

Preparation and Characterization of a High Performance Emulsion Using a Polymeric Emulsifier and AKD

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An alkylketene dimer (AKD) emulsion was prepared using a neotype polymeric emulsifier. The water resistance, surface tension, stability, grain diameter, and contact angle of the obtained AKD emulsion were investigated under different conditions, such as emulsification temperature, emulsification time, solids content, and amount of emulsifier. The experimental results demonstrated that the sizing effect of the AKD emulsion was fairly good under the following conditions: emulsification temperature, 75°C; emulsification time, 9 min; solids content, 10%; and the amount of emulsifier, 3%.

Keywords: Emulsification; AKD; Polymeric emulsifier

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INTRODUCTION

Traditional acidic papermaking has gradually declined because of its many associated problems. With the continuous development of papermaking technology, an increasing number of researchers have shown interest in using medium and alkaline papermaking due to its unique advantages, such as high paper hydrophobicity, lower sizing reversibility, and paper durability. Therefore, the use of sizing agents has also witnessed a shift from previous rosin sizing to alkenyl succinic anhydride (ASA) sizing and alkyl ketene dimer (AKD) sizing (Lee and Luner 2005; Chen *et al.* 2012; Song *et al.* 2012; Hubbe 2014).

Emulsified AKD is the most widely used neutral sizing agent in China. The word “emulsion” is used here, despite the fact that AKD is a solid at room temperature, because the material is briefly heated above its melting point as it is being dispersed into an aqueous suspension that must contain some form of stabilizer. Although the mechanism of the reaction is not entirely understood, the hydrophobic linear alkyl groups of AKD emulsion are believed to arrange themselves on the surface of paper as it is being dried to form a layer of water resistant film, while its lactone ring reacts with starch or cellulose. This special molecular structure allows the emulsion to be spread on paper. AKD can be applied to paper to provide water resistance and excellent printability; therefore, it is necessary to obtain AKD emulsions with excellent performance, good stability, and low cost (Neimo 1999; Mohlin *et al.* 2006).

The most important thing in preparing emulsions is to find a suitable emulsifier. Different emulsifiers have different hydrophilic lipophilic balance (HLB) values; for

instance, an HLB value of 3 to 8 is suitable for a water-in-oil emulsion and an HLB value of 8 to 18 is suitable for an oil-in-water emulsion. While a single emulsifier is sometimes insufficient for achieving a good emulsion, the emulsification effect of a composite emulsifier is always better, leading to an emulsion with better stability and lower interfacial tension (Shen 2004; Xu *et al.* 2005; Foudazi *et al.* 2011; Tian *et al.* 2011; Wang and Fang 2013).

An increasing amount of research studies have focused on the stability of the AKD emulsion dispersal system in recent years because of the thermodynamic instability of emulsions. The stability of the AKD emulsion is affected by the oligomer content of AKD, and the thermal stability of the system is reduced by the presence of the by-products of dispersants. Additionally, the stability of the emulsion is influenced by thermodynamics and other dynamics besides the emulsifier. The mechanical strength of the interfacial membrane, a high interfacial charge, a thick hydration layer, and the use of various dispersants make the emulsion more stable (Al-Sabagh *et al.* 2002; Derkach 2009; Al-Sabagh *et al.* 2013; Wang and Fang 2013; Zhang and Ni 2014; Al-Sabagh *et al.* 2016).

EXPERIMENTAL

Materials

The emulsifying agent was a copolymer of diallyldimethylammonium chloride and diallylamine, which was prepared in the laboratory. The diallylamine was adjusted to a pH of 5 with glacial acetic acid and then mixed well with DMDAAC at a ratio of 4:100, placed in a water bath and kept at 80 °C, and 0.1% ammonium persulfate was slowly added dropwise over 3 h. After that period of reaction, the solution of sodium bisulfite was added dropwise and the material was held for 0.5 h after discharging. AKD wax powder (industrial grade purity) was purchased from Wilmar Speciality Chemical Co., Ltd. (Lianyungang, China). Surface sizing starch (industrial grade purity) was obtained from Qingzhou Chenming Modified Starch Co., Ltd. (Weifang, China).

Methods

AKD (5%, 7.5%, 10%, 12.5%, 15%, or 17.5%), laboratory-made surfactant (6%, 7%, 8%, 9%, or 10%), and water (270 g) were simultaneously added to a beaker and then heated to 75 °C in a constant temperature water bath. The reaction was carried out with stirring at 3000 rpm for 1 min, using a JRJ300-D-I high-speed shear emulsifier (Shanghai Biaoben, Shanghai, China). The remaining heated deionized water was added with stirring (11000 rpm, 9 min). The AKD emulsion was cooled rapidly with cold water to obtain the sizing agent.

The paper was coated using a K101 CONTROL COATER (RK Print Coat Instruments Ltd, Litlington, Royston, Herts. U K) for surface sizing. It was then placed in an oven at 105 °C for 5 min to remove the water. A YXQ-125 circular sampler (Changchun Yongxing Test Instrument Manufacturing Co., Ltd, Changchun, China) was used to cut out paper samples of 100 cm². A ZBK-100 type paper surface absorbance weight tester (Changchun Yongxing Test Instrument Manufacturing Co., Ltd, Changchun, China) was used to test the water resistance of the sized paper. The Cobb value is weight of absorbed water.

Characterization

Water-resistance analysis

The water-resistance performance of the emulsion of sizing agent is represented by the Cobb value, which refers to the amount of water that is absorbed by the surface of a unit area of paper or cardboard at a certain time under certain pressure and temperature (g/m^2).

The Cobb value was measured in accordance with the national standard GB/T 1540-2002. Each sample was individually soaked in 100 mL of water for 45 seconds.

Surface tension analysis

The water-resistance performance of the emulsion of sizing agent can be also represented by the surface tension, which refers to the tensile force of a unit length boundary line perpendicular to the liquid surface (mN/m). It was measured using a fully automatic surface tensiometer (Shanghai Fangrui Instrument Co., Ltd. QBZY-1, Shanghai, China).

Stability analysis

An emulsion is a thermodynamically unstable system, and viscosity and liquidity are important indicators of its stability. Therefore, the effect of different composite ratios of the AKD emulsion on the evolution of viscosity was observed for some of the samples. The other batch of samples was centrifuged at room temperature. Finally the formation of the emulsion layer was observed.

TEM analysis

The AKD emulsion prepared using the high molecular mass emulsifier was analyzed by transmission electron microscopy (TEM; Japanese Electronics Co., Ltd, JM-2100, Japan), to observe the size and shape of micelles. The emulsion was diluted with deionized water to 0.1% of the solids content, and the diluted emulsion was applied to a coated copper net. TEM analysis was carried out after drying.

Contact angle analysis

The contact angle was measured to determine the angle at which the water droplets spread over a solid surface, which reflects the wettability of the solid surface and the relationship between the surface tension of the liquid and the free energy of the solid surface.

The contact angle was determined by a static contact angle-measuring instrument (Chengde yote Instrument Sales Co. Ltd, JY-Pha, Chengde, China) on the emulsion-coated paper.

SEM analysis

Scanning electron microscopy (SEM) was used to characterize the distribution of AKD and starch on the surface of the paper after coating with the emulsion. SEM images were taken on a JSM-6700F scanning microscope (Japanese Electronics Co., Ltd, Japan). The sample was coated with a thin layer of gold in vacuum before examination.

RESULTS AND DISCUSSION

Water-Resistance Analysis

The initial reaction conditions were set to AKD 28.5 g, macromolecule emulsifier 1.5 g, total solids content 10%, emulsification for 10 min, and shear emulsifier rotation speed 11000 r/min. The AKD was heated and melted with the emulsifier. Hot water was prepared in another beaker. The emulsification temperature was increased from 65 °C to 85 °C. However, as the reaction temperature was increased beyond 75 °C, the AKD was hydrolyzed, resulting in decreased AKD content and a poorer sizing effect (Fig. 1a, b, c, d) (Dai and Zheng 1999).

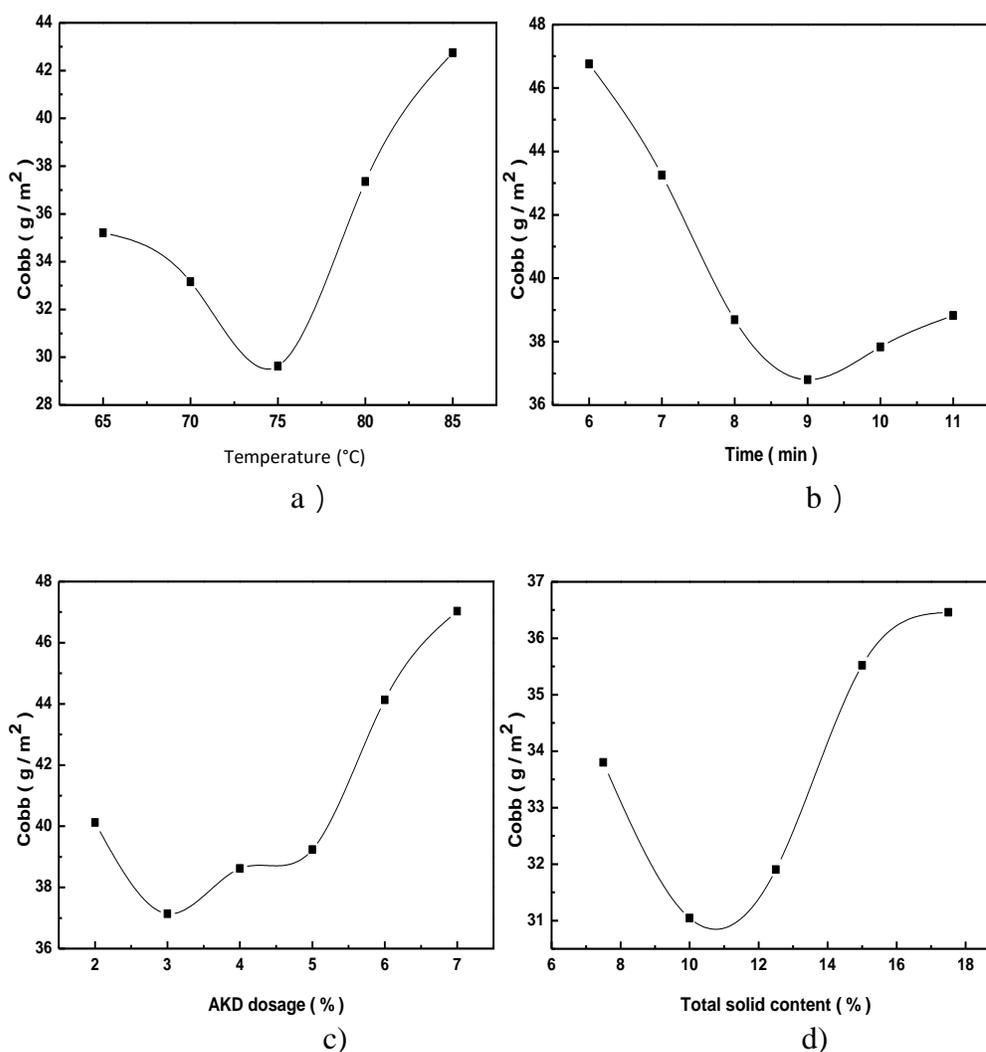


Fig 1. Effects of a) emulsification temperature, b) emulsification time, c) emulsifier dosage and d) AKD dosage on the water-resistance performance of paper

As shown in Fig. 1a, when the temperature was 75 °C, the Cobb value of the paper was 29.6 g/m². As shown in Fig. 1b, shortening the emulsification time reduced the energy consumption and improved the reaction efficiency. However, some AKD did not participate in the emulsification, so the sizing effect of the AKD emulsion was poor when the emulsification time was 6 to 9 min. As the emulsification time was increased, the sizing

effect of the AKD emulsion was improved because the AKD emulsion was emulsified completely. Moreover, the Cobb value of the paper was not changed greatly with increasing time above 9 min, which indicated the complete emulsification of the AKD emulsion. However, if the emulsification time was too long the emulsion water resistance showed an upward trend and had a negative effect on the operation of the paper machine. With these considerations, the optimum emulsification time was 9 min.

Emulsifiers can reduce the interfacial tension, forming an electric double layer and a protective film; thus, the choice of an appropriate emulsifier plays an important role in emulsion stability. Feng *et al.* (2011) found that the strength of the interfacial film is related to the amount of emulsifier. As shown in Fig. 1c, the Cobb value of the paper decreased at first and then increased with increasing emulsifier dosage. This effect shows that a low concentration of emulsifier failed to achieve a good emulsifying effect, while a very high concentration of emulsifier would lead to a small amount of free hydrophilic emulsifier.

As indicated in Fig. 1d, the Cobb value of the paper decreased at first and then increased with increasing solids content. This result could be explained by the fact that the emulsion is a thermodynamically unstable system. This is due to the lower solids content of the emulsion. The dense AKD water-resistive film cannot be formed, and the sizing effect is poor. If the solids content of the emulsion is too large, the AKD micelle particles in the entire system are large, and the effective collision probability between the two particles is increased, the emulsion is easily destabilized, and the sizing effect is become worse.

Surface Tension Analysis

Emulsions from experiment 1 were evaluated. Figure 2a shows that the emulsion surface tension declined with increasing emulsification temperature at first. The molecular energy increased, and the irregular motion of the molecules accelerated, overcoming the internal contraction force of the liquid. However, with further increasing temperature, the emulsion surface tension also rose, and the emulsion lost its stability. Figure 2b illustrates that the emulsion surface tension at first declined with increasing emulsification time, and it reached the smallest value after 9 to 10 min. At the beginning of the emulsification, the emulsification of AKD was not sufficient, and the emulsion still contained free AKD molecules with higher surface tension and lower emulsion stability. With increasing emulsification time, the emulsification of AKD was becoming sufficient, and the surface tension gradually decreased. However, further increasing emulsification time led to gradual hydrolysis and demulsification of the emulsion at high temperature and under high speed stirring, and the emulsion stability then worsened while the emulsion surface tension began to rise again.

Figure 2c shows that the emulsion surface tension declined first and then increased slightly with increasing emulsifier dosage. At the beginning, the amount of emulsifier was too low and could not disperse and emulsify the AKD properly, while the emulsion surface tension was overly high. Therefore the emulsion was unstable against demulsification.

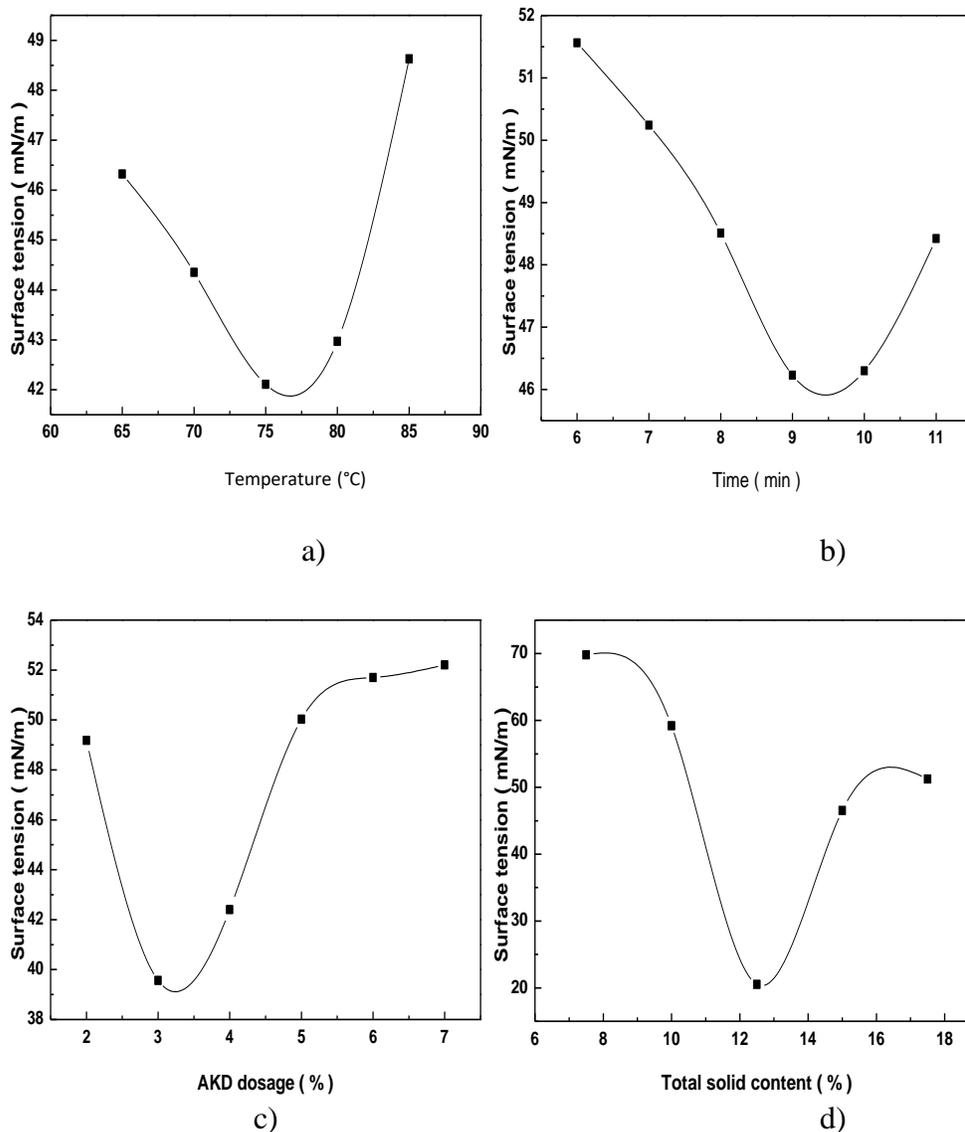


Fig. 2. Effects of a) emulsification temperature, b) emulsification time, c) emulsifier dosage and d) emulsification dosage on the water-resistance performance of paper

With increasing emulsifier dosage, the dispersion and emulsification of AKD improved and the emulsion surface tension decreased while the micelle content in the emulsion was low. As the emulsifier dosage was further increased, the micelle content in the emulsion increased and the emulsion particle size declined, while the specific surface area and the emulsion surface tension also was boosted.

Finally, the micelle content in the emulsion became stable and the emulsion surface tension tended to increase slightly. The increase of the solids content in the emulsion means a higher content of emulsifier in the water. The emulsifier that was used in this test can reduce the surface tension of the active material. The surface tension of the emulsion decreased gradually because of an increased solids content; therefore the emulsion will lose stability, so the surface tension of the emulsion started to rise and then reached a plateau.

Stability Analysis

As shown in Fig. 3, the emulsion viscosity varied slightly as a function of temperature, time, emulsifier dosage, and emulsification dosage. The viscosity was basically stable and did not change much, maintaining a value of about 10 mPa.s with increasing storage time. In general, it showed an upward trend. The results showed that the AKD emulsion prepared in this experiment was relatively stable and could be stored for a long time. This is of great importance for long distance transportation of the emulsion and for its application in the industry.

TEM Analysis

As shown in Fig. 4, the micelles formed in the emulsion were of spherical shape without rods and irregular particles, which indicates that the emulsion had good dispersity.

The outermost layer observed in Fig. 4 is the emulsifier, revealing that the emulsifier molecules wrapped around the AKD. Thus, the emulsifier used in this experiment had a good emulsifying effect on the AKD. At the same time, the shear strength of the emulsion and the emulsion grain diameters were different as a function of the rotational speed.

The emulsion grain diameters were mostly above 1 μm when the speed of emulsification was 4500 rpm. In this case, the stability of the emulsion was poor and it was prone to demulsification because of the large grain diameters.

When the speed of emulsification was 11000 rpm, the shear strength of the emulsion was higher, and the emulsion grain diameters were under 1 μm , which indicates a nano-level emulsion. The emulsion grain diameters were uniform and mostly around 500 nm, suggesting a narrow grain diameter distribution and leading to an improvement in the stability of the emulsion. This evidenced a good emulsification effect and dispersion performance.

Contact Angle Analysis

As shown in Fig. 5, the contact angle of the sized paper with conventional emulsion was slightly lower than that of the sized paper with the new type emulsion upon initial contact of the water droplets with the surface of the paper. With increasing time, the water droplets spread on the surface of sized paper with conventional emulsion, and the contact angle quickly decreased to 20°. The water droplets did not spread on the surface of the sized paper, and the contact angle remained substantially unchanged at a value greater than 90°, demonstrating good water resistance of the sized paper with new type emulsion and the effectiveness of the emulsion under study.

SEM Analysis

The SEM images presented in Fig. 6 revealed that the surface of the paper became smoother after being subjected to the surface sizing process, compared to that of the initial cellulosic paper. This is strong evidence that, after surface sizing of paper, the fibers on the surface were wrapped, impeding the contact of the fibers' hydrophilic groups with water and thus reducing the water absorption ability of the paper. Consequently, the sized paper exhibits a certain degree of water resistance, which also has a good effect on the printing of paper.

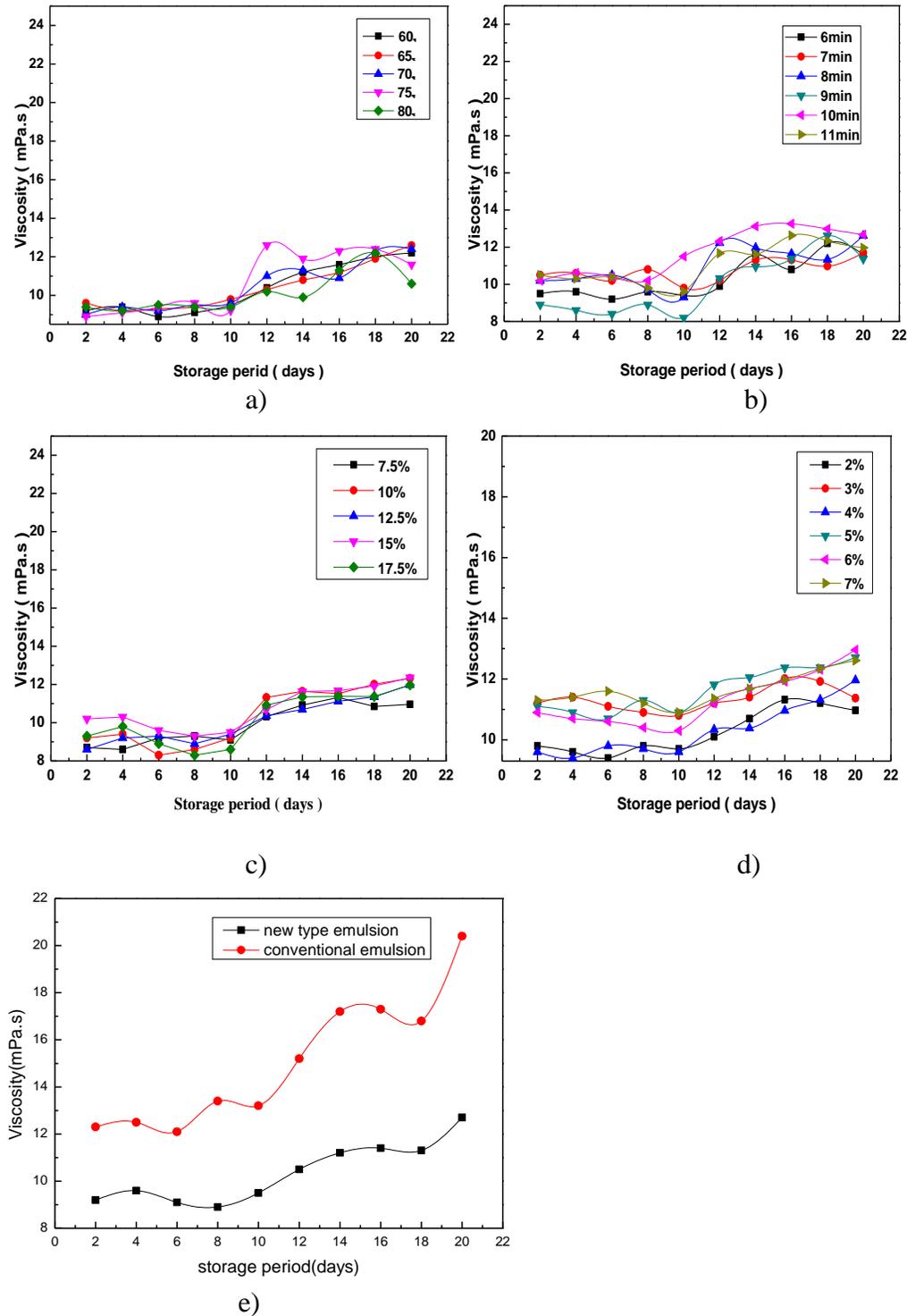


Fig. 3. Effects of a) emulsification temperature, b) emulsification time, c) emulsifier dosage and d) AKD dosage on viscosity, e) new type emulsion compared with conventional AKD emulsion on viscosity.

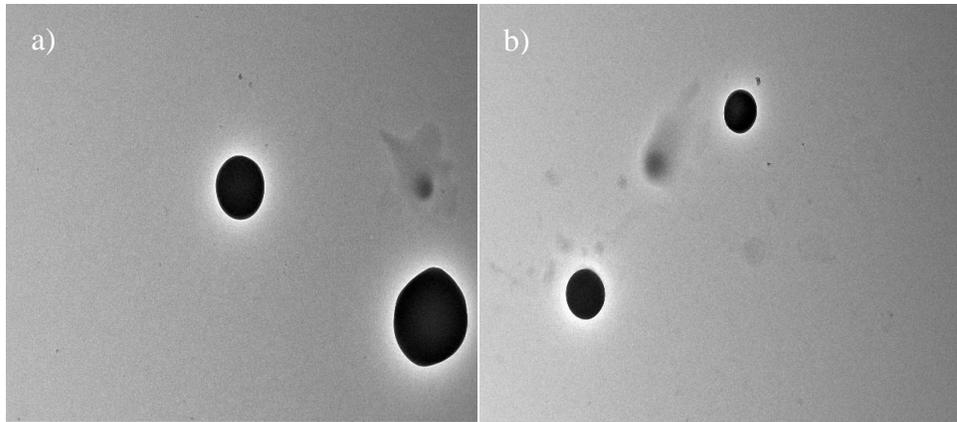


Fig. 4. TEM images of the emulsion at an emulsification speed of a) 4500 rpm, and b) 11000 rpm

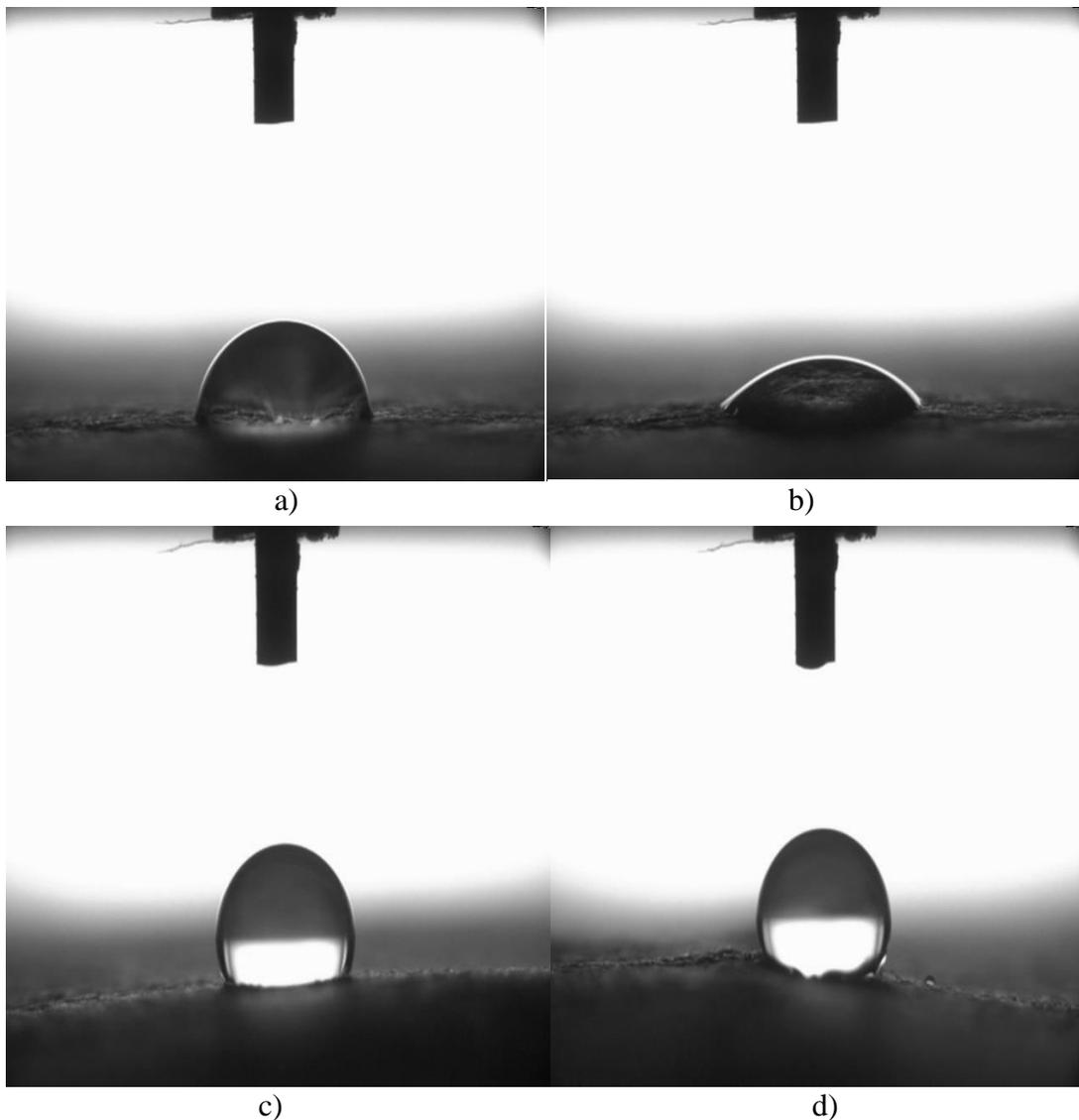


Fig. 5. Contact angle images of a) water droplet upon impact with the surface of sized paper with conventional emulsion; b) same after 2 min contact with the surface of sized paper with conventional emulsion; c) same upon impact with the surface of sized paper with new type emulsion; d) and same after 2 min contact with the surface of sized paper with new type emulsion

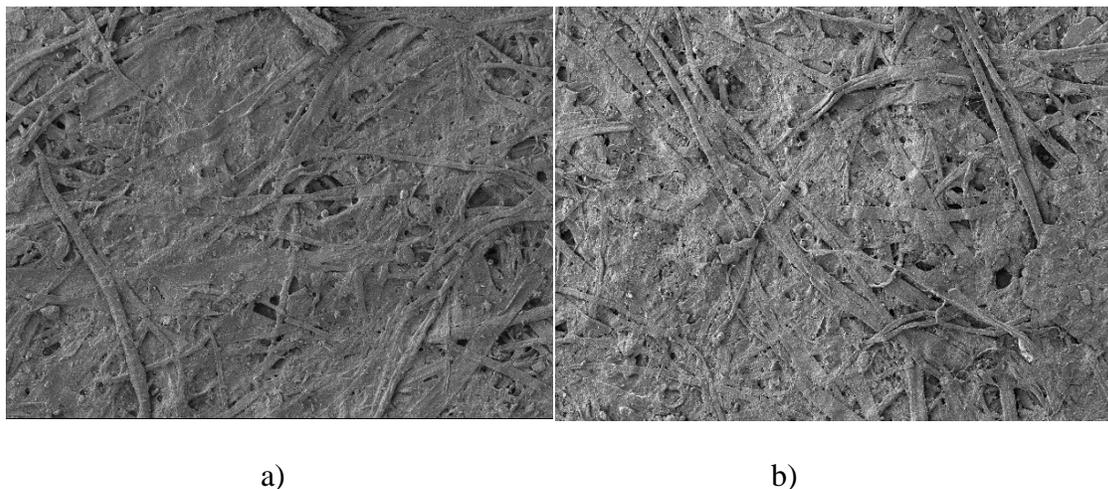


Fig. 6. SEM images of paper (a: surface of unsized cellulosic paper; b: surface of sized paper)

CONCLUSIONS

1. The study reported on the preparation of an AKD emulsion using a neotype polymeric emulsifier. The water resistance, surface tension, and stability of the AKD emulsion were investigated under different conditions, such as emulsification temperature, emulsification time, solids content, and amount of emulsifier.
2. Experimental results demonstrated that the sizing effect of the AKD emulsion was fairly good under the following optimum conditions: emulsification temperature: 75 °C, emulsification time: 9 min, solids content: 10%, and amount of emulsifier: 3%. Under these conditions, the Cobb value of the paper was the lowest – of 29.63 g/m². Moreover, the surface tension of the emulsion was quite low and the emulsion was stable, the emulsion grain diameters were small and the shapes of the micelles were regular.

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