

Melamine Formaldehyde/Polyvinyl Alcohol Composite Fiber: Structure and Properties Manipulated by Hydroxymethylation Degree

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ABSTRACT: Composite fibers made of different hydroxymethylation degree (HMD) melamine formaldehyde (MF) resins and polyvinyl alcohol were prepared by wet spinning. The structures of MF resins and composite fibers were studied using Fourier transform infrared spectrometer, optical microscope, scanning electron microscope, differential scanning calorimetry, X-ray diffraction, and Kjeldahl. The fibers' mechanical properties, fire retardant properties, softening point in hot water, and thermal stability were also tested. Results show that with the increase of HMD, the compatibility between MF and PVA gets better; the breaking strength and thermal stability of the fibers increase, while the nitrogen-loss rate, the elongation at break, and SP decrease. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40678.

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INTRODUCTION

Melamine formaldehyde (MF) resin and its derivatives are always considered to be an excellent flame retardant material because of its low thermal conductivity, low smoke toxicity, high nitrogen content, halogen absence, and nonformation of molten drops or noncontraction in the fire, or at high temperature.^{1–4} As a typical thermosetting resin, MF resin is usually stiff and brittle after being cured, and is always used as coating, adhesive, finishing agent, etc.^{5–8} To expand the application of MF resin and fully use its favorable nonflammability, melamine fiber, which has excellent flame retardancy, was conceived and has been attracting a lot of attention.^{2,3} Being a low molecular weight thermosetting resin, MF prepolymer always should be modified to improve its spinnability and toughness before being spinned.^{2,3} Due to the complexity of processing, only one kind of melamine fiber, Basofil, has attained industrial-scale production. The MF resin for Basofil is synthesized by using alkane-modified melamine, which can provide the cured resin with much toughness.^{9–12} However, the spinnability of this modified resin is not good enough. Therefore, Basofil can only be produced by centrifugal spinning as irregular staple fiber.

To obtain MF filament with satisfactory mechanical properties, many methods had been attempted. One feasible way is to use polyvinyl alcohol (PVA) as fiber-forming agent mixed with MF resin and get MF/PVA composite filament fiber via wet spinning process.¹³ However, a neglected problem that MF resin would

dissolve in coagulation bath during spinning impedes the application of this method. The dissolving-out of MF resin, also called “nitrogen loss,” would induce the deteriorations of fibers' mechanical and fire retardant properties, and contaminate the coagulation bath.

This study tries to improve the compatibility of MF resin and PVA to reduce the nitrogen loss in the coagulation bath by changing the hydroxymethylation degree (HMD) of MF resin. The structures and the properties of MF/PVA composite fibers consisting of MF resins with different HMD have been characterized and tested.

EXPERIMENTAL

Materials

PVA (DP = 2000, alcoholysis degree > 99%), industrially pure, was obtained from Sichuan Vinyon Workers, China, which was washed in advance by water; Melamine, formaldehyde solution (concentration: 35~38 wt %), triethylamine, sodium hydroxide, hydroxylamine hydrochloride, triethanolamine, and hydrochloric acid (98 wt %), all chemically pure, were purchased from Kelong Chemical Reagent Factory, Sichuan, China; Sodium sulfate, industrially pure, was obtained from Sichuan Chuan Mei, China.

Preparation of MF Resin with Different HMD

Formaldehyde solution was adjusted to pH 9~10 by triethylamine before being used. The formaldehyde and melamine

Table I. The Compositions of MF Resins

Sample number	1#	2#	3#	4#	5#	6#
Formaldehyde (N) : Melamine (N)	2:1	2.5:1	3:1	3.5:1	4:1	4.5:1

solution (the molar ratio of formaldehyde and melamine is summarized in Table I) were poured into the 500 mL three-necked flask, which was equipped with a stirrer and a condenser, then the mixture was heated to 80°C and kept stirring. When the mixture became colorless and transparent, the MF resin was obtained. The pH of product was adjusted to 9~10 by triethylamine.

Preparation of Spinning Dope

PVA was dissolved in water with a concentration of 15 wt % at 96°C for about 4 h, and then the solution was cooled to 70°C. The MF resin solution was added to the PVA solution and mixed together to form the spinning dope. The temperature of spinning dope was kept at 70°C. The mass ratio of MF resin and PVA is 1:1.

Preparation of MF/PVA Cast Film

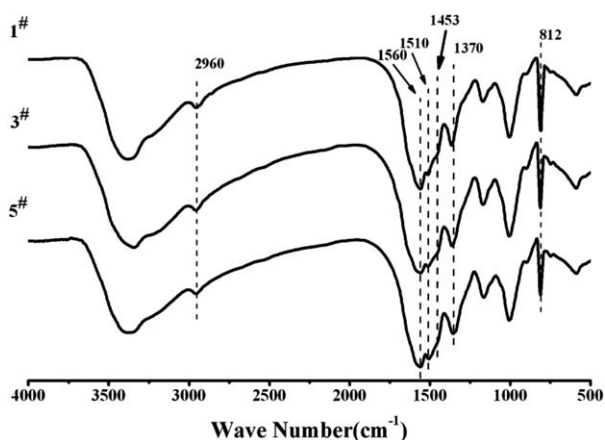
The prepared spinning dope was poured onto a polytetrafluoroethylene board to form a thin sheet. After being dried in the air, the MF/PVA cast film was obtained.

Preparation of MF/PVA Fiber

The spinning dope was extruded into a saturated sodium sulfate coagulating bath at 45°C from a spinneret (the diameter of capillary hole is 0.1 mm) to form the as-spun composite fiber. After being dried, the as-spun fibers were subjected to heat setting at 220°C for 3 min. Then, the final MF/PVA composite fiber was obtained by washing and drying.

Characterization

The molecular structures of synthesized MF resins were observed by Fourier transform infrared spectrometer (FTIR) (Magna 560, Nicolet, USA). The scan was range from 4000 cm^{-1} to 400 cm^{-1} with resolution of 2 cm^{-1} . The morphology of the composite fibers and membranes were observed using optical microscope (OM) (BK-POLR, OPTTEC, China) and scanning electron microscope (SEM) (JSM-5900, JEOL, Japan) whose

**Figure 1.** FTIR spectra of MF resins with different HMD.

accelerating voltage was 5 kV. The fiber samples for SEM were cut by blade to expose the cross-sections. The composite cast films were also analyzed using energy-dispersive X-ray spectroscopy (EDS) (INCAPentaFETx3, OXFORD, UK) to distinguish between the MF resin and PVA phase region. The composite fibers were also measured using differential scanning calorimetry (DSC) (DSC200, NETZSCH, Germany) at the ramping rate of 10°C/min in the range of 0~300°C in N_2 atmosphere. The crystal structures of the fibers were tested with X-ray diffraction (XRD) experiments (X'Pert Pro, Philips, Holland) in the 2θ range of 5~40° at a scanning rate of 12°/min with nickel filtered Cu-K_α radiation ($L = 1.54 \text{ \AA}$) at room temperature. The thermal stability of fibers was studied with thermogravimetric analysis (TGA) (Q600, TA, USA) at the ramping rate of 10°C/min in the range of 0~700°C in N_2 atmosphere. The nitrogen content was tested by nitrogen tester (K-06, ShenSheng, China) according to Kjeldahl. The nitrogen loss rate was obtained by comparing the nitrogen content of composite cast films and fibers. The mechanical properties of fibers were measured using a tensile strength tester (YG001A, HDFY, China). The initial length was 20 mm; drawing speed was 20 mm/min. The limiting oxygen index (LOI) of the fibers was measured using oxygen index tester (JF-3, JiangNing, China). The fibers were twisted into plaits 50 mm long, 6 mm wide, and 3 mm thick for testing. The composite fibers were boiled in distilled water at 100°C for 30 min, and then the quality change before and after were identified to calculate the gel content.

HMD Test

HMD was calculated by measuring the free formaldehyde in MF resin solution. Its test procedures are described as follows: First, 10 mL of MF resin solution and the reference solution (formaldehyde solution [37 wt %]) were adjusted to a pH of 7 with HCl standard solution (0.1 mol/L) or triethanolamine solution (6.5 wt %). The pH of the solution was monitored using pHmeter (STARTER3C, OHAUS, China). Second, 10 mL hydroxylamine hydrochloride solution (0.25 mol/L) was mixed with solutions obtained from the first step, and the mixture was shaken together in an iodine flask and kept at 40°C for 30 min. Finally, NaOH standard solution (0.1 mol/L) was used to titrate

Table II. Homogeneous Time and HMD of MF Resins

Samples	Homogeneous time ^a (min)	HMD
1#	15	0.49
2#	4	0.72
3#	3	0.92
4#	1	1.04
5#	0.67	1.15
6#	0.39	1.23

^a Homogenous time: the time that the mixture of melamine and formaldehyde solution takes to become homogenous in reaction.

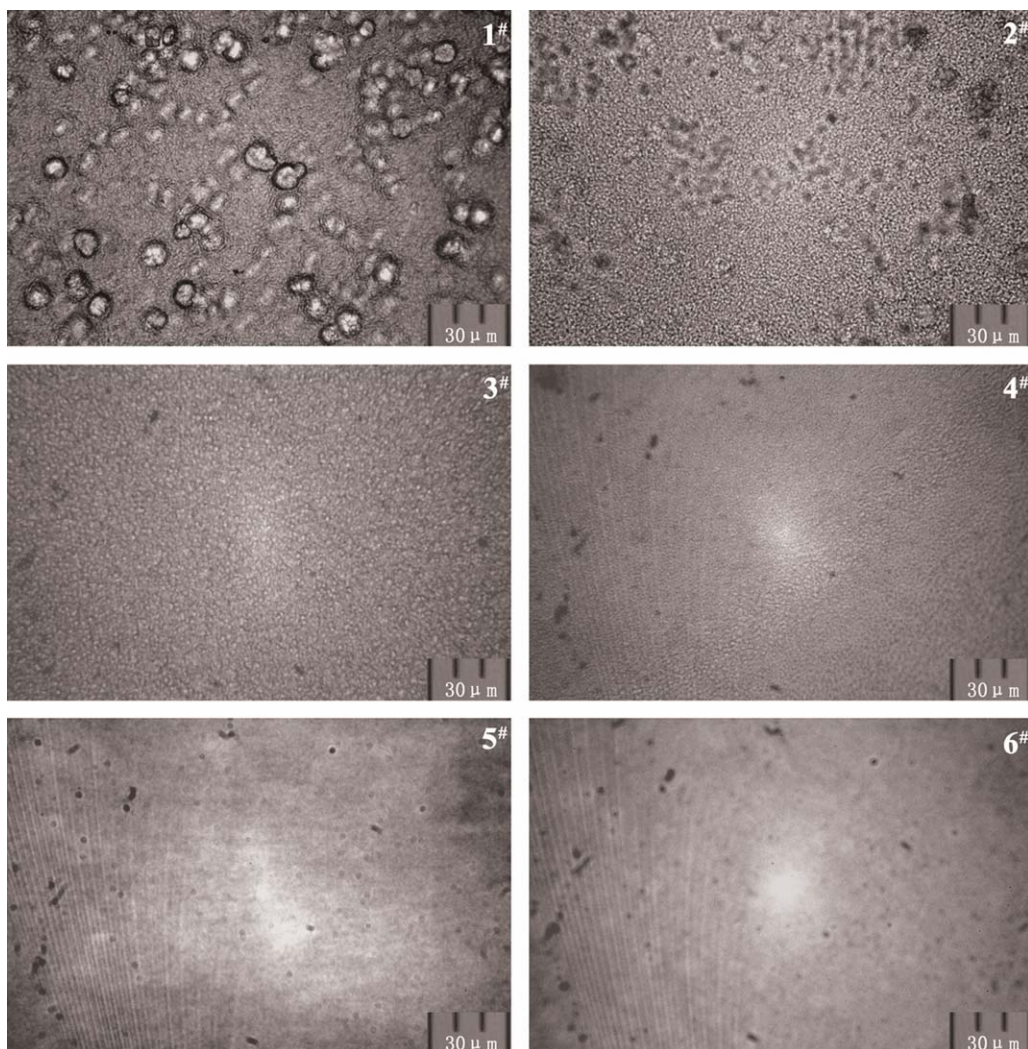


Figure 2. OM images of spinning dopes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

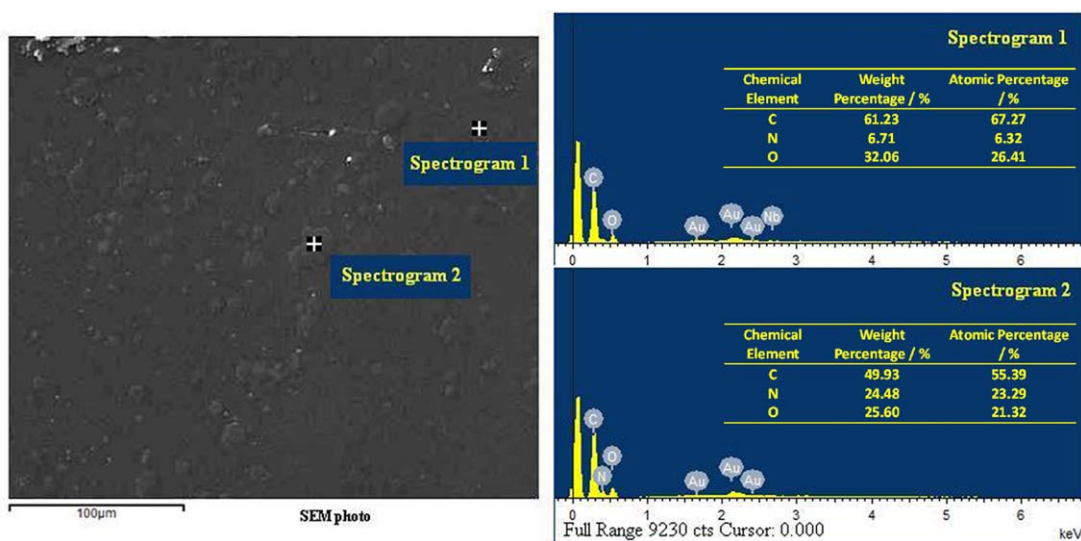


Figure 3. EDS spectrograms of Sample 1#. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

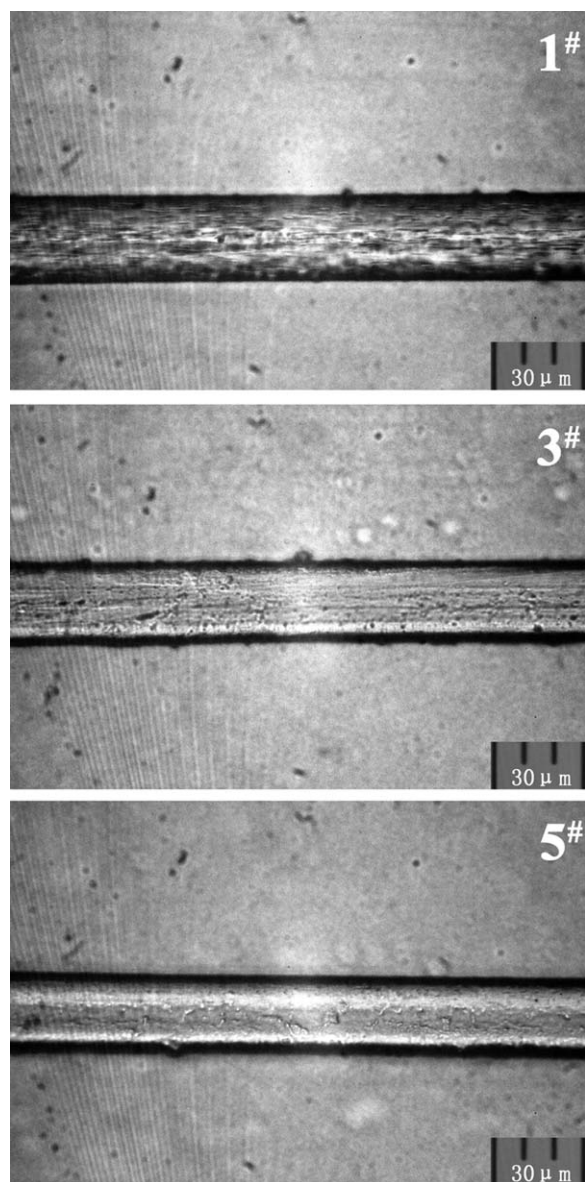


Figure 4. OM images of fibers made of different MF resins.

the moles of hydrochloric acid, which was released from the reaction between free formaldehyde and hydroxylamine hydrochloride. The HMD was figured out by the following formula (1):

$$\text{HMD} = \frac{(V_1 - V_2) * C * \frac{V}{10}}{m/126} \quad (1)$$

where V_1 represents the NaOH standard solution consumed volume of the reference solution (mL); V_2 represents the NaOH standard solution consumed volume of MF resin solution to be examined (mL); V represents the total volume of the test resin solution (mL); 10 represents the volume of the test sample (mL); m is the mass of melamine added (g); C is the concentration of NaOH standard solution (0.1 mol/L); 126 represents the molar mass of melamine (g/mol).

Water Resistance Test

Softening point in hot water (SP) was defined as a measurement for the hot water resistance of fibers. SP was tested with

methods described as follows: a bundle of fibers with length of 20 mm was tied to a regulus lead and then put into 20°C water. The ratio of regulus lead's weight to fiber's linear density was 1.8 mg/dtex. The water was heated at a heating rate of 2°C/min as soon as the fibers were put in the water. Record the temperature of the water when the deformation of the fibers reached 2 mm (either elongation or shortening) as SP.

RESULTS AND DISCUSSION

Characterization of Molecular Structure

Figure 1 is the IR spectrum of MF resins with different HMD. It can be seen that the stretching vibrations peaks of C—H at 2960 cm^{-1} and flexural vibration peak of C—H at 1453 cm^{-1} all belong to the $-\text{CH}_2-$; the flexural vibration peak at 812 cm^{-1} and the stretching vibration peak at 1560 cm^{-1} all belong to the triazine ring; the stretching vibration peak at 1510 cm^{-1} and 1370 cm^{-1} belong to the C—N of the inner and outer part of triazine ring, respectively. All of these peaks show that hydroxymethyl reaction has occurred between melamine and formaldehyde. Compared to the peak at 2960 cm^{-1} , the reduction of the peak at 812 cm^{-1} and 1560 cm^{-1} shows an increase of HMD. No peaks appear from 1150 cm^{-1} ~1060 cm^{-1} , which means that no etherification reaction has happened and all the MF resins are in hydroxymethyl stage. With the increase of formaldehyde amount, the time that the reaction system takes to become homogeneous reduces and the HMD of resin increases, which are summarized in Table II.

Compatibility of MF Resin and PVA

Figure 2 shows the OM images of spinning dope. It shows that when the HMD of MF resin is at low level, the MF resin and PVA solution are immiscible. In the spinning dope, MF resin microphase regions scatter in the PVA solution with clear interface, such as Sample 1#. With the increase of HMD, the compatibility of MF resin and PVA solution gradually improves; the interface between MF resin and PVA solution becomes blurred and the size of MF resin phase reduce, which can be seen from Samples 2# to 4#. When the mass ratio of formaldehyde and melamine reaches 4:1 or more, MF resin and PVA solution are mutually soluble, and the spinning dope becomes homogeneous, as Samples 5# and 6#. These results suggest that the increase of HMD is beneficial to the compatibility between MF resin and PVA.

To clarify the regions of MF resin and PVA, energy-dispersive X-ray spectroscopy (EDS) test was conducted in the SEM observation process of Sample 1#. The result is as shown in Figure 3. It shows that the nitrogen element content in area 1 is 6.71%, while that in area 2 is 23.29%. It indicates that the MF resin is the dispersed phase in the spinning dope.

Figure 4 is the OM photos of the composite fibers after heat treatment, and Figure 5 is the SEM photos of the cross-sections of the composite fibers after heat treatment. These two figures also show that MF resin with higher HMD tends to have better compatibility with PVA. From the OM photos, it can be seen that the composite fiber made of high HMD resin (Sample 5#) is homogeneous and transparent, while the fiber with low HMD (Samples 1# and 3#) is heterogeneous, and the lower HMD

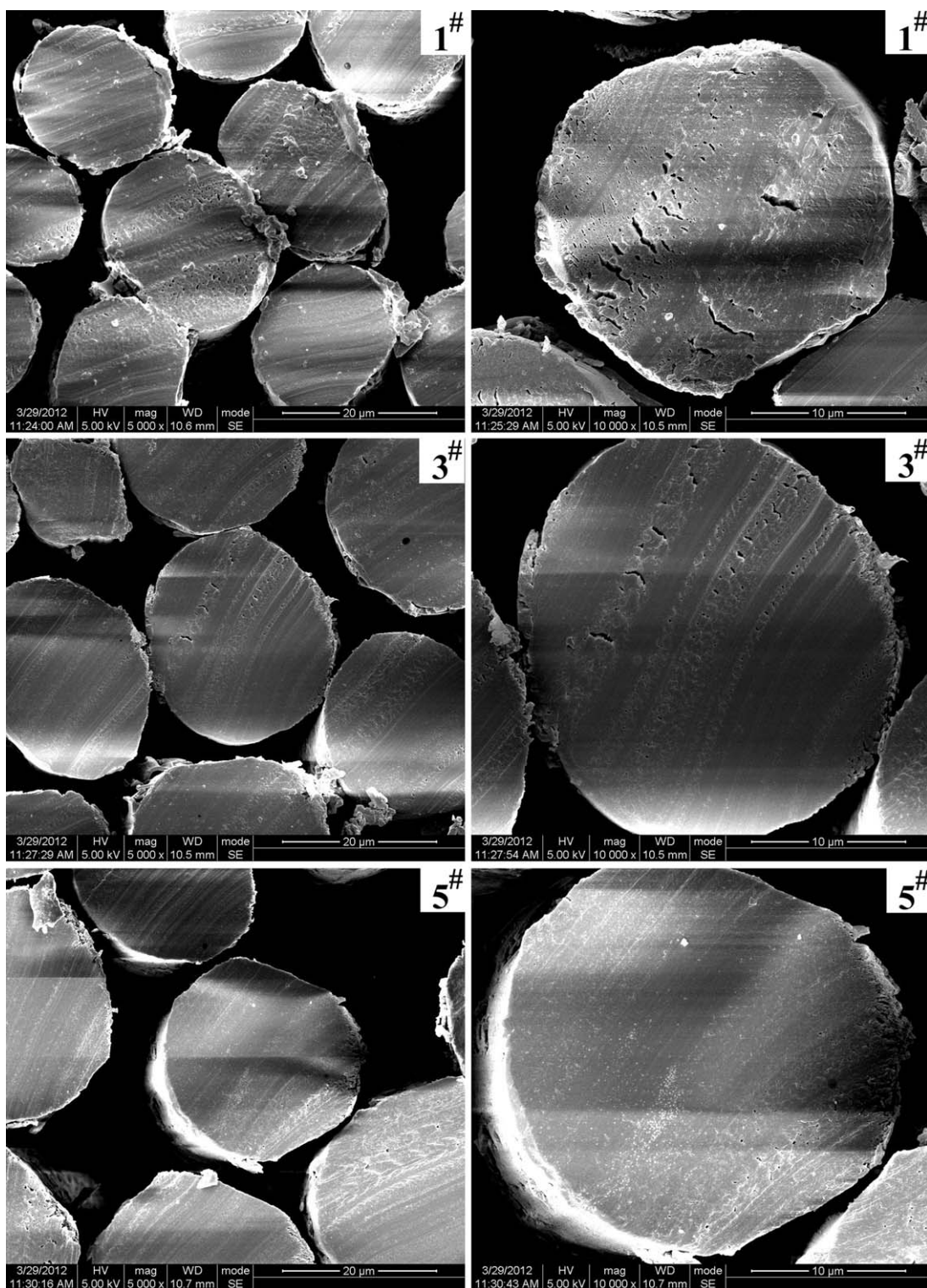


Figure 5. SEM photos of the cross-sections of fibers made of different MF resins.

induces the larger phase separation degree. Figure 5 clearly shows that there are more flaws and defects inside the fiber with low HMD than that in the fiber with high HMD.

Figure 6 is the DSC analysis results of composite fibers. All the curves have the only endothermic peak at $220\sim 240^{\circ}\text{C}$; with the

increase of HMD, both the area and the peak temperature of this peak descend. This result also demonstrates that the compatibility of MF resin and PVA is improved by raising the HMD of MF resin. The endothermic peak should be due to the melting of PVA crystal; if MF resin has good compatibility with PVA, it would retard the crystallization of PVA, which will cause

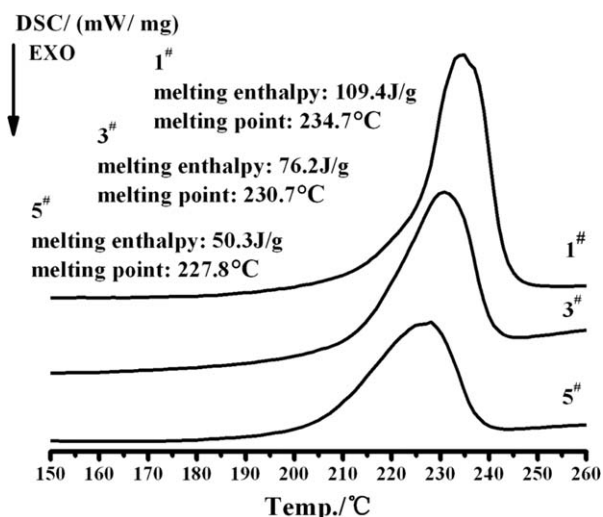


Figure 6. DSC curves of fibers made of different MF resins.

the decrease of melting enthalpy and melting temperature of PVA crystal; on the contrary, the crystallinity of PVA is less impeded when MF resin does not dissolve in PVA.

The influence of HMD on the crystallinity of fibers also can be proved by the outcome of XRD shown in Figure 7. The superimposition of the X-ray diagrams shows that the signal characteristics of the fibers are quasi similar however the HMD of MF resin changes. On the XRD diagrams, peaks appear at $2\theta = 11.3^\circ$, 16.1° , 19.7° , 22.7° , 27.4° , and 34.4° . The peaks at $2\theta = 11.3^\circ$, 16.1° , 19.7° , and 22.7° were reported as the theoretical positions of PVA.^{14,15} The crystallinities of samples were calculated using MDI Jade 5.0 software with the peak at $2\theta = 19.7^\circ$ selected as the only crystalline diffraction peak, and the crystallinities of Samples 1#, 3#, and 5# are 62.01%, 57.47%, and 49.58%, respectively. The variation tendency of crystallinity is the same as the results of DSC tests.

All the photos and test results show that the MF resin with higher HMD has a better compatibility with PVA. It is believed that the higher the HMD is, the more similar polarities of MF resin molecules and PVA molecules will be, which is good for the improvement of the compatibility.

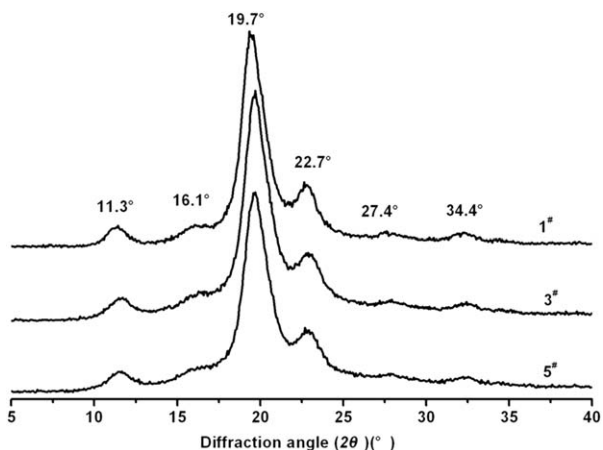


Figure 7. XRD curves of fibers made of different MF resins.

Table III. Nitrogen Loss Rates of Fibers Made of MF Resins with Different HMD

Samples	Nitrogen content of membranes (%)	Nitrogen content of fibers (%)	Nitrogen loss rate (%)
1#	45.96	33.76	26.55
2#	44.27	37.35	15.64
3#	44.07	40.04	9.14
4#	42.50	40.55	4.58
5#	41.66	41.58	0.20
6#	40.73	40.63	0.20

Nitrogen Loss Rate of the Fibers

The rising compatibility also contributes to the decrease of nitrogen loss rate, which is summarized in Table III. With the MF resin HMD increasing, the fiber nitrogen loss rate fell to 0.20% from 26.14%. But a further increase in HMD does not reduce the wastage of MF significantly. This is because, with the increase of MF resin HMD, the hydrogen bond density between MF resin and PVA also increases, which causes the improvement of intermolecular force. The hydrogen bond is stable in the coagulation bath at 45°C , hence the MF resin with high HMD is nearly all that remains in the fiber. When the molar ratio of formaldehyde and melamine attains 4:1, the nitrogen loss rate is only 0.20%, which can be considered that no MF resin has dissolved in the coagulation bath.

Properties of the Fibers

The properties of fibers are summarized in Table IV. All samples have 100% gel content, which means that all fibers were completely crosslinked. Fibers made of higher HMD MF resins have lower SP, because high HMD lead to low crystallinity of fibers, and hydroxyls in amorphous regions of fiber increase, which make the water resistance of fiber to decrease. The samples with higher HMD have a stronger breaking strength and shorter elongation at break. The breaking strength of Sample 5# reaches up to 3.19 cN/dtex, and the elongation at break is 25.1%. This is because that higher HMD resin has better compatibility with PVA, which reduces the defects in fibers. And higher HMD resin has more active groups, which contribute to the crosslink density of composite fibers. The LOI of different MF fibers does not have an obvious change, and they are all above 33.0.

The TGA curves of these MF fibers are shown in Figure 8. There exist two weight loss stages during the thermal

Table IV. The Properties of Fibers Made of MF Resins with Different HMD

Sample	Gel content (%)	Breaking strength (cN/dtex)	Elongation at break (%)	LOI	SP ($^\circ\text{C}$)
1#	100	2.75	38.1	33.5	96
3#	100	2.88	29.4	33.6	89
5#	100	3.19	25.1	33.2	86

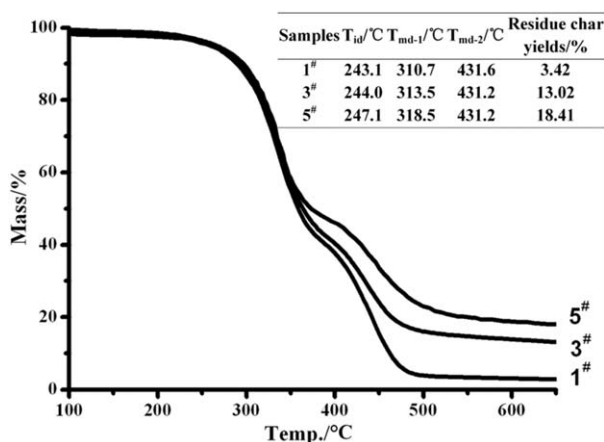


Figure 8. TGA curves of MF fibers made of different MF resins.

decomposition of composite fibers. The first stage is due to the decomposition of PVA and second stage belongs to the decomposition of MF resin. With the HMD of MF resin deepening, the char yield increases from 3.42% to 18.41% at 650°C. The initial thermal decomposition temperature (5% weight loss) and the first maximum temperature of thermal decomposition also have an increasing trend, although no significant changes of the second maximum temperature of thermal decomposition has been observed. The fiber made of higher HMD resin has better thermal stability, which should be caused by the lower loss rate of MF resin and the higher crosslinking degree of fiber.

CONCLUSION

Raising the mass ratio of formaldehyde and melamine benefits the increase of HMD. With an increase in HMD, the compatibility of MF resin and PVA is improved and the nitrogen loss rate of fibers is gradually reduced. When HMD increases to 1.15, the nitrogen loss rate will reduce to 0.20%, which can be considered as no dissolution of MF resin in coagulation bath. With the increase of HMD, the mechanical and thermal properties of fibers became better, whereas the crystallinity and water resistance of fiber decreased. The properties of fiber prepared by MF with HMD of 1.15 are as follows: the breaking strength is 3.19 cN/dtex; the elongation at break is 25.1%; the LOI is 33.2; the SP is 86°C; the initial thermal degradation temperature and char yield in nitrogen at 650°C are 247.1°C and 18.41%.

The problem of MF resin dissolving out in spinning has been successfully solved in this study. The water resistance of the fiber is unsatisfactory, but with desirable mechanical properties, good thermal properties, and excellent flame retardancy, this kind of composite MF fiber has the potential to be applied in some flame retardant textiles.

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