The Impact of Synthesis Conditions on the Structure and Properties of Di-(Stearylamidoethyl) Epoxypropyl Ammonium Chloride

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Both alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA) are widely used neutral papermaking sizing agents. However, AKD has the issue of sizing hysteresis, while ASA requires on-site emulsification. In addition, both reagents are readily hydrolyzed. Di-(stearylamidoethyl) epoxypropyl ammonium chloride (DSEAC) has been applied as a fabric softener, but it is a potential sizing agent which leads to good sizing without sizing hysteresis. It could be synthesized by a two-step process starting from stearic acid and diethylenetriamine. During the process, the stearamide structure obtained from the first step plays a key role in the second process as well as sizing. This paper focuses on the impact of the synthetic process of the first step on the structure and sizing properties of DSEAC. Single factor experimental results demonstrated that the optimal temperature should be 160 °C while the optimal reaction time should be less than 3.5 hours. Orthogonal analysis experiments indicated that the optimal synthetic process was maintaining 100 °C for 30 min, and then increasing the temperature to 160 °C for 3.5 hours. Dosages of the catalysis and antioxidant were 0.5% and 0.6% of stearic acid, respectively.

Keywords: Stearylamidoethyl; DSEAC; Structure; Properties

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INTRODUCTION

Paper is vulnerable to water or other fluids. To overcome the inherent wettability, sizing chemicals are added to the paper surface or to the aqueous slurries containing cellulosic fibers (Hansen and Björkman 1998; Truong *et al.* 2003; Yu and Garnier 2002; Basta 2003; Wang *et al.* 2003). Alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA) are widely used sizing agents in industry (Lindfors *et al.* 2007). AKD products are generally prepared by the dimerization of stearoyl chloride (Hodgson 1994). Similar to the ASA products, AKD is required to be emulsified in the presence of cationic starch as well as other cationic polymers before adding it to the paper machine system (Guan 2002; Lee and Shin 1991). The inventors of AKD sizing technology strongly believed that a chemical reaction takes place between the active ingredient and the hydroxyl groups on the fiber surface (Davis *et al.* 1956). However, AKD is much less reactive than that of ASA with respect to the reaction time and the temperature. For this reason, AKD has the issue of sizing hysteresis, and the emulsification can be carried out at a central facility, allowing the shipment of ready-to-use AKD dispersions to paper mills (Hubbe *et al.* 2006). To be effective, the ASA oil is required to form an emulsion before its addition to the paper machine system (Hubbe *et al.* 2006; Isogai and Morimoto 2004).

On the other hand, DSEAC, which poses neither a sizing hysteresis nor a hydrolysis issue, has the application potential as neutral papermaking sizing agent (Xu *et al.* 2012). DSEAC could be prepared by a two-step reaction. Firstly, diethylenetriamine can form stearamide through an amidation reaction with stearic acid. The secondary amine from the stearamide could further form quaternary ammonium after a ring open reaction of epichlorohydrin. In the structure of stearamide, the first step played a key role for cationic processes and sizing. This paper mainly dealt with the impact of the synthetic process of the first step on the stearamide structure by keeping consistent conditions in the second step.

EXPERIMENTAL

Materials

Stearic acid was purchased from Guoyao Chemical Co., Ltd., China. Epichloro-hydrin and diethylenetriamine were supplied by the Nanjing Chemical Co., Ltd., China. Paper which had a Cobb$_{60}$ value of 72 g/m^2 was used for sizing in this study and was supplied by the Shanying Co., Ltd., China. All of the other chemicals were analytical reagents (Shanghai Chemicals Co., Ltd, China) and were used directly without further purification.

Methods

The synthesis of stearamide (stirring)

Stearic acid (28.488 g added) is a white solid with a melting point between 67 °C and 72 °C. It needed to be melted before the reaction. Diethylenetriamine (6 mL) was added dropwise into the liquefied stearic acid in a flask while the temperature was held constant at 72 °C. To complete the reaction, the reaction mixture was maintained at 100 °C for 10 to 30 min. After that, the temperature needed to be elevated sequentially until it reached the exact temperature. Either toluene-p-sulfonic acid, phosphoric acid, or ethyl acetate (0.25% to 0.5% of the amount of stearic acid) was used as a catalyzer. Sodium borohydride, sodium hydrogen sulfite, or a 50%:50% mixture of sodium boro-hydride and sodium hydrogen sulfite (0.2% to 0.6% of the amount of stearic acid) was used as the antioxidant (Chen *et al.* 2007).

Cationic process of stearamide

Stearamide (6.72 g) was added to a 100 mL four-mouth flask equipped with a mechanical stirring bar, thermometer, dropping funnel, and condensing tube. The temperature was gradually raised to create a molten state. Epichlorohydrin (1 mL) was dropped into the flask while the temperature was kept at 70 °C for 2 h (Chen *et al.* 2002).

Surface sizing procedure and Cobb$_{60}$ value test

Surface sizing was performed using a K-type coating method. The sizing weight was controlled by adjusting the power and speed in the sizing process. All sheets were dried on a standard drier set at 105 °C for three minutes and then stored in a conditioned environment (23 °C and 50% RH) for 24 h until further analysis.

The Cobb$_{60}$ value of paper after surface sizing was measured. The quantity of the sizing agent was 0.3%. Cobb$_{60}$ value test was according to TAPPI standard T 441 om-09.

Melting point analysis (MP)

The capillary tube, which was filled with a small amount of sample power, was then placed in the middle of the B tube along with a thermometer. The B tube was heated by an alcohol lamp. Record the temperature as the initial temperature when the sample power began to be melted. Record the temperature as the final temperature when the sample power was all melted.

Contact angles analysis (CA)

Smooth solid surfaces were used to the contact angles analysis which was made from Stearamide or DSEAC. The contact angles were measured by the sessile drop method with an instrument equipped with a CCD camera. The water droplet in each measurement was about 5 µL and was generated with a micro-syringe. The average CA value was determined by measuring five different positions of the same substrate (Li *et al.* 2012).

FT-IR analysis

FT-IR analysis was carried out with an IR-360 instrument from Thermo Nicolet. Samples were placed into a vacuum drier for 48 h before being observed by the infrared detector.

NMR analysis

The sample was purified before an NMR analysis. For solid state MAS NMR measurements, the samples were pressed into 4 mm zirconia rotors and spun at 14 kHz. The measurements were conducted on a Bruker AvanceIII 400 spectrometer (Bruker BioSpin, Rheinstetten, Germany) with a resonance frequency of 100.62 MHz for ^{13}C. The signal-to-noise ratio was enhanced by applying cross polarization. The contact time was 1000 µs, and the relaxation delay was 20 s; a ramp-contact and spinal 64 decoupling pulse program was used. The spectra were recorded as the sum of 1603 scans and calibrated using the methine carbon atoms of adamantane as an external standard ($\delta =$ 29.47 ppm).

RESULTS AND DISCUSSION

DSEAC was synthesized through two steps. Firstly, the stearamide in Fig.1 was formed by an amidation reaction between diethylenetriamine and stearic acid. The carbon skeleton of stearic acid provided hydrophobicity due to a long chain that had 17 carbon atoms. Structurally, diethylenetriamine contains two primary amine functional groups and one secondary amine functional group. The secondary amine functional group of diethylenetriamine could further form quaternary ammonium with epichlorohydrin. Secondly, as shown in Fig. 2, stearamide could interact with epichlorohydrin to produce DSEAC. The hydrophobicity of DSEAC was determined by the first step. However, stearamide obtained by the first step, which had high melting point, was difficult to disperse in water or to distribute on the paper surface. However, stearamide gained better dispersibility and a lower melting point after the cationic reaction. Therefore, good sizing could be achieved after a two-step reaction. The stearamide structure was the key factor for the cationic reaction due to the fact that the cationic reaction could not be completed without free amino functional groups. Consequently, this paper mainly dealt with the

impact of synthetic processes on stearamide by keeping consistent conditions in the second step.
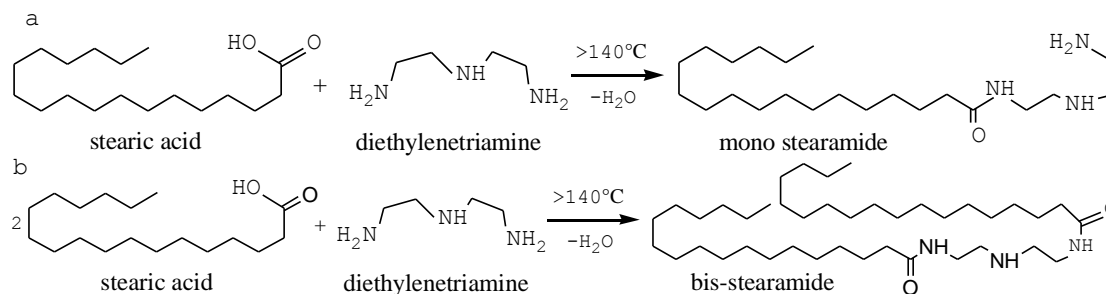
Fig. 1. Synthesis routes and chemical structures of (a) mono stearamide, and (b) bis-stearamide

The synthesis of stearamide is shown in Fig. 1. The ammonium salt was initially formed at 100 °C by mixing stearic acid with diethylenetriamine. Consequently, the temperature of the reaction was increased to melt the salt. The dehydration process did not begin until 140 °C. Theoretically, diethylenetriamine containing two primary amines could form bis-stearamide, as shown in Fig. 1(b); however, it was difficult to avoid forming mono-stearamide, as shown in Fig. 2(a) (Yan *et al.* 2013). Thus, the stearamide gained after the first step was a mixture of bis-stearamide and mono-stearamide.
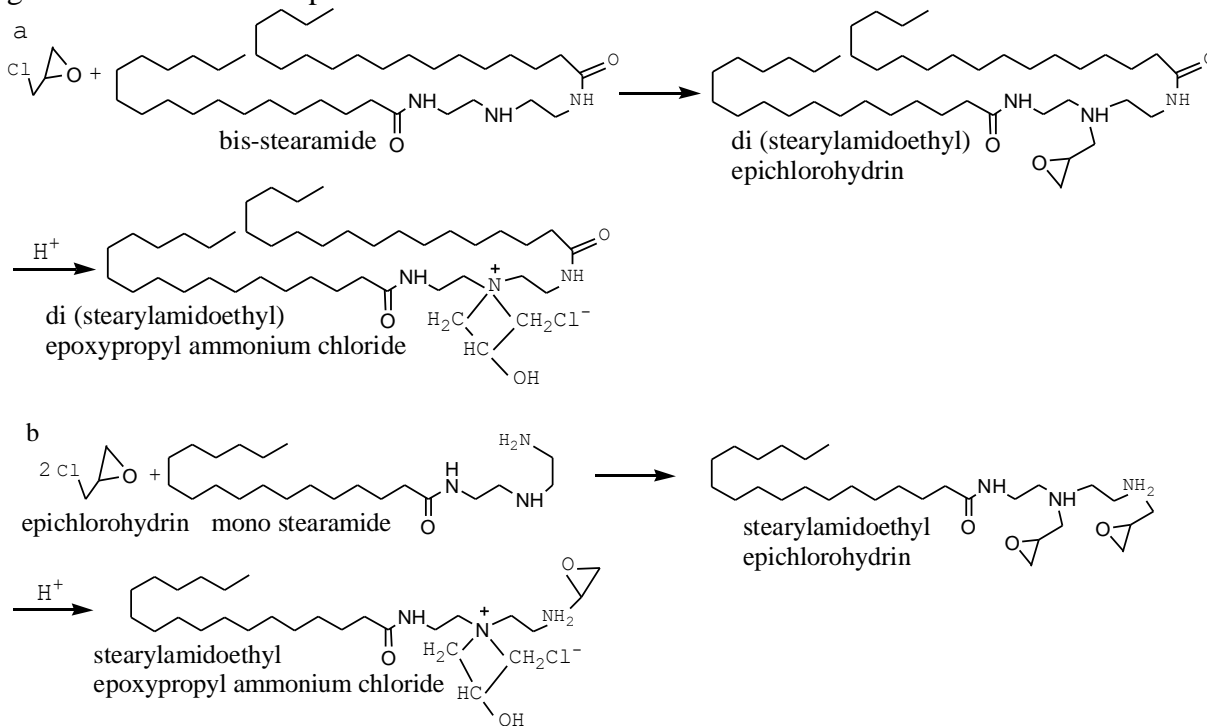
Fig. 2. The synthesis routes and chemical structure of (a) DSEAC and (b) stearylamidoethyl epoxypropyl ammonium chloride

As shown in Fig. 2, mono-stearamide, with low melting point, reacted readily with epichlorohydrin, and the cationic product had good dispersity in water or on the paper surface. Bis-stearamide exhibits good hydrophobicity, and it has a high melting point and low reaction activity, but the cationic product was difficult to disperse in water

and on the paper surface. Different synthetic conditions resulted in various ratios between bis-stearamide and mono-stearamide. The optimal proportion of bis-stearamide and mono-stearamide was therefore considered in this paper. Similarly to PAE, epoxy group in the di(stearylamidoethyl) epichlorohydrin can be transformed to a quaternary ammonium salt when the emulsion process is carried out under the acid conditions.

Single Factor Experiment Analysis and Orthogonal Experimental Design

The impact of reaction conditions on the stearamide synthesis, as revealed by the results of single-factor experiments is shown in Table 1. When the reaction temperature was greater than 140 °C, water was removed and stearamide was, therefore, formed. The results in Table 1 showed that the extent of the dehydration condensation strengthened as the temperature was increased. The reaction time played a key role in water removal. The longer time the reaction was held, the more dehydration condensation was achieved. Raw material proportion was a key factor for the proportion of hydrophobic groups. Results of CA analysis in Table 1 show the water-resistance of stearamide. Compared with CA analysis, $Cobb_{60}$ value of DSEAC demonstrated product hydrophobicity and disperse-bility on the paper surface. The higher ratio of stearic acid led to a higher melting point, and a greater contact angle for the product. Thus, the product could be dehydrated completely at 160 °C for 3.5 h.

Table 1. The Impact of Reaction Conditions on the Stearamide Synthesis by Single Factor Experiment

SA/DI	T /°C	Time /h	Color	MP of stearamide /°C	CA of stearamide / °	$Cobb_{60}$ of DSEAC /g·m^{-2}
2：1	160	3	yellow	108-118	99	38
1.75：1	160	3	yellow	102-110	80	35
1.5：1	160	3	yellow	94-106	67	41
1.25：1	160	3	white	92-100	55	45
1：1	160	3	white	88-98	53	47
1.5：1	150	3	yellow	96-104	68	41
1.5：1	140	3	yellow	98-104	69	40
1.5：1	160	3.5	yellow	96-103	70	39
1.5：1	160	2.5	yellow	98-104	67	41

* SA/DI was the mole ratio of stearic acid and diethylenetriamine. The p-toluenesulfonic acid was used as a catalyst.

Reaction time, temperature, and material proportion are basic factors for stear-amide synthesis. Holding time, antioxidant, and catalyst are also the factors for the stearamide molecular structure. Therefore, to further understand the impact of the synthetic process on stearamide, an orthogonal experiment was employed. Table 2 shows results of the synthetic process for stearamide, carried out according to an orthogonal experimental design, dealing with the impact of the reaction temperature, time, anti-oxidant type and dosage, catalyst type and dosage, and holding time on the properties of stearamide. According to Table 1, sizing was best when the mole ratio of stearic acid to diethylenetriamine was 1.8:1.

Table 2. Process Chemistry of Stearamide Designed by the Orthogonal Experiment

NO.	T /°C	Time /h	Kind of antioxidant	Dosage of antioxidant /%	Kind of catalyzer	Dosage of catalyzer/%	Holding time /min
1	140	2	sodium borohydride	0.2	p-toluenesulfonic acid	0.25	10
2	140	3	sodium bisulfite	0.4	ethyl acetate	0.5	20
3	140	4	composite	0.6	phosphoric acid	0.75	30
4	160	2	sodium borohydride	0.4	ethyl acetate	0.75	30
5	160	3	sodium bisulfite	0.6	phosphoric acid	0.25	10
6	160	4	composite	0.2	p-toluenesulfonic acid	0.5	20
7	180	2	sodium bisulfite	0.2	phosphoric acid	0.5	30
8	180	3	composite	0.4	p-toluenesulfonic acid	0.75	10
9	180	4	sodium borohydride	0.6	ethyl acetate	0.25	20
10	140	2	composite	0.6	ethyl acetate	0.5	10
11	140	3	sodium borohydride	0.2	phosphoric acid	0.75	20
12	140	4	sodium bisulfite	0.4	p-toluenesulfonic acid	0.25	30
13	160	2	sodium bisulfite	0.6	p-toluenesulfonic acid	0.75	20
14	160	3	composite	0.2	ethyl acetate	0.25	30
15	160	4	sodium borohydride	0.4	phosphoric acid	0.5	10
16	180	2	composite	0.4	phosphoric acid	0.25	20
17	180	3	sodium borohydride	0.6	p-toluenesulfonic acid	0.5	30
18	180	4	sodium bisulfite	0.2	ethyl acetate	0.75	10

*Raw material ratio of stearic acid and diethylenetriamine was 1.8:1. Amount of antioxidant and catalyzer was based upon mass of stearic acid.

Impact of Synthetic Process on Melting Points and Cobb$_{60}$ Value of DSEAC

Color, melting point, and the Cobb$_{60}$ value of stearamide and DSEAC are shown in Table 3. The results in Table 3 show that reaction conditions had a great impact on the product structure. The main impact of the independent variables on the melting points is shown in Fig. 3. The dosage of the catalyst, holding time, and reaction time in the first step were the key factors for the melting points of DSEAC. With increasing temperature, the dehydration was promoted while the melting points of stearamide decreased. The holding time and dosages of the catalyst had a great influence on the ratio of mono-stearamide to stearic acid diamide. That was because the mixability of stearic acid and diethylenetriamine was determined by the holding time. The results demonstrated that the melting points of the product decreased when the catalyst dosage was 0.5% or the holding time was 20 min. That was due to the higher proportion of mono-stearamide under these conditions.

Table 3. Color, Melting Point, and Cobb60 Value of Stearamide and DSEAC

NO.	Color	MP of stearamide /°C	MP of DSEAC /°C	CA of stearamide /°	CA of DSEAC/°	Cobb$_{60}$ of stearamide /g·m^{-2}	Cobb$_{60}$ of DSEAC /g·m^{-2}
1	brown	100-102	94-102	70	87	62	30
2	pale yellow	94-100	66-72	45	54	65	58
3	pale yellow	102-106	80-90	88	97	60	26
4	puce	102-108	84-96	72	97	57	37
5	sandy beige	100-109	85-94	89	95	64	37
6	puce	100-105	72-77	104	103	61	42
7	puce	104-115	74-86	97	102	58	38
8	puce	98-104	82-90	73	98	62	37
9	puce	100-106	74-82	92	92	60	42
10	pale yellow	100-102	74-84	61	97	60	31
11	white	100-106	74-82	86	103	63	35
12	puce	104-108	78-84	103	98	59	29
13	puce	103-106	74-78	99	102	63	37
14	pale yellow	104-110	78-92	92	88	63	39
15	puce	102-108	66-70	104	93	59	40
16	brown	98-104	70-80	92	99	55	37
17	puce	100-105	72-80	86	86	58	39
18	puce	98-102	72-78	100	104	53	39

*Cobb$_{60}$ value of paper after surface sizing was measured. The quantity of the sizing agent was 0.3%.
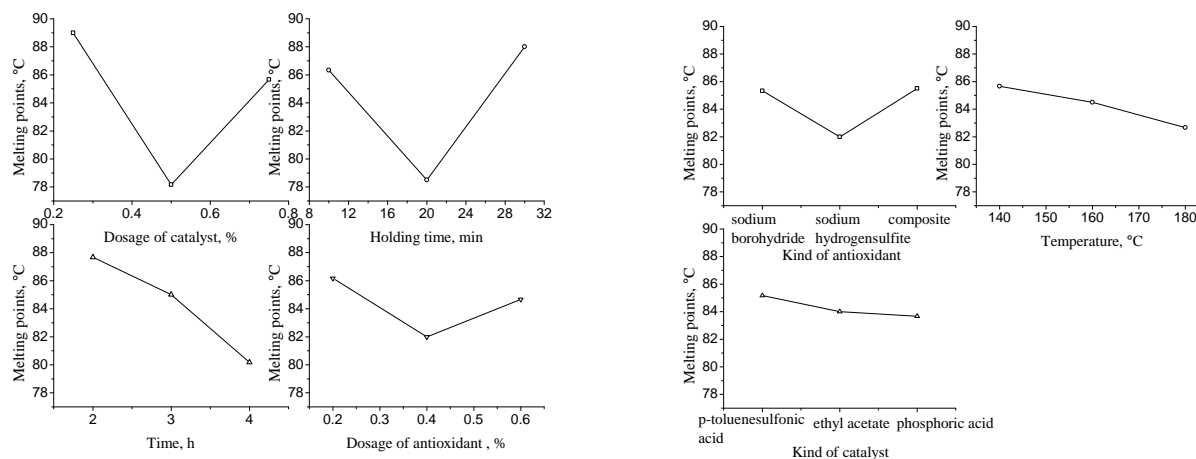
Fig. 3. The main effects of the independent variables on melting points

The main effects of the independent variables on the Cobb$_{60}$ test are shown in Fig. 4. The holding time, catalyst dosage, reaction time, and catalyst type in the first step were the key factors influencing the sizing performance of DSEAC. Consistent with results of the melting points, the holding time and catalyst dosage had a great impact on the ratio of single stearamide and stearic acid diamide. The higher ratio of mono-stearamide in the stearamide resulted in a poorer hydrophobicity than that of DSEAC. The sizing efficiency

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of p-toluenesulfonic acid was almost the same as that of phosphoric acid. However, the product color was lighter when using phosphoric acid as the catalyst.

According to Figs. 3 and 4, dosages of catalyst and holding time were respectively the most important factors for melting point and $Cobb_{60}$ value. Thus, the dosages of the catalyzer and holding time were respectively 0.5% based on the stearic acid mass and 30 min. Controlling the final temperature at 160 °C by using phosphoric acid as catalyst for 4 h was beneficial to both melting points and $Cobb_{60}$ value. Results showed that composite antioxidant can effectively enhance sizing. Therefore, the optimal synthetic process was maintained at 100 °C for 30 min, and was increased to 160 °C for 3.5 h. The dosages of the catalyzer and composite antioxidant were respectively 0.5% and 0.6% of the stearic acid mass by using phosphoric acid as catalyst.
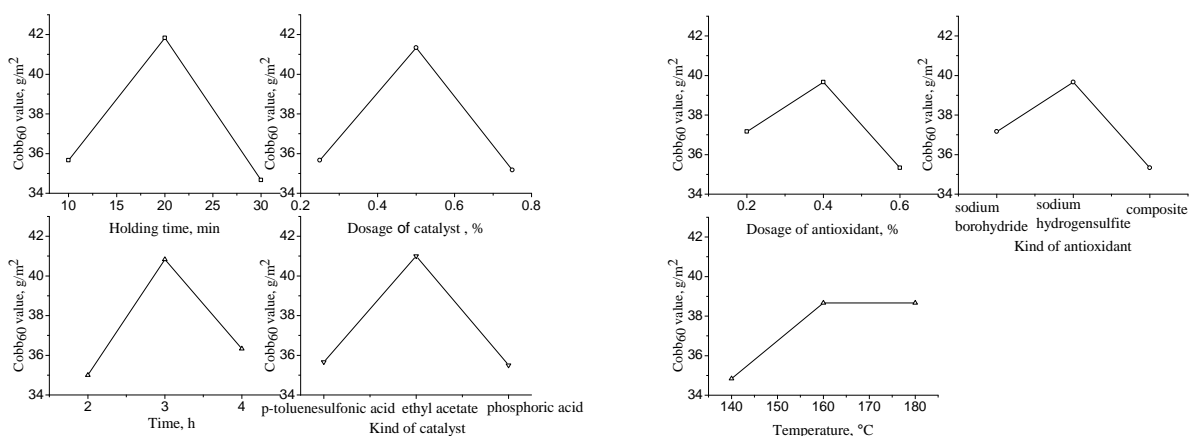
Fig. 4. Main effects of the independent variables on the $Cobb_{60}$ value

## Impact of Synthetic Processes on the Stearamide Structure

The $Cobb_{60}$ value was 27 when the quantity of the sizing agent was 0.3%, and the melting point ranged from 74 to 80 under the above synthetic conditions. The IR spectra and NMR results of the optimal product were recorded and analyzed. The IR spectra of diethylenetriamine, stearamide, and stearic acid are shown in Fig. 5. As shown in Fig. 5 (2), the appearance of the stretching vibration of C=O at 1680 cm^{-1} indicated the carboxyl group in stearic acid, and it was displaced in Fig. 5 (3). As shown in Fig. 5 (1), a broad band at 3300 cm^{-1} was assigned to the N-H of diethylenetriamine. Single or double absorption peaks at 3300 cm^{-1}, respectively indicated that the product contained either secondary or primary amine functional groups. Compared with the double absorption of diethylenetriamine at 3300 cm^{-1}, stearamide only had the single absorption peak due to amide formation. As shown in Fig. 5 (3), the continuous absorption peaks at 1650 cm^{-1} and 1310 cm^{-1} were the characteristic absorption peaks of the acylamino group. The absorption peak at 1640 cm^{-1} was the telescopic vibrating peak of C=O. The telescopic vibrating absorption peak of N-H was at 3300 cm^{-1}, and the single absorption peaks at 3300 cm^{-1} indicated that the product contained a secondary amine functional group. The absorption peaks at 2919 cm^{-1} and 2850 cm^{-1} were the characteristic absorption peaks for the methylene functional group. The absorption peak at 720 cm^{-1} would appear when continuous methylene groups (>4) existed in the product. The absorption peak at 2960 cm^{-1} and 1380 cm^{-1} were the characteristic peaks of the methyl group. At 1128 cm^{-1}, there was the telescopic vibrating absorption peak of C-N. The IR spectra demonstrated that

the product contained a long carbon chain with repeated methylene functional groups. According to the IR spectra, the acylamino groups were formed and the secondary amine groups were intact.
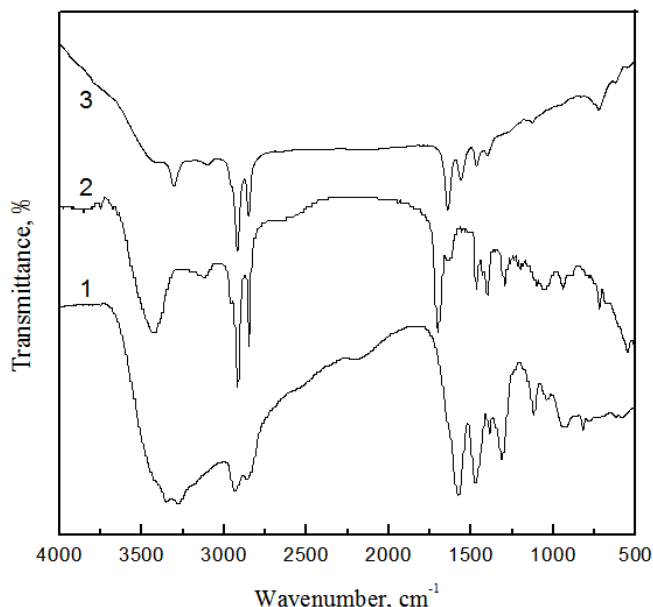
Fig. 5. IR spectra of diethylenetriamine (1), stearamide (2), and stearic acid (3)
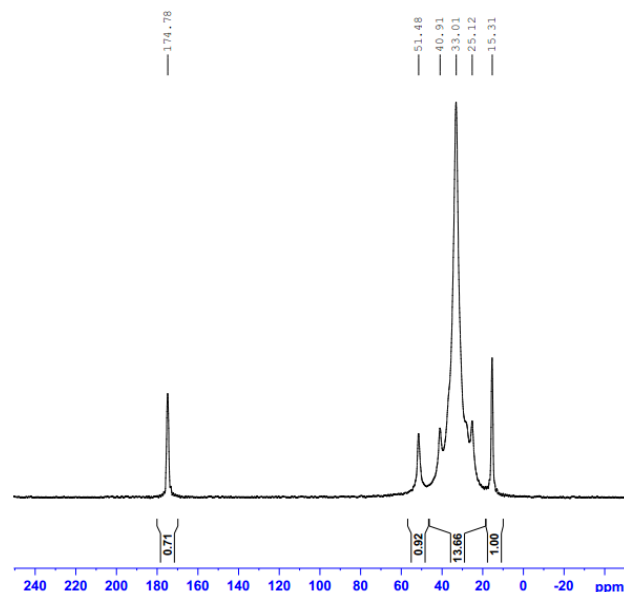
Fig. 6. ^{13}C NMR results for stearamide

An NMR analysis was employed in order to determine whether stearamide or other by-products possibly were formed. In general, the chemical displacement of carbon in the long alkyl chain was less than 40 ppm. Due to the electron withdrawing groups, the chemical displacement of the adjacent carbon atom would migrate. The chemical displacement of the carbon, which was adjacent to the amido group in stearamide, was around 51 ppm. The chemical displacement of carbon might shift to 77 ppm if the oxygen in the air reacted with the free amino group in mono-stearamide. In stearic acid, the chemical displacement of the carboxyl group was about 177 ppm, while the chemical shift was about 174 ppm in stearamide. For imidazole, the chemical displacement of intra-annular C-N double bonds would be around 164 ppm. Based on all these logical analyses, NMR spectra were obtained to distinguish stearamide and other by-products possibly formed. The NMR analysis results demonstrated that no stearic acid was found and no imidazole was generated, indicating good control. One peak observed at 15.31 ppm was attributed to the final carbon in a long alkane chain. One big band from 25 to 41 ppm was ascribed to the carbon atoms in a long alkane chain. One peak at 51.48 ppm and 174 ppm showed that stearamide was formed. No absorption at 77, 164, or 177 ppm in the NMR spectra indicated there was no stearamide oxidative formation, no imidazole formation, and no stearic acid residue formed, respectively. From the NMR spectra, it was difficult to distinguish mono-stearamide from bis-stearamide; however, the peak intensity at 174.78 ppm was different from that of 51.48. According to raw material ratio and NMR, we can conclude that the stearamide was a mixture of mono-stearamide and bis-stearamide.

CONCLUSIONS

1. The exploration of the synthetic process of stearamide showed that stearamide could have an application prospective as a neutral papermaking sizing agent. Single factor experimental results showed that the reaction time and temperature played a key role for condensation action. As shown in the orthogonal experiment, holding time, dosages of catalyzer, and antioxidant were the main factors affecting the stearamide structure.

2. According to an orthogonal experiment, the optimal synthetic process involved maintaining the temperature at 100 °C for 30 min, and then increasing the temperature to 160 °C for 3.5 h. The dosages of the catalyzer and composite antioxidant were respectively 0.5% and 0.6% of the stearic acid mass by using phosphoric acid as catalyst. The $Cobb_{60}$ value was 27 when the quantity of the sizing agent was 0.3%, and the melting point ranged from 74 to 80 under the above synthetic conditions.

3. The FTIR analysis under the optimal conditions showed that the carboxyl group of stearic acid and the primary group of diethylenetriamine disappeared while the amide group was formed. The NMR analysis results demonstrated that the proposed stearamide structure was actually generated and no other possible by-product, such as imidazole was formed when using optimal process conditions.

ACKNOWLEDGMENTS

REFERENCES CITED

Basta, H. (2003). "The role of chitosan in improving the ageing resistance of rosin sized paper," *Restaurator* 24(2), 106-117.

Chen, C.-Y., Wu, Q., and He, L. (2002). "Synthesis of di-(stearylamidoethyl) epoxypropyl ammonium chloride," *Journal of Beijing Institute of Petro-chemical Technology* 10(3), 39-42.

Chen, X.-K., Wu, H.-K., Shi, H.X., and Xiang, J.-P. (2007). "Synthesis of ethylene bis-stearamide through direct amidated reaction," *Chem. Prod. Technol*. 14(3), 21-29.

Davis, J. W., Roberson, W. H., and Weisgerber, C. A. (1956). "A new sizing agent for paper – Alkylketene dimers," *Tappi J*. 39(1), 21-23.

Guan, Y. (2002). "Effect of cationic starch on ASA emulsification," *China Pulp Paper* 2002(5), 17-20.

Hansen, C. M., and Björkman, A. (1998). "The ultrastructure of wood from a solubility parameter point of view," *Holzforschung* 52(4), 335-344.

Hodgson, K. T. (1994). "A review of paper sizing using alkyl ketene dimer versus alkenyl succinic anhydride," *Appita J*. 47(5), 402-406.

Hubbe, M. A. (2006). "Paper's resistance to wetting. A review of internal sizing chemicals and their effects," *BioResources* 2(1), 106-145.

Isogai, A., and Morimoto, S. (2004). "Sizing performance and hydrolysis resistance of alkyl oleate succinic anhydrides," *Tappi J*. 3(7), 8-12.

Lee, G. H., and Shin, D. S. (1991). "Effects of degree of substitution of cationic starches on ASA sizing in alkaline papermaking," *J. TAPPIK* 23(2), 5-14.

Li, F., Geng, X. G., Chen, Z., and Zhao, L. (2012). "A novel and expeditious method to fabricate superhydrophobic metal carboxylate surface," *Appl. Phys. A* 106, 35-40.

Lindfors, J., Salmi, J., Laine, J., and Stenius, P. (2007). "AKD and ASA model surfaces: Preparation and characterization," *BioResources* 2(4), 652-670.

Truong, Y. B., Shen, W., and Parker, I. (2003). "Effect of primary fines and surface charge of hardwood pulps on AKD sizing," *Appita J*. 56, 30-34.

Wang, F., Kitaoka, T., and Tanaka, H. (2003). "Supramolecular structure and sizing performance of rosin-based emulsion size microparticles," *Colloids Surf. A* 221, 19-28.

Xu, M., Dai, H.-Q. Wu, W.-B., and Wang, S.-M. (2012). "Effect of process parameters on cationic ethylene stearamide," Proceeding of the 4th International Conference on Pulping, Papermaking and Biotechnology, Nov, 7-9, 2012, Jiangsu Provincial Key Lab of Pulp & Paper Science & Technology, Nanjing Forestry University, Nanjing, China, pp. 526-530.

Yan, X.-H., Ji, Y.-X., and He, T. (2013). "Synthesis of fiber crosslinking cationic latex and its effect on surface properties of paper," *Progress in Organic Coatings* 76, 11-16.

Yu, L., and Garnier, G. (2002). "The role of vapour deposition during internal sizing: A comparative study between ASA and AKD," *J. Pulp Pap. Sci*. 28(10), 327-331.