

The Influence of Gas Diffusion Mechanisms on Foam Stability for Foam Forming of Paper Products

Wuling Zhao, Qiupeng Hou, and Xiwen Wang*

Foam forming is an innovative process for papermaking that yields various paper products with excellent formability and porosity. The stability of the foam is a critical factor in foam forming technology. The effects of different surfactants and gases (N₂ and CO₂) on the ability of the foams to coalesce and the stability of the foams were studied. The properties of the liquid film were investigated *via* high-speed camera observation and infrared spectrum. The CO₂ foam was less stable than the N₂ foam under the same conditions, especially for the polyvinyl alcohol surfactant. The infrared spectra and high-speed camera observation showed that the main factor that resulted in CO₂ foam instability was the bubble coalescence caused *via* the gas diffusion in the foam column, although the process of liquid film thinning was performed simultaneously. The greater the liquid film permeability coefficient of the foam, the easier the gas was able to spread throughout the liquid film. Foam forming technology will likely be employed in many potential pulp and papermaking mill processes.

Keywords: Foam forming; Stability; Foam drainage; Gas diffusion

Contact information: School of Light Industry Science and Engineering, State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China; *Corresponding author: wangxw@scut.edu.cn.

INTRODUCTION

Foam forming technology has potential use in the pulp and papermaking industry. In this work, a methodology was developed to estimate the effects of gas diffusion on the stability of the foam in those applications. The methodology and estimates could potentially be used for future planning and research.

Foam forming is an innovative papermaking process that effectively prevents fiber flocculation for long and synthetic fibers, and its products are characterized by excellent uniformity of formation. In addition, this method can be utilized with renewable materials. Foam forming technology was first developed by Radvan and Gatward in the 1970's (Gatward and Radvan 1973; Radvan *et al.* 1973). They found that fibers could be dispersed uniformly in a water-based foam, even with high concentrations of long fibers. At the same time, the Radfoam process was employed to manufacture paper sheets (Smith *et al.* 1974). In the pulp and papermaking industry, this method has been further improved to include many kinds of fibers (Rodman and Lessmann 1988; Mao *et al.* 2008; MacFarlane *et al.* 2012). Recently, foam forming technology has been applied to both paper and paperboard production, in realistic conditions at VTT's pilot plant environment (Alimadadi and Uesaka 2016).

Foam has been applied in many industries, but due to its thermodynamically unstable nature, the stability of the foam is one of the most important features. Therefore, it is vital to effectively evaluate and understand the mechanisms of foam stability. There are two decay mechanisms of foam: foam drainage and gas diffusion. Both are related to

the liquid film properties as well as the interactions between the liquid film and the Plateau boundary (Rao *et al.* 1982; Weaire and Hutzler 1999).

In general, foam stability is evaluated by parameters such as the height or volume of the foam column (Khristov *et al.* 2001; Stubenrauch and Khristov 2005; Ruízhenestrosa *et al.* 2008), and the half-life of the foam (Vilkova and Kruglyakov 2008). In addition, a variety of modern experimental techniques, including interfacial rheology (Monteux *et al.* 2004; Espinosa and Langevin 2009), resonance Raman scattering, and X-ray reflection, have been used to investigate foam stability mechanisms (Heydarifard *et al.* 2016). In addition, the Gibbs-Marangoni effect (Deshpande *et al.* 2000; Tan *et al.* 2005) is widely used to explain dynamic foam stability. Also, the viscoelasticity of liquid film is thought to be an important factor that affects the foam drainage process and the stability of liquid films (Kovalchuk *et al.* 2005). In this paper, the effects of different surfactants and gas (N₂ and CO₂) on the ability of the foams to coalesce and the stability of the foams were studied. Moreover, the properties of foam liquid film were investigated *via* high-speed camera observation and infrared spectrum (FT-IR).

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVOH) was purchased from Kuraray Co., Ltd, Chiyoda, Tokyo, Japan. Sodium dodecyl sulfate (SDS) and Cetyl-trimethyl ammonium bromide (CTAB) were obtained from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China, and were both dissolved in distilled water at a pH 7 without further purification. In addition, 95% purity CO₂ and N₂ gases were used.

Foam stability

The stability of the CO₂ and N₂ foams were evaluated *via* the Waring-Blender method. The foam stability was analyzed *via* a foam decay curve, which described the changes in volume of the foam column over time. The half-life time of the foam column was also recorded (Bhattacharyya *et al.* 2000; Koehler *et al.* 2000; Duan *et al.* 2004). The amount of surfactant solution used for each batch was 200 mL, and 1000 mL of CO₂ or N₂ gas was filled with a sealed cylinder *via* use of a mass flow meter. Then, an aqueous foam was generated from a mixture of distilled water (pH = 7) and either the PVOH, or one of the surfactants sodium dodecyl sulfate (SDS) or cetyl trimethylammonium bromide (CTAB) respectively, and then mechanically agitated for 5 min (1600 rpm) in a cylindrical vessel with a 10 cm diameter. For this experiment, the temperature was regulated at 25 °C.

Foam coalescence

The coalescence behavior of the air bubbles was studied in a defined amount (100 mL) of surfactant solution. The bubbles were grown on two parallel facing stainless steel capillaries with a 1.0 mm inner diameter. Gastight precision syringes were used as an air reservoir, to ensure the initial bubble size was always adjusted to the same volume. Then, the bubbles were brought into contact with each other by moving the syringe piston (Duerr-Auster *et al.* 2009). The stability and coalescence structure of the two facing bubbles were observed with a high-speed camera operated at 40 fps (frames per second), and the effects of gas diffusion on the stability of the foam was investigated by liquid film.

Foam film

The properties of the foam film were measured by Fourier Transform Infrared Spectroscopy (FT-IR; Hyperion, Tensor27). In the quartz tube (90 mm length, 8 mm width), a single layer of liquid film was formed *via* a capillary blowing method. The quartz tube was placed in an infrared light path, scanned at regular intervals, and recorded the infrared absorption spectrum. The spectral resolution was set to 1 cm^{-1} , the scanning spectral range from 4000 cm^{-1} to 400 cm^{-1} and scanned 32 times.

RESULTS AND DISCUSSION**Foam Stability**

Table 1 summarizes the observations on the stability of the CO_2 and N_2 foams. Under the same conditions, the half-life of the CO_2 foam was much shorter than the N_2 foam, which indicated that the CO_2 foam was less stable than the N_2 foam. In addition, when the concentration of the PVOH was increased from 0.3% to 1.0%, the half-life of the CO_2 foam barely changed. However, the half-life of N_2 foam increased with an increase in PVOH solution concentration, showing improved foam stability. This is because, as far as foam stability is concerned, the concentration of surfactant depends on the adsorption of surfactant molecules on the gas-liquid interface and their diffusion in surfactant solution (Chistyakov *et al.* 2001; Bailon-Moreno *et al.* 2005). In this experiment, the stability of the CO_2 foam was not affected by the concentration of PVOH, indicating that the PVOH concentration was not the main factor responsible for the stability of the CO_2 foam.

Table 1. Foam Stability of CO_2 Foam and N_2 Foam in Different Foaming Systems

Concentration (% m/v)	CO_2 Foam Half-life (min)	N_2 Foam Half-life (min)
0.3 PVOH	1.0	1.5
0.5 PVOH	1.0	1.5
0.7 PVOH	1.5	4.5
0.3 SDS	1.5	3.0
0.5 SDS	1.5	2.5
0.7 SDS	1.5	2.5
0.3 CTAB	8.0	> 30
0.5 CTAB	3.5	> 30
0.7 CTAB	3.0	> 30

The decay curve of the general foam is generally divided into three stages (Deshpande and Barigou 1999); I. Drainage stage: the foam drains under the condition of gravity and capillary forces, there is essentially no bubble burst, and the foam volume only decreases slightly, II. Foam rupture stage: the foam continues to drain, but there was some bursting of bubbles, and the volume of foam column rapidly decreases, and III. Foam metastable stage: the foam drainage has essentially stopped, and the liquid film gradually forms a Newtonian black film (NBF), which remained stable in the absence of external interference.

As shown in Fig. 1, all three of the additives (the PVOH and the surfactants) used in the experiment showed that the decay curve of the N_2 foam was consistent with the decay curve of the general foam. The stability of the CO_2 foam was less stable than the N_2 foam

under the same conditions, especially for the PVOH. Figure 2 shows that, for the 0.7 % m/v PVOH foaming system, the volume of the N₂ foam slowly decreased from 480 mL to 295 mL after the foam foamed. The diffusion rate of N₂ through the liquid film was slow, approximately 0.62 mL/s. The liquid film thinning process caused by gravity was the main factor for the foam instability. However, the decay curve of the CO₂ foam dropped rapidly, and the both the bubble size and the foam volume rapidly decreased. The volume of the CO₂ foam decreased from 480 mL to 0 mL after the foam foamed, and the diffusion rate of CO₂ through the liquid film was 1.6 mL/s under the same conditions. Because the CO₂ molecule had relatively high water solubility, the gas diffusion rate of CO₂ foam was obvious. The rapid gas diffusion rate increased the foam decay process, which resulted in foam instability. In a parallel comparison experiment, the authors found that the impact of the gas diffusion rate on the foam stability in PVOH systems was notable. Therefore, the differences between the decay curve of N₂ foam and CO₂ foam was the largest in PVOH systems, followed by SDS surfactant systems, and then CTAB surfactant systems under the same conditions.

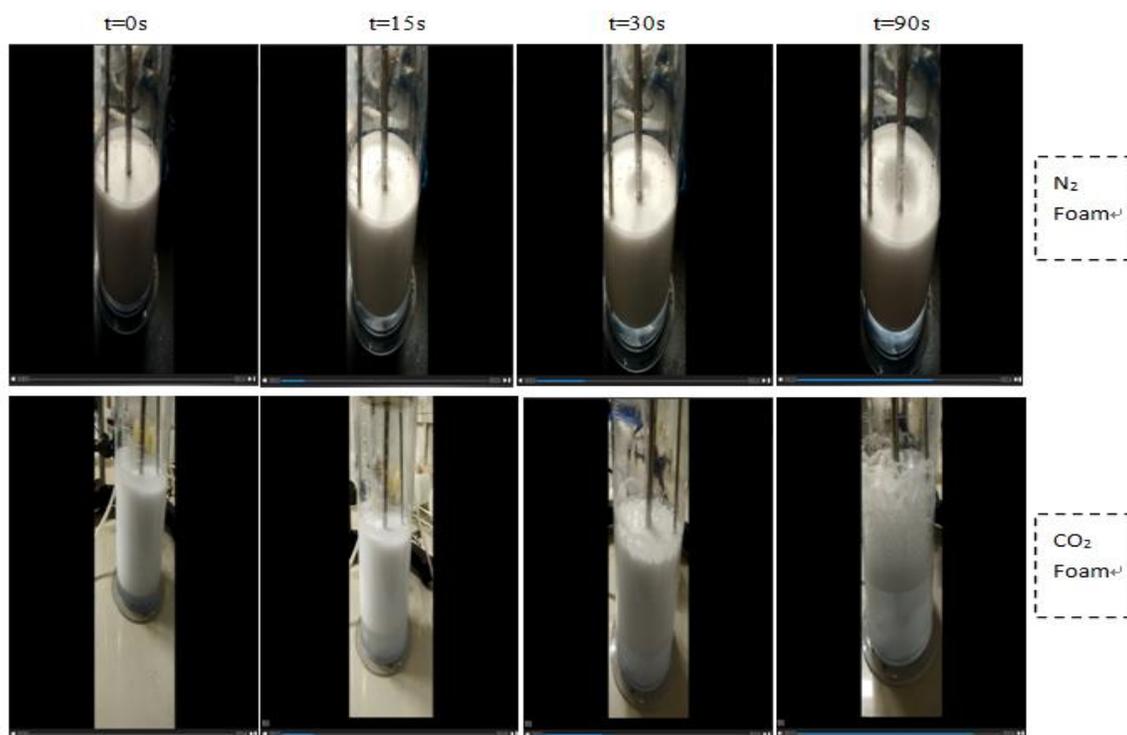
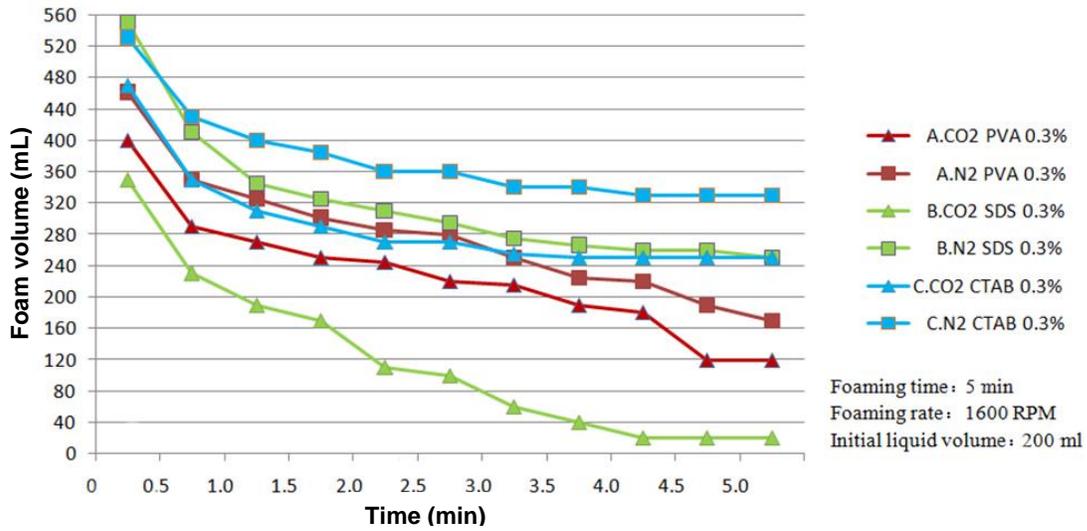


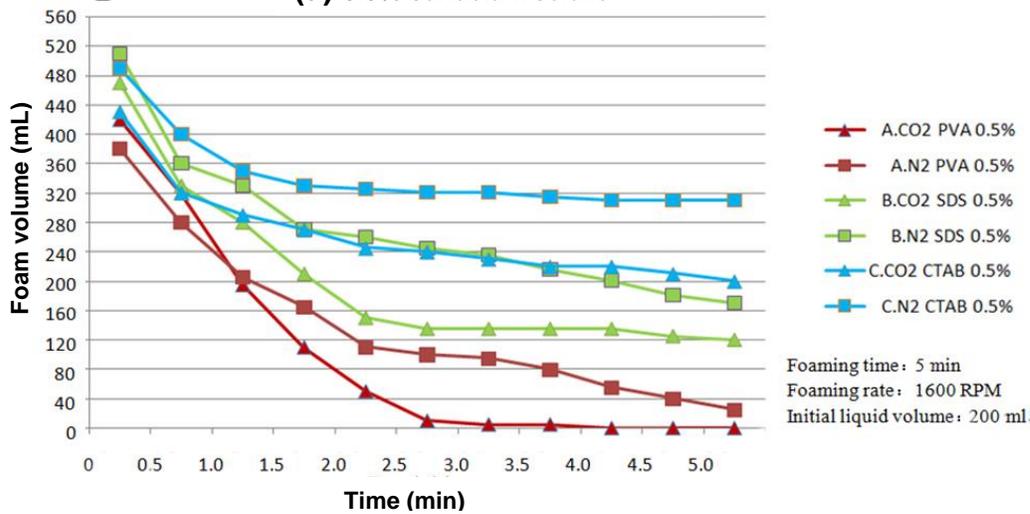
Fig. 1. The drainage process of N₂ foam and CO₂ foam

Foam coalescence

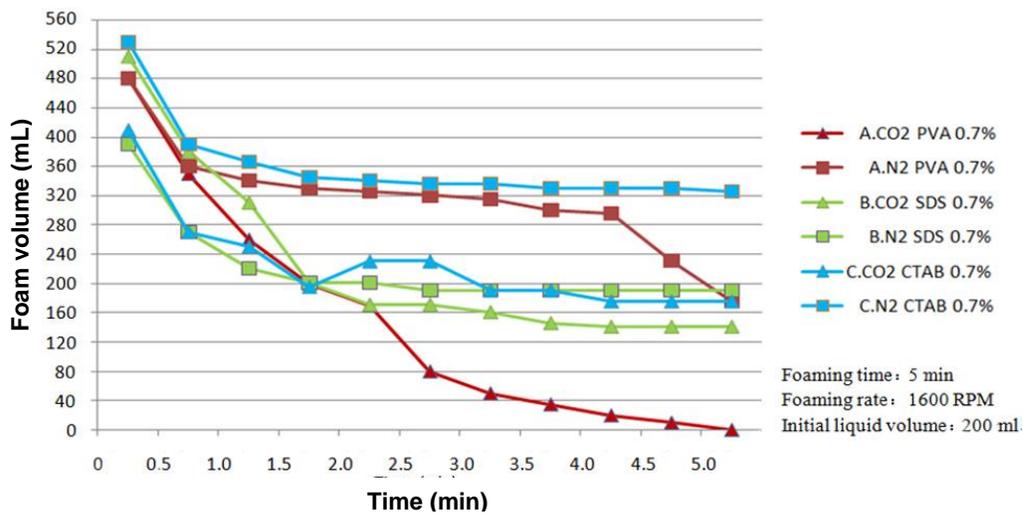
As shown in Fig. 3, the foam coalescence phenomenon increased when the CO₂ foam bubbles were in contact with each other. A large bubble was formed *via* the coalescence of two small bubbles, which then rose above the gas-liquid interface until they ruptured. When the N₂ foam sources contacted, the two small bubbles dropped below the gas-liquid interface and formed a larger bubble until it ruptured.



(a) 0.3% surfactant solution



(b) 0.5% surfactant solution



(c) 0.7% surfactant solution

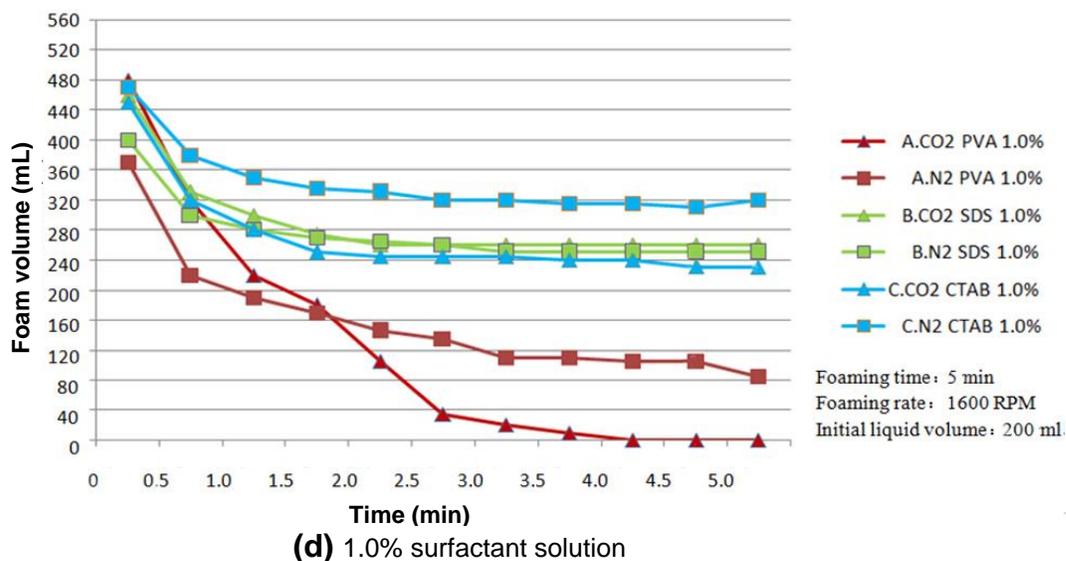
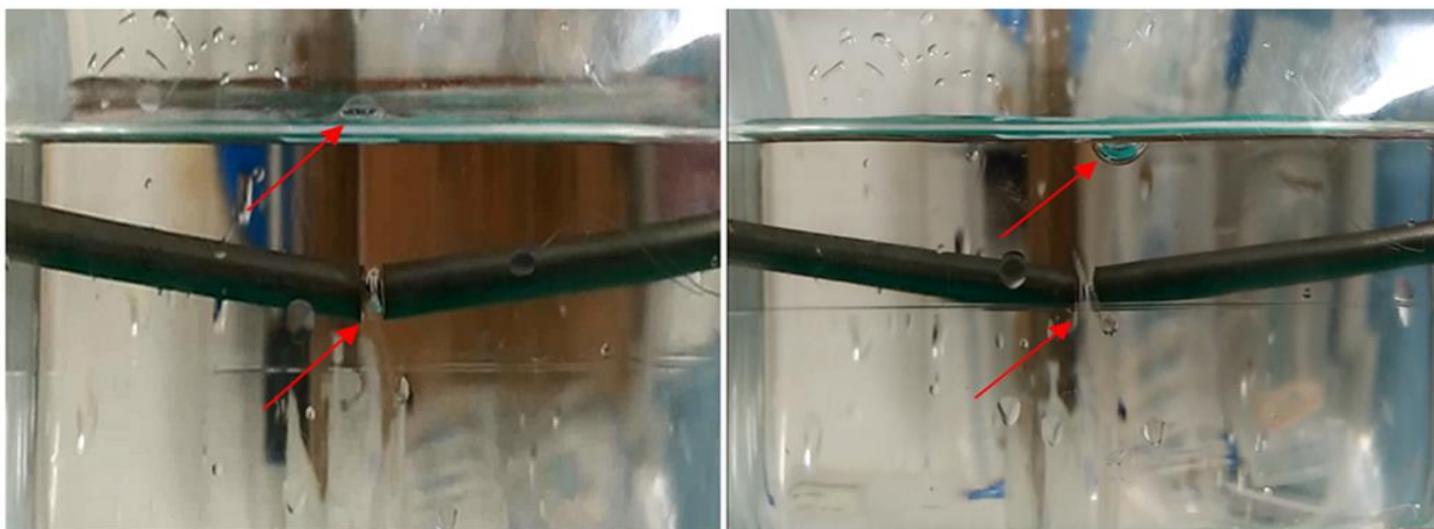


Fig. 2. Foam decay curves of PVOH, SDS, and CTAB in CO₂ and N₂ systems

The theoretical mechanism of foam decay and its factors that affected the stability of the foam can be explained as follows. In a water-based foam system, the CO₂ molecules competed with the polar groups of the surfactant for water molecules and then reduced the surfactant hydrophilicity, which resulted in the aggregation of surfactant molecules on the liquid film. In addition, due to the formed gas-permeable channel, the CO₂ molecules easily diffused through the liquid film, which caused an increased rate of foam coalescence and much less stable foam.



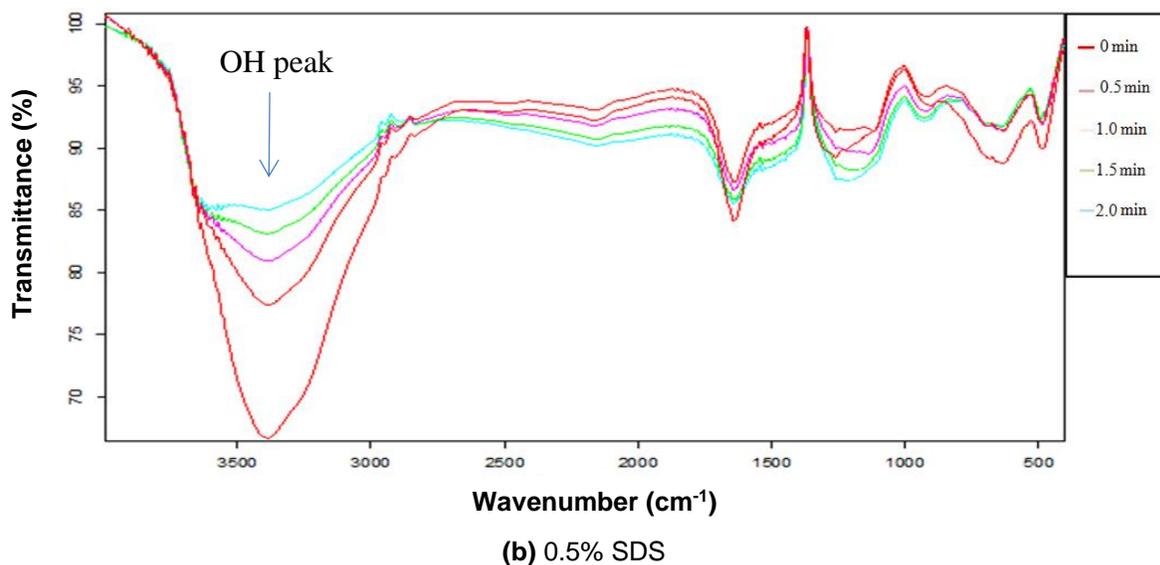
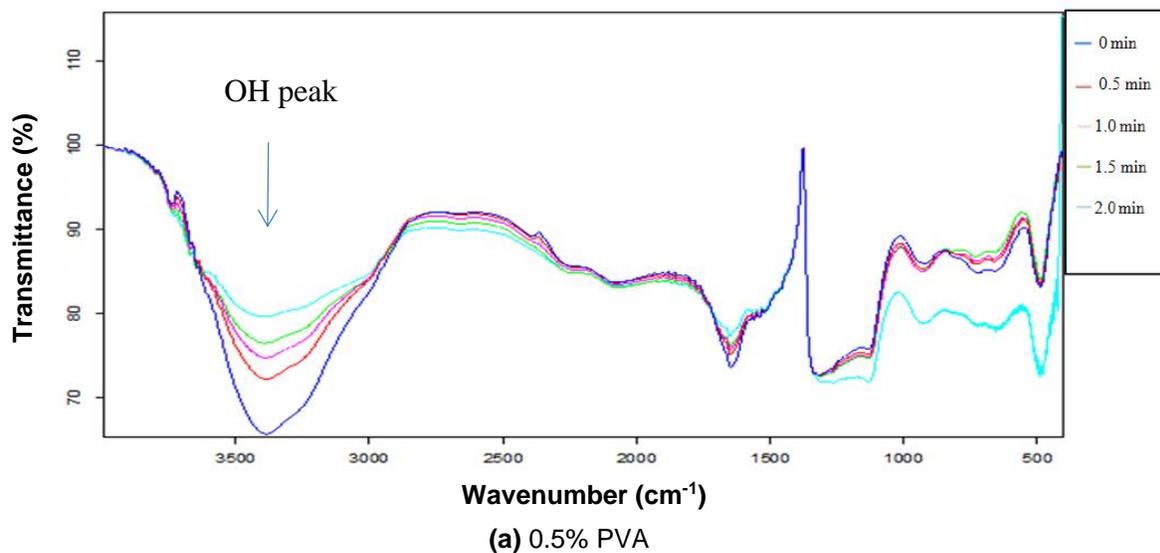
(a) CO₂ foam coalescence

(b) N₂ foam coalescence

Fig. 3. Photography of CO₂ foam and N₂ foam coalescence

Foam film

As shown in Fig. 4, the location of the 3400 cm^{-1} band represented the vibration absorption peak of an OH group, and the other bands were characteristic absorption peaks of the PVOH or surfactants used.



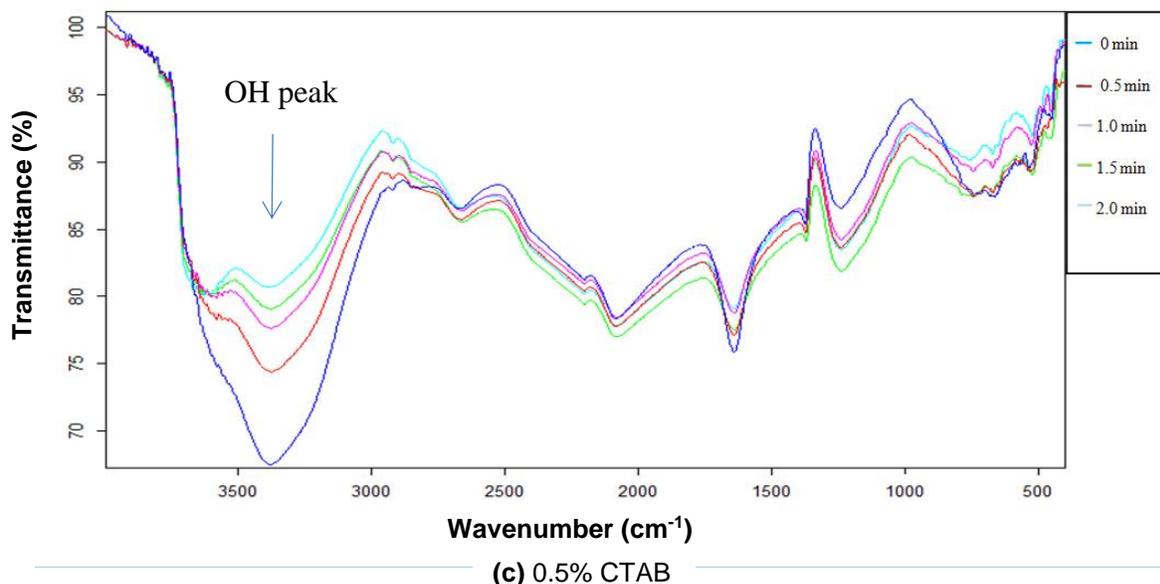


Fig. 4. FT-IR spectra of foam film formed from (a) PVOH, (b) SDS, and (c) CTAB solutions

The results showed that when the liquid film was newly formed, the absorption peak for OH in the SDS liquid film was the strongest, followed by CTAB, and PVOH being the weakest. The SDS liquid film had an excellent fluid-carrying capacity and was able to hold a large amount of water in the liquid film. But, as the foam drainage progressed, the absorption peaks of OH in the SDS and CTAB liquid film sharply decreased after 2 min. This showed that the fluid-carrying capacity of SDS and CTAB liquid film was poor and that the liquid drainage process occurred quickly. The absorption peak of OH in the PVOH liquid film slowly decreased, and very little drainage process occurred. This meant that either the single liquid film or the foam had a strong liquid holdup capacity in the PVOH system, and the foam was stable. This further demonstrated that the gas diffusion rate of the foam had a strong effect on the stability of the foam.

Foam decay mechanism

The foam decay mechanism mainly includes the foam drainage process and the gas diffusion process (Boud and Holbrook 1958). These two processes are related to the properties of the liquid film, and the liquid film permeability coefficient has been found to be an important parameter to characterize the gas diffusion extent of the foam (Koehler *et al.* 2000). The CO₂ molecules have high water solubility, 50 times greater than the N₂ molecules under the same conditions, while the difference between their diffusion coefficients in the liquid phase was small. The liquid film permeability coefficient of the CO₂ foam is much larger than that of the N₂ foam, which was the main factor in the differences in the stability of each foam (Li *et al.* 2013).

The effects of the gas diffusion rate on the stability of the foam came from two aspects. First, the gas inside the bubble was partially dissolved in the liquid film. Second, the greater the liquid film permeability coefficient of the foam was, the more easily the gas was able to spread throughout the liquid film, which resulted in a rapid decrease in bubble size and foam volume. In the foam drainage process, the trace amount of liquid that flows into the liquid film can affect the gas diffusion rate. In the foam rupture process, the bubble began to burst from the top of the foam column and the upper side of the foam film was

always convex. Thus, the film was very sensitive to the effects of gas diffusion, and it ruptured when a critical thinness was reached. The foam coalescence caused by gas diffusion also affected the foam stability. Both of these effects led to an increase in bubble size and an accelerated foam drainage rate, which eventually caused a decreased foam rupture rate.

CONCLUSIONS

1. The CO₂ foam was less stable than the N₂ foam under the same conditions. For 0.7 % m/v PVOH surfactant foaming system, the volume of the N₂ foam slowly decreased from 480 mL to 295 mL after foaming. The diffusion rate of the N₂ molecules through the film was slow, approximately 0.62 mL/s, and the half-life of the N₂ foam exceeded 4.5 min. However, the volume of the CO₂ foam rapidly decreased from 480 mL to 0 mL after foaming. The diffusion rate of the CO₂ molecules through the film was 1.6 mL/s and the half-life of the foam was 1.5 min.
2. The liquid film permeability coefficient of the CO₂ foam was much greater than that of the N₂ foam; thus, the CO₂ molecules were easily diffused through the liquid film, which led to increased foam coalescence, the main reason for the difference in foam stability.
3. The gas diffusion rate had a strong effect on the stability of the foam. One aspect of stability, was that the gas inside the bubble was partially dissolved in the liquid film.
4. In addition, the greater the liquid film permeability coefficient of the foam, the easier the gas was able to spread throughout the liquid film. Both these effects rapidly decreased the bubble size and the foam volume. Foam forming technology will likely be employed in many potential pulp and papermaking mill processes. The development of its application will require continued public and private investment in the research and development of foam stability mechanisms, which can be utilized in commercial production.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (31470608) and the fundamental Research Funds for the Central Universities (201522117).

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Article submitted: May 22, 2019; Peer review completed: September 18, 2019; Revised version received and accepted: October 10, 2019; Published: October 29, 2019.
DOI: 10.15376/biores.14.4.9893-9903