Molecular Weight of Amphoteric Polyacrylamide: How it is Influenced by the Variables in Synthesis, and its Impacts on the Dry Strength of Paper Sheets

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Amphoteric polyacrylamide (AmPAM) is a linear water-soluble polymer that has been applied in papermaking as an agent for flocculation, retention, filtration, and dry-strength improvement. However, AmPAM with different ranges of molecular weight (MW) have different properties in these processes. In this study, a series of AmPAMs were constructed with an anionic monomer, itaconic acid (IA), a cationic monomer, methacryloxyethyl-trimethyl ammonium chloride (DMC), and a main backbone of acrylamide (AM). Four factors influencing free radical polymerization, *i.e*., reaction temperature, pH, initiator load, and the concentration of monomers, were systematically investigated *via* an orthogonal test to determine their effects on the MW of AmPAM. Spectroscopy and isoelectric point assays were used to characterize the structure of the produced AmPAM, and the MW was assessed by calculating the viscosity. The reaction temperature had the greatest influence on the MW of AmPAM, followed by the solution pH and the initiator load. To determine the dry strength of papersheets containing AmPAM, the breaking length of handsheets was assessed after adding 0.5% AmPAM (based on fiber) with different MWs. The maximum value, 4.05 km, was 15.0% higher than the control and was obtained using AmPAM with a MW of 330 kDa.

Keywords: Amphoteric polyacrylamide; Molecular weight; Dry strength; Orthogonal experimental design

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INTRODUCTION

The percentage of recycled fiber used in paper and paperboard has been increasing for decades, and now it has become the most important material for the paper industry. Its consumption greatly exceeds that of either chemical pulp or mechanical pulp (Göttsching and Pakarinen 2000; Pöyry 2011). The fiber strength and quality decrease each time the fiber is recycled due to fibers being cut and worn down during the beating and the hornification that occurs during drying (Scallan and Tigerström 1992).

Thus, it is necessary to modify secondary fibers for improved strength. Nazhad (2005) found that a caustic treatment modifies the surface of fibers to improve the strength of the produced paper; cationic starch treatment also helps the flocculation of fines and fibers. In terms of improving fiber bonding, the cationic starch treatment was much more effective than the caustic treatment. Cationic polyacrylamide (CPAM) and cationic starch have been used as dry strength agents for many years in papermaking. However, CPAM is more suitable than cationic starch due to its lower required dosage.

Recently, amphoteric polyacrylamide (AmPAM) has been used as a dry strength agent in the paper industry and other fields. AmPAM is a typical polyampholyte, carrying both basic groups and acid groups along the same molecular chain (Dobrynin *et al.* 2004; Song *et al.* 2006; Hubbe *et al.* 2007; Silva *et al.* 2009; Song *et al.* 2010; Zhu *et al.* 2015). In an aqueous solution, the acid groups of AmPAM dissociate and adsorb cations from the white water in the wet end, while the basic groups dissociate and anchor onto anionic fibers. With this unique feature, AmPAM can interact with fibers without interference from other cations.

The properties of AmPAM, *e.g.* molecular weight (MW), charge density, and types of ionic monomer used, have significant impacts on its function. Sezaki *et al.* (2006a,b) synthesized an AmPAM series with the same charge ratio and similar MW (approximately 3×10^6 D) but with various charge densities; the colloid behavior differed greatly between different AmPAMs. Song *et al.* (2006) applied those AmPAMs in papermaking and found that those AmPAMs with a moderate charge density contributed more to the dry strength of paper sheets. Higher MW does not necessarily improve paper tensile strength (Abdelmouleh *et al.* 2002).

In this study, a series of AmPAMs were developed with a molecular ratio of 86% monomeric acrylamide, 10% methacryloxyethyltrimethyl ammonium chloride and 4% itaconic acid but with various final MWs. To find the optimal MW for paper dry strength improvement, an orthogonal test was designed, and the impacts of individual factors on the MW were investigated.

EXPERIMENTAL

Materials

Monomeric acrylamide (AM), Methacryloxyethyltrimethyl ammonium chloride (DMC), and itaconic acid (IA) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), the Tokyo Chemical Industry Co., Ltd (Tokyo, Japan), and Tianjin Chemical Reagent Co., Ltd (Tianjin, China), respectively. The initiator ammonium persulfate was obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Sodium hydrogen sulfite was purchased from Sinopharm. Terahydrofuran (THF) was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were analytical reagent grade and used as they were received without further purification.

Synthesis of AmPAM

Free radical copolymerization took place in a four-neck flask equipped with a reflux condenser. The molar ratio of monomers was 86% AM, 10% DMC, and 4% IA. The flask was heated in a water bath to a temperature of 60 to 90 °C in an N_2 atmosphere. The pH of the reaction was adjusted with 1 M NaOH. The initiator consisted of ammonium persulfate and sodium hydrogen sulfite (mass ratio of 5:4). Sodium hydrogen sulfite was added first, and then the ammonium persulfate was added dropwise 10 min later. The reaction was stopped after 4 h. Solid AmPAM samples were obtained after drying at 60 °C. The experimental parameters were designed using an orthogonal experimental design (Table 1).

Characterization of AmPAM

Molecular weight of AmPAM

A 0.1% solution of AmPAM in 1 M NaCl solution was prepared. The viscosity of aqueous AmPAM solutions was measured using an Ubbelohde viscometer (Nanjing, China) in a water bath at 30 °C. The flow time of AmPAMs and the 1 M NaCl solutions in the viscometer was recorded. The molecular weight (MW) of AmPAM was calculated as follows, where $[\eta]$ represents intrinsic viscosity.

$$\mathrm{MW} = 802[\eta]^{1.25} \tag{1}$$

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectra

FTIR spectra were obtained with a Bruker VERTEX80 spectrometer (Karlsruhe, Germany). Approximately 1 mg of the sample and 200 mg of KBr were mixed and pressed into disks for the test preparation. For NMR analysis, aqueous AmPAM solutions were purified by precipitation in THF, and samples were prepared as described by Song *et al.* (2006). ^{1}H-NMR spectra were acquired on a Bruker 600 MHz spectrometer (Karlsruhe, Germany).

Measurement of isoelectric point (IEP)

The IEP of AmPAMs was obtained *via* particle charge detector (PCD; model PCD-03, BTG, Wessling, Germany). A PCD can detect the surface charge of particles or macromolecular charges. The charge of AmPAMs was measured under a different pH, which was adjusted by 1 M NaOH and/or 1 M H_2SO_4 aqueous solution. The curve of potential *versus* pH was plotted. On this curve, the potential is 0 at a certain pH value, which is the estimated IEP.

Handsheet Preparation and Performance of AmPAMs

Bleached hardwood kraft fibers were provided by Asia Symbol (Shandong, China) and were beaten with a laboratory valley beater (TD6-23, Xianyang Tongda Light-Industry Equipment Co., Ltd. Xiangyang, China) to a beating degree of 35° SR (GB/T 3332-1982). Before handsheet preparation, 1000 mL of slurry (with 0.2% oven-dried fiber) was blended with 10 mL of 1000 ppm AmPAM solution (0.5 wt.% load based on fiber) and stirred for 5 min. Handsheets were prepared in an automatic rapid Köthen sheet machine mold (Frank-PTI, Birkenau, Germany) with a base weight of 68 g/m^2. The wet handsheets were dried for 15 min.

The breaking length (standard of GB/T 12914) of the handsheets was measured on a tensile machine (Qingtong Instrumental Co., Ltd. Hangzhou, China). Before measurements, handsheets were stored at 23 °C and 50% humidity for more than 48 h. The handsheets were cut into pieces of 15 mm (width) by more than 150 mm (length). The pulling force of paper sheet tensile failure was recorded to calculate the breaking length.

RESULTS AND DISCUSSION

Experimental Design and Data Analysis

A five-factor, four-level orthogonal experimental design ($L_{16}(4^5)$) was employed to study the impacts of temperature (T), pH, monomer concentration (C_m), and dosage of initiator (D_i) on the MW and to produce a series of AmPAM samples with different MWs. A total of 16 experiments were performed; the influencing factors and their respective levels are listed in Table 1. The resulting AmPAM MW is also reported in Table 1. The minimum and maximum MW were 1.3 and 663.6 KDa, respectively, and these values are consistent with the reported MW range of the strength agent, 10^5 Da to 10^6 Da (Abdelmouleh *et al.* 2002).

Table 1. Results from the $L_{16}(4^5)$ Experimental Design for AmPAM Synthesis

Run	*T* (°C)	pH	C_m (%)	D_i (%)	Blank Row*	MW (×10^4; D)
1	60	4	15	0.2	1	28.8
2	60	4.5	20	0.4	2	54.4
3	60	5	25	0.6	3	33.55
4	60	5.5	30	0.8	4	56.94
5	70	4	20	0.6	4	21.44
6	70	4.5	15	0.8	3	19.65
7	70	5	30	0.2	2	27.04
8	70	5.5	25	0.4	1	66.36
9	80	4	25	0.8	2	0.13
10	80	4.5	30	0.6	1	10.65
11	80	5	15	0.4	4	23.59
12	80	5.5	20	0.2	3	25.08
13	90	4	30	0.4	3	19.07
14	90	4.5	25	0.2	4	27.74
15	90	5	20	0.8	1	15.51
16	90	5.5	15	0.6	2	22

*used for error calculation

Effect of reaction temperature on the MW of AmPAM

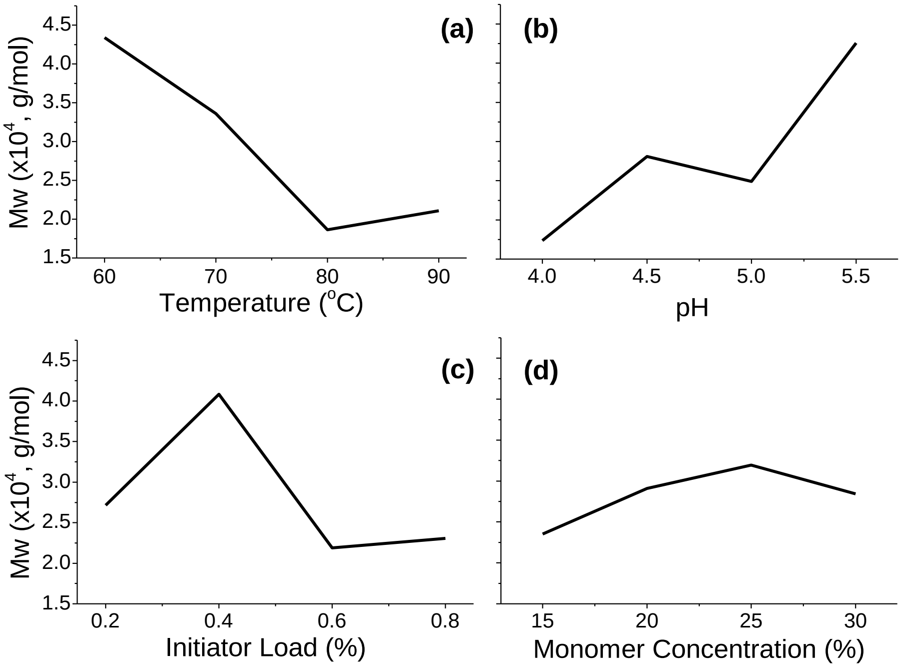

Fig. 1. Effect of temperature (a), pH (b), initiator load (c), and monomer concentration (d) on AmPAM MW

In a general chemical reaction, the reaction temperature and time, concentration of each agent, pH, *etc*., affect the final product. Other variables, such as the reaction time, the stirring speed, *etc.* may contribute to some extent to the MW of the produced AmPAM, but they will not be discussed in this article.

Temperature is always important in polymerization reactions. As illustrated in Fig. 1(a), higher MW AmPAM was obtained usually at a lower temperature. Generally, monomer activity increases with an increasing reaction temperature. The major constituent AM has a high activity even at a low temperature such as 10 °C. Therefore, it reacts too rapidly at a higher temperature, forming PAM segments with a small molecular weight in the solution. This phenomenon is called implosion, and it is harmful for the MW growth of PAM. Therefore, the activity of AM in polymerization should be restricted, while the activity of IA is very low. In some polymerization reactions involving IA, the temperature usually is controlled around 80 °C. Because the activity of AM and IA components seemed incompatible, it was necessary to compromise to achieve a product with high MW and all IA segments embedded in the chains. Because AM is the major constituent in the polymerization, its polymerization governs the trend of the MW of the produced AmPAM.

Effect of medium pH on the MW of AmPAM

The pH also influences the copolymerization of AM, DMC, and IA for the following reasons: (1) the amide group in AM tends to be hydrolyzed when the pH is higher than 7; (2) as DMC as a basic monomer, the pH of the solution affects the dissociation of the basic group and its activity; and (3) IA has low activity and double acid groups, such that the acid group dissociation at high pH leads to more IA activity. The MW of AmPAM increased with the reaction pH in the investigated range of a pH of 4 to 5.5 (Fig. 1(b)). A pH value higher than 5.5 but lower than 7 was expected to be more suitable for the MW of AmPAM, but that pH range was too close to neutral and very difficult to maintain.

Effect of initiator load on the MW of AmPAM

The initiator dosage also affected the MW (Fig. 1(c)). The polymerization was initiated by $(NH_4)_2S_2O_8$ and $NaHSO_3$ with a weight ratio of 1.5 to 1.2. $(NH_4)_2S_2O_8$ is the main effective initiator, while the reducible $NaHSO_3$ inhibits the oxidization of PAM. In the free radical reaction, an initiator molecule reacts with and activates an AM molecule. This activated AM reacts with another AM molecule and becomes a new active center. The chain reaction continues until PAM activity decreases too much to connect to another monomer. Therefore, more initiator creates more polymer chains and results in a final product of lower MW. However, insufficient initiator results in unreacted monomers. The optimal initiator load for polymerization was 0.4 wt.% for all monomers.

Effect of monomer concentration on the MW of AmPAM

The concentration of monomers affects the reaction dynamics and the viscosity of AmPAM in solution (Fig. 1(d)). With increased viscosity, the mobility of the monomers and the activated AmPAM chains decrease. The reaction may stop when the viscosity is high enough with the increasing MW. Therefore, there is a balance between the dynamics and the viscosity. In the investigated range of monomer concentration, 25% was the optimal value for MW growth of AmPAM.

ANOVA

ANOVA results for the calculated models are shown in Table 2. The orthogonal design table used in this investigation is an L16 (4^5) table, but only four factors were considered. Therefore, the residual error (4527.66) was calculated first from the blank column. Because the variance from concentration of monomers was less than the residual error, it was combined with the residual error to calculate the pooled error, and therefore the degree of freedom of pooled error increased to 9. ANOVA indicated that the temperature was the most important factor in determining AmPAM MW because its F value (12.315) was greater than the F_{critical} value of 9.78 ($P < 0.01$). With regard to the pH and initiator load, the F values were 8.438 and 5.714, respectively, which were greater than the F_{critical} 4.76 ($P < 0.05$), but lower than the F_{critical} 9.78 ($P < 0.01$). Thus, their influence on the MW of AmPAM was also statistically significant but not as closely correlated as temperature. Only the influence of monomer concentration was not statistically significant.

Table 2. ANOVA of the Variables Influencing AmPAM MW

Factors	Variance	Freedom	F ratio	F_{critical}
T	1958.810	3	12.315	**
pH	1341.852	3	8.438	*
C_m	(147.546)	(3)	(0.928)	
D_i	908.883	3	5.714	*
Error	4527.66	6		
F_{critical}		$F(a = 0.01) = 9.78$	$F(a = 0.05) = 4.76$	

**Statistically significant ($P < 0.01$); *statistically significant ($P < 0.05$)

Characterization of Produced AmPAM

FTIR characterization

Because all samples had the same proportion of monomers and the structure of the produced AmPAM is quite similar, they were assumed to possess similar FTIR spectra. Therefore, FTIR spectra were collected for only one sample, but with different drying approaches, *i.e.* freeze-dried or hot air-dried at 60 °C (Fig. 2).

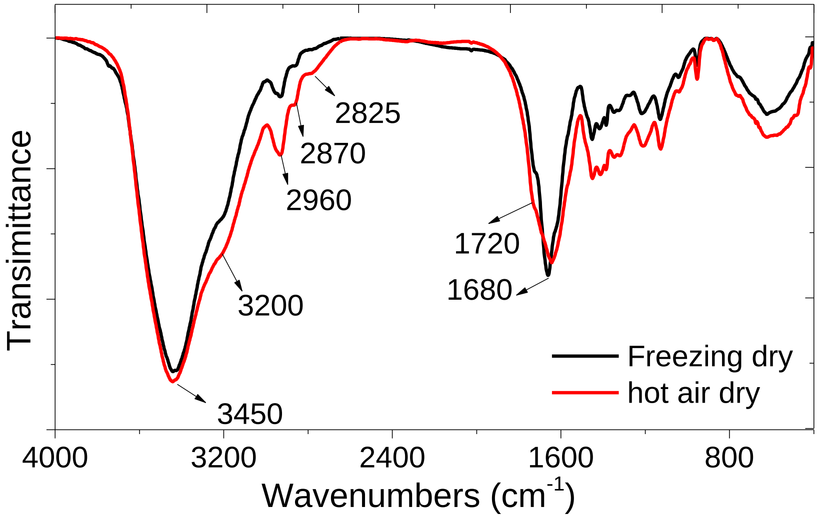

Fig. 2. FTIR spectra of AmPAM sample 16 that was freeze-dried or hot air-dried

The adsorption peaks at 3450 cm^{-1} and 3200 cm^{-1} were assigned to the stretching vibration of N-H and -NH_2, respectively, in the AM moieties. The adsorption peaks caused by C-N at 2960 cm^{-1} and 2870 cm^{-1} belonged to -N-CH_3 and -N-CH_2 in the DMC moieties, respectively. A wide and weak adsorption peak at 2825 cm^{-1}, which was caused by O-H in -COOH, belonged to the IA moieties. Therefore, the characteristic peaks of AM, DMC, and IA moieties were found in the FTIR spectra. In addition, the peaks at 1720 cm^{-1} and 1680 cm^{-1} were assigned to the stretching vibration of C=O. More specifically, the peak at 1720 cm^{-1} was assigned to the -COOH group, while 1680 cm^{-1} was assigned to the -$CONH_2$ group. These differences are discussed below in the context of the isoelectric point.

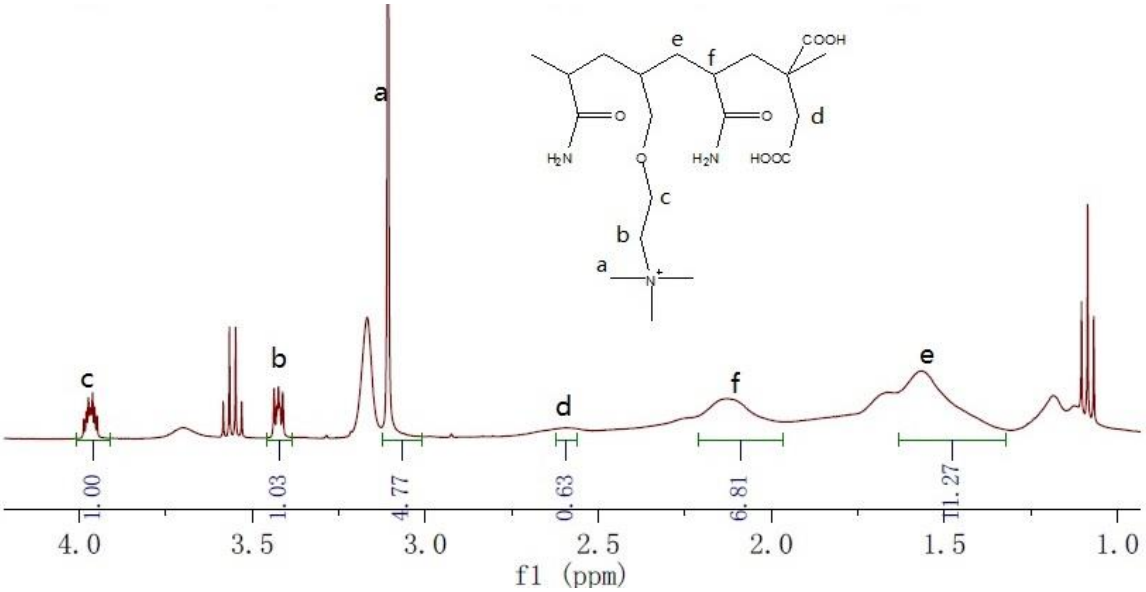

Fig. 3. ^{1}H-NMR spectra of AmPAM sample of Run 8

NMR characterization

For the reasons discussed above, the ^{1}H-NMR spectra of only one sample (Run 8) was investigated; the peak assignments and integration areas for most protons of AmPAM are presented in Fig. 3. Assuming the area of c proton from DMC moieties is 1, the areas of other protons based on NMR DMC, IA and AM are listed in Table 3 along from with their theoretical values, respectively. The calculated integration areas agreed roughly with the theoretical values. They did not exactly match because the broad d, e, aid f peaks may have overlapped. This result suggests that all monomers in the system are involved in the copolymerization reaction and that the proportion of each moiety is close to the monomer input ratio.

Table 3. Comparison of the Integration Area for Each Proton of AmPAM from ^{1}HNMR Spectra with Theoretical Value

	DMC			IA	AM	
	a(3.1-3.3)	b(3.4-3.5)	c(3.9-4.0)	d(2.5-2.7)	e(1.3-1.6)	f(2.0-2.4)
C10A4	4.77/4.5	1.03/1	1.00/1	0.63/0.4	11.27/10	6.81/4.8

Isoelectric point (IEP) test for selected AmPAM samples

IEP was measured for selected AmPAM samples without drying and with hot air drying at 60 °C (Fig. 4). Fresh, undried samples had an IEP close to 7; after hot air drying, the IEPs of the same samples were reduced to between 4 and 5. A decrease in basic groups or an increase in acid groups can shift the IEP to a lower pH, where the pH boosts basic group dissociation and limits acid group dissociation. The AM moieties tend to be hydrolyzed in an aqueous solution, especially when it contains O_2 and an active substance like $(NH_4)_2S_2O_8$.

In the FTIR spectra, the absorption peaks located at 2825 cm^{-1} and 1720 cm^{-1} corresponded to the O-H and the C=O of -COOH, respectively. The peaks at 2825 cm^{-1} and 1720 cm^{-1} of samples dried in hot air were stronger than those of the freeze-dried samples. This result implies that hydrolysis and oxidation of the AmPAM samples transforms $CONH_2$ into –COOH during hot air drying. Thus, the IEP shifts to a lower pH after hot air drying.

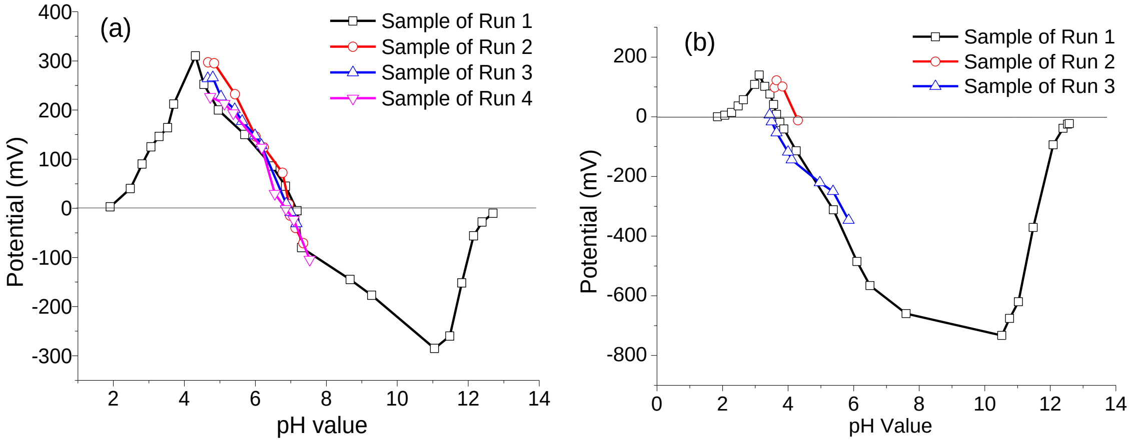

Fig. 4. Isoelectric point of selected AmPAM samples that were (a) freeze-dried or (b) hot air-dried

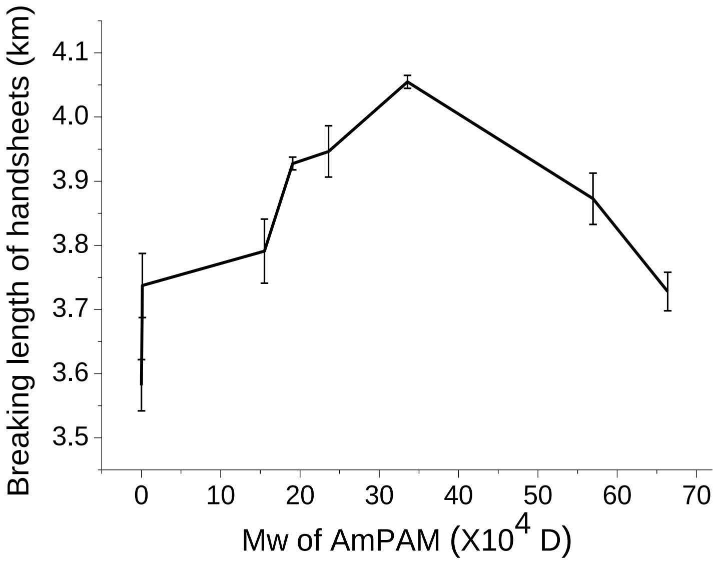

Fig. 5. Breaking length of AmPAM samples with various molecular weight

Dry Strength Performance for AmPAM with Various MWs

Handsheets were prepared by adding 0.5% AmPAM (based on fiber weight) during papermaking. The dry strength performance was expressed as the breaking length of handsheets, which was plotted against the AmPAM MW (Fig. 5). In the first stage, the breaking length of handsheets increased with increasing MW; this result was attributed to the better bridging effect of amphoteric polymers with longer chains and higher MW. At AmPAM MW greater than 330 kDa, the handsheet breaking length decreased with increasing MW. This result may reflect the flocculation of AmPAM, which decreases the homogeneity of handsheets. The optimal AmPAM MW for the dry strength of paper sheets was close to 330 kDa, where the bridging and flocculation effects of AmPAM were balanced. For this sample, the breaking length reached 4.05 km at a very small dosage (0.5%), which was 15.0% better than the control.

CONCLUSIONS

1. FTIR and ^{1}H-NMR analyses showed both IA and DMC are involved in polymerization. The anionic and cationic groups that were calculated from the ^{1}H-NMR was consistent with the original ratio of IA, DMC, and AM at addition.
2. An orthogonal test showed that the reaction temperature has the most influence on the MW of AmPAM. The solution pH and initiator load also contribute greatly to MW, while the concentration of monomers is not of much significance.
3. Regarding the dry strength performance of AmPAM with different MWs, there was an optimal MW range around 330 KD. For this sample with optimal MW, its breaking length reached up to 4.05 km, 15.0% longer than the control, at a very small dosage of AmPAM with 0.5% fiber.

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