantor Performance Materials Poland S.A., molecular weight equal to 240 000 g/mol). In order to enable the hydrophilic-hydrophobic transition the addition of salt was required. For this purpose potassium chloride was used (pure for analysis, Avantor Performance Materials Poland S.A.).

In order to verify the polymer dosage impact on the flocculation performance three different dosages were investigated, *i.e.* 10 mg/g, 100 mg/g and 1000 mg/g. Unfortunately the natural

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consequence of different polymeric acid concentrations was a change of the solution's pH. This in turn influenced the location of the UCST point. During thermo-sensitive aggregation the driving force of flocs creation results from the hydrophobic interactions between the solid particles. The magnitude of these interactions depends directly on the temperature. Therefore, it was decided that in all the experiments a constant UCST value will be preserved at the expense of a pH value change (Table 1). Contrary to the standard flocculation experiments in which the flocculation performance is investigated from the moment of polymer addition, in the presented cases the polymer solution with a strictly determined UCST point had to be prepared before the aggregation experiments. Next, the solid particles in the form of a dense sludge were introduced to the mixing tank and the observations initiated. The final concentration of solid particles during all the experiments was equal to 12 g/dm^3.

The flocculation experiments were performed in a thermostated mixing tank equipped with 4 baffles and a mechanical 3-blade marine propeller (400 RPM). The key dimensions of the laboratory setup are presented in Fig. 1. During solution preparation it was found that the value of the UCST depends on a very delicate balance between the component concentrations. Even a small change in the salt concentration or pH value influenced the UCST substantially.

Therefore, it was decided to analyze the UCST flocculation on the basis of microscopic photographs. The authors of this work were aware that a large part of the suspension particle population of submicron size were not visible on the photographs. However, the proposed approach yielded results which proved the scientific goal of this work. It has to be emphasized that the biggest disadvantage of laser sizer measurements of particle size distribution is the possibility of sample contamination by residuals left in the sample circulation loop of the apparatus.

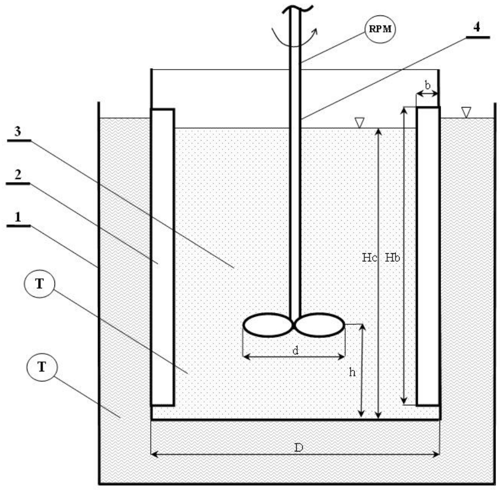

Fig. 1. Mixing tank scheme: 1) thermostated jacket, 2) baffle, 3) mixing tank, 4) propeller. Dimensions: D = 0.098 mm, d = 0.038 m, b = 0.01 m, H_c = D, H_b = D, h = ⅓H_c.

The measurements were made as follows. First, the polymer solution, together with salt addition, was heated to 318 K. Next, the titanium oxide sludge was transferred into the tank. From that moment the suspension was mixed for 10 minutes. After this period of time a sample was taken using a preheated plastic pipette with a wide end and transferred on to a custom-made thermostated microscope slide. The photographs of the aggregates were taken using a biological Olympus CH30 microscope with a CMOS camera. 10 samples in total were collected for each polymer dose. 10 photographs were taken of each sample.

Next, the temperature was decreased to 298 K and once again after 10 minutes 10 samples were taken. The time needed to investigate one sample (taking a sample using a pipette, placing it on the microscope slide and taking 10 photographs) was equal to approximately 20 seconds. The measurements were repeated several times in order to prove their repeatability.

During the next step the photographs were digitally processed using MultiScanBase software. First, all the photographs were converted into grayscale. Second, for each photograph different

Table 1. Experimental data for the polymer solutions.

Polymer dose [mg·g^{-1} TiO_2]	Polymer concentration [% w/w]	pH	Salt concentration [M]	UCST [K]
1000	1	2.42	1.50	308
100	0.1	3.11	0.43	309
10	0.01	3.88	0.55	310

kinds of anomalies were manually removed (e.g. noises etc.) using a set of filters (median filter for noise reduction, averaging background brightness filter and sharpening filter - if necessary). Subsequently, they were transformed into black and white figures. The number and size of the aggregates were determined using a dedicated algorithm included in the software. Finally, the fractal dimension of the aggregates was determined using the same figures. For this purpose HarFA 5.4 (Harmonic and Fractal Analyzer) software was used [11] which employs a box counting method (2D fractal dimension).

RESULTS AND DISCUSSION

Regardless of the polymer dosage all the polymer-treated TiO_2 suspensions behaved similarly at temperature above the UCST (Fig. 2).

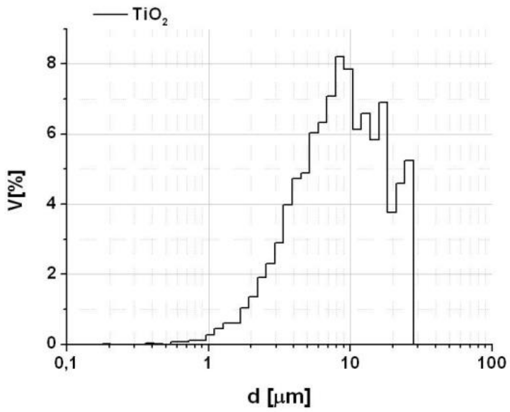

Fig. 2. Particle Size Distribution of the TiO_2 suspension in water without polymer addition.

The primary suspension had the Sauter diameter equal to 6.11 μm. The fractal dimensions of the particles were equal to 1.87 (std. dev. 0.05). The diluted suspension of TiO_2 has a positive zeta potential at low pH values [12]. Therefore, after addition of PAA some aggregation is present for all the dosages due to charge neutralization and bridging (compare Fig. 2, 3 and 4).

The particle size distribution is only slightly dependent on the dosage which clearly indicates that poly(acrylic acid) has a limited flocculation ability at elevated temperatures. The Sauter diameters were equal to 47.44 (fractal dimension equal to 1.53, std. dev. 0.10), 41.91 μm (fractal dimension equal to 1.57, std. dev. 0.12) and 67.17 μm (fractal dimension equal to 1.81, std. dev. 0.11) for 10 mg/g, 100 mg/g and 1000 mg/g dosages, respectively.

When the temperature was reduced to 25°C (below the polymer's UCST) the aggregation could be seen with the naked eye for the two highest

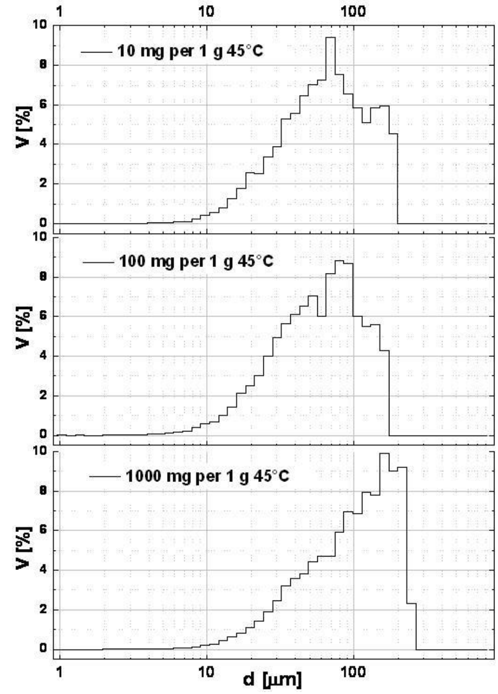

Fig. 3. Particles Size Distribution of TiO_2 with different PAA dosage. At 45°C (above the UCST) the polymer is in the hydrophilic form.

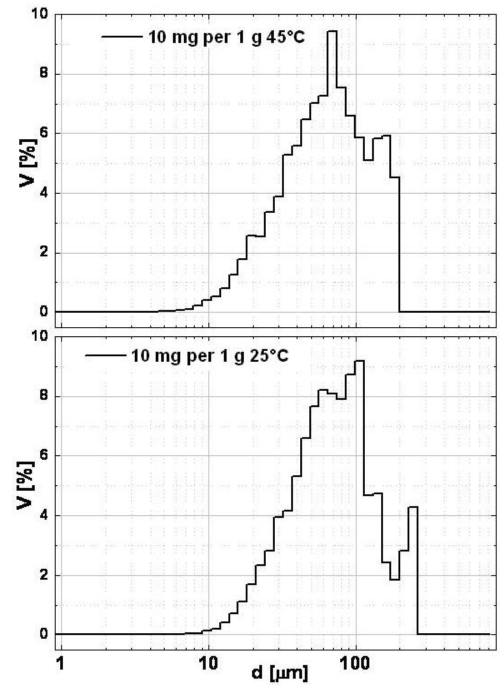

Fig. 4. Particle size distribution of TiO_2 with PAA (10 mg/1g dose) at 45°C (top panel) and 25°C (bottom).

polymer doses. In the case of a 10 mg/g dosage a shift in Particle Size Distribution can be observed upon cooling (Fig. 4).

The mean diameter achieved a value equal to 54.81 μm (fractal dimension equal to 1.70, std. dev. 0.08). In the case of higher PAA dosages (100 mg/g and 1000 mg/g) the formation of very large aggregates (Fig. 5) clearly indicates that the polymer starts to act as a very effective flocculant after cooling below the UCST. The PSD (as well as the mean diameter and fractal dimension) at 25°C for these dosages are not presented because with such large aggregates (exceeding the size of the camera frame) it was not possible to obtain images allowing for a meaningful analysis. However, it has to be emphasized that one can easily find aggregates larger than 1 mm.

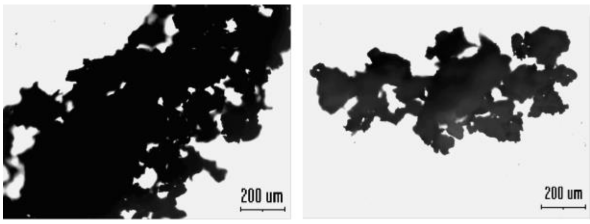

Fig. 5. Aggregates observed at 25°C with a 100 mg/1g PAA dosage.

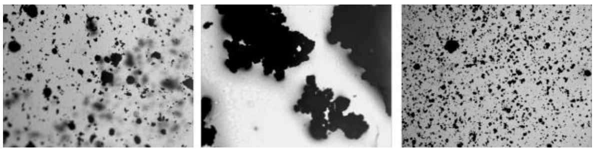

Fig. 6. Reversibility of the thermoresponsive UCST flocculation: TiO_2 suspension with 1000 mg/g of poly(acrylic acid) at 45°C (left), 25°C (middle) and after heating back to 45°C (right).

After cooling the suspension obtained with 1000 mg/g PAA the sludge was heated back to 45°C. The large aggregates present at 25°C are absent from the images taken after heating, proving the reversibility of the UCST-type thermoresponsive flocculation which is crucial from the point of view of the potential practical applications (Fig. 6).

CONCLUSIONS

A reversible flocculation process was demonstrated on a UCST polymer – poly(acrylic acid) and TiO_2 solid aqueous suspension. For all the studied polymer dosages (10, 100 and 1000 mg/1g of TiO_2) the suspension was stable at a temperature above the polymer's UCST (45°C) and aggregation was observed in all the samples upon cooling to 25°C (below the UCST). In the case of medium and high polymer dosage very large (> 2 mm) aggregates were formed. Breakage of the aggregates was observed after heating the sediment providing a clear proof of the process reversibility. The experimental results presented herein show that UCST-type thermosensitive polymers can be used as flocculating agents in analogy with their more popular LCST counterparts which imply possible applications in separation, process control and catalysis.

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ТЕРМОЧУВСТВИТЕЛНА ФЛОКУЛАЦИЯ НА ВОДНИ СУСПЕНЗИИ С ИЗПОЛЗВАНЕТО НА UCST ПОЛИМЕР

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(Резюме)

В тази работа се изследва термочуствителното агрегиране и разпадане на моделна суспензия от TiO_2 във вода в присъствие на поли-акрилова киселина – полимер с висока критична температура на разтворимост (USCT). Противно на флокулацията при ниска критична температура на разтворимост (LCST), в разглеждания случай суспензията е стабилна при висока температура и частиците се агрегират при охлаждане. При проведените експерименти суспензията се дестабилизира в смесителен съд с прегради при механично разбъркване и термостатиране. Поради голямата чувствителност на системата агрегирането беше изследвано чрез цифров анализ на микроскопски снимки. Намерено е, че UCST-термочувствителната агрегация във водна среда е обратима и подходяща за работа в цикличен режим.