

## Melamine formaldehyde/polyvinyl alcohol composite fiber: Structures and properties controlled by reaction-induced phase separation

Weixing Xu, Cihang Yu, Xiangsen Zhao, Jianjun Xu, Mengjin Jiang

College of Polymer Science and Engineering State Key Laboratory of Polymer Materials Engineering of China, Sichuan University, Chengdu, Sichuan 610065, China

Correspondence to: M. Jiang (E-mail: memoggy@126.com)

**ABSTRACT:** Melamine–formaldehyde resin (MF)/polyvinyl alcohol (PVA) composite fibers with different phase structures and properties were prepared through reaction induced phase separation by wet spinning. Raman spectroscopy, rotary viscometer, and miscibility index were used to characterize the MF resins with different reaction degrees (RD). The phase structures of composite spinning dopes and composite fibers were observed by optical microscope (OM) and scanning electron microscope (SEM). Mechanical properties, flame retardant properties, and thermal stability of the composite fibers were also tested. Results show that the composite fibers made from MF resins with different RD have different phase structures and properties; when the miscibility index (MI) of MF resin is 1.60, the obtained MF/PVA composite fiber shows a sea-island phase structure, which endues the fiber with the best comprehensive properties: the breaking strength, breaking elongation, rupture work and limiting oxygen index (LOI) are 4.29 cN/dtex, 13.55%,  $8.46 \times 10^{-5}$  J/dtex and 43.1%, respectively. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42918.

**KEYWORDS:** crosslinking; fibers; mechanical properties; phase behavior; thermosets

Received 11 May 2015; accepted 4 September 2015

DOI: 10.1002/app.42918

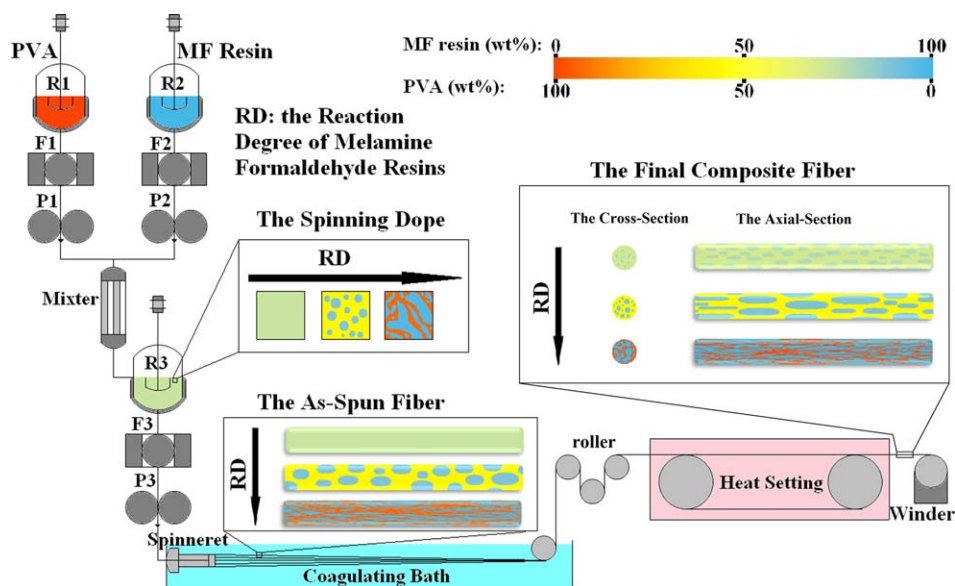
### INTRODUCTION

Melamine–formaldehyde resin (MF) fiber is a kind of outstanding intrinsic flame-retardant fiber due to its low thermal conductivity, no smoke toxicity, no molten drops, and low shrinkage in fire or at high temperature.<sup>1–4</sup> Moreover, it is a halogen free and environment friendly flame retardant fiber that attracts people's attention increasingly.<sup>5</sup> Although MF fiber has so many advantages, it is difficult to be prepared because of the poor spinnability and brittleness of MF resin.<sup>1,6</sup> Since the mid-19th century, many organizations have attempted to research and develop MF fiber with high performance for textile application, and some of them have made positive results. One successful example is the first real melamine fiber developed by BASF, "Basofil," which is made from MF resin grafted by long-chain alkyl. Basofil has made a great progress in the development of MF fiber, but it can only be made by centrifugal spinning, and is just irregular staple fiber.<sup>7–10</sup>

To further improve the spinnability and toughness of MF resin and obtain filament MF fiber, many other modification methods for MF resin were tried. One feasible way is to adopt polyvinyl alcohol (PVA) as the fiber-forming and toughening agent mixed with MF resin and spin MF/PVA composite fiber by wet spinning.<sup>11,12</sup> PVA is a flexible linear polymer with good spinnability, and it has nice toughening effect on MF resins.<sup>13</sup> The

hydroxyl groups of PVA can react with the hydroxymethyl groups of MF resin, which is helpful to reinforce the interface interaction between PVA and MF resin. However, there is always a need for a large proportion of PVA to provide MF resin with enough toughness and spinnability, which will deteriorate the fire retardancy and water resistance of the composite fiber.<sup>14</sup> Thus, to ensure the good thermal stability of MF/PVA composite fiber, the proportion of PVA in composite fiber must be low. Then, it deserves studying how to make PVA provide enough spinnability and toughness at a low proportion.

It is worth noting that MF/PVA composite fiber is a system of thermoset (TS) toughened by thermoplastic (TP), whose properties are dramatically affected by its phase structures. For TS/TP, the reaction induced phase separation (RIPS) is considered as an effective way to regulate its phase structure.<sup>15–17</sup> With the curing degree of TS growing, the compatibility between TS and TP changes, and TS/TP composite will evolve into various phase structures.<sup>18</sup> Ordinarily, the composites would have better toughness when phase separation happens and TP forms continuous phase structure.<sup>19,20</sup> Thus, it is essential for PVA to form a continuous phase structure in composite fiber so as to enhance fiber's toughness, especially when the loadings of PVA are low. Additionally, continuous PVA phase is also helpful to improve the spinnability of composite spinning dopes.



**Scheme 1.** The wet spinning progress of MF/PVA composite fiber and the phase structure evolution of MF/PVA composites system controlled by reaction induced phase separation. R, reaction kettle; F, filter; P, metering pump. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

In this study, we try to observe the structural evolution of MF/PVA composite system in the process of RIPS, and reveal the relationship between the structures and the properties of MF/PVA composite fiber which has a relative low PVA content. Through this study, the toughening effect of PVA in composite fiber was expected to be elevated. The RIPS of MF/PVA composite system was conducted *ex situ* in this study, which means that the curing process of MF resin was independent, when the MF resin reached a certain reaction degree (RD), it was mixed with PVA solution to form a spinning dope with a certain phase structure. The *ex situ* curing of MF resin is to reduce or avoid the reaction between MF resin and PVA before spinning, and prevent the gelation of spinning dope. The spinning dopes with different phase structures were wet spun and heat-set to form composite fibers with different phase structures. The design of this study and the formation of fibers' phase structure are showed in Scheme 1.

## EXPERIMENTAL

### Materials

Industrial-grade PVA (DP = 2000, alcoholysis degree > 99%), was obtained from Sichuan Vinyon Works, China, and was washed by deionized water before use; Melamine, formaldehyde solution (concentration: 35 wt % ~ 38 wt %), triethylamine, dimethyl sulfoxide and acetone were all chemical pure and purchased from Kelong Chemical Reagent Factory, Sichuan, China; Sodium sulfate was industrial-grade and obtained from Sichuan Chuan Mei, China.

### Preparation of MF Resins with Different RD

Formaldehyde solution was adjusted to pH 9~10 by triethylamine before being used. The formaldehyde solution and melamine (the mole ratio of formaldehyde and melamine is 2 : 1) were poured into a 500 mL three-necked flask equipped with a

stirrer and a condenser, then the mixture was heated to 80°C and kept being stirred. After the mixtures turn colorless and transparent, the reactions continued for 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, and 30 h to get MF resins with different RD which were labeled as R0, R3, R6, R9, R12, R15, R18, R21, R24, R27, and R30, respectively.

### Preparation of Spinning Dopes

PVA was dissolved in water with a concentration of 20 wt % at 98°C for about 5 h, then the PVA aqueous solutions were cooled to 70°C. The MF resin solutions were poured into the PVA solutions and mixed together to form the spinning dopes. The temperatures of spinning dopes were kept at 70°C. The mass ratios of MF resins and PVA were 7 : 3. The pH of spinning dopes were adjusted to 9~10 by triethylamine. The composite dopes made from R0~R30 resins were labeled as D0~D30, respectively.

### Preparation of MF/PVA Cast Films

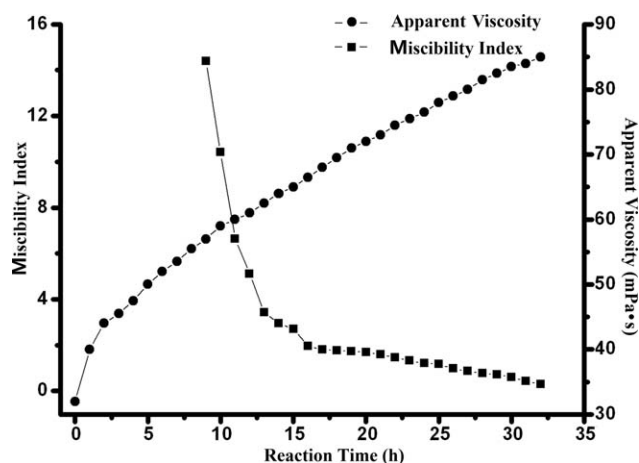
The prepared spinning dopes were cast on a polytetrafluoroethylene board to form thin films. After being dried in the air, the MF/PVA cast films were obtained.

### Preparation of MF/PVA Fibers

The spinning dopes were extruded into a sodium sulfate coagulating bath from a spinneret with 200 nozzle holes (nozzle diameter: 0.1 mm) to form the as-spun composite fibers. After being dried, the as-spun fibers were subjected to heat setting at 220°C for 200 s. Then, the final MF/PVA composite fibers were obtained by washing and drying. The composite fibers made from D0~D30 were labeled as F0~F30, respectively.

### Measurements and Instruments

Apparent viscosities of MF resin solutions and spinning dopes were tested by rotary viscometer (DV II+Pro, Brookfield, USA). The molecular structures of synthesized melamine formaldehyde



**Figure 1.** Miscibility index and apparent viscosity of MF resins with different reaction time.

resins were observed by Laser Raman spectrometer (LabRAM HR, HORIBA Jobin Yvon S.A.S., France); the range of wave number was from  $200\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ ; the resolution was  $1\text{ cm}^{-1}$ ; semiconductor laser with wavelength of  $785\text{ nm}$  was the excitation source; the grating was  $600\text{ gr/mm}$ . The morphologies of the composite fibers and membranes were observed with optical microscope (OM) (BK-POLR, OPTEC, China) and scan electron microscope (SEM) (JSM-5900, JEOL, Japan) whose accelerating voltage was  $5\text{ kV}$ . The composite fibers were also analyzed by energy-dispersive X-ray spectroscopy (EDS) (INCAPentaFETx3, OXFORD, UK) to distinguish the MF resin and PVA phase regions. The nitrogen contents were tested by nitrogen tester (K-06, ShenSheng, China) according to Kjeldahl. The nitrogen losses were gotten by comparing the nitrogen contents of composite cast films with that of fibers. Linear densities of fibers were measured with the torsion balance (JN-B, China). The mechanical properties of fibers were tested with a tensile strength tester (LLY-06E, Laizhou, China); the initial length is  $20\text{ mm}$ ; drawing speed is  $20\text{ mm/min}$ . The limiting oxygen indexes (LOI) of the fibers were tested with oxygen index tester (JF-3, Jiangning, China); the fibers were twisted into plaits of  $50\text{ mm}$  long,  $6\text{ mm}$  wide, and  $3\text{ mm}$  thick for testing. The LOI is the minimum concentration of oxygen, determined in a flowing mixture of oxygen and nitrogen that will just support the plaits burning down in  $150\text{ s}$ . The thermal stability of fibers was studied with thermogravimetric analysis (TGA) (Q600, TA) at a heating rate of  $10^\circ\text{C/min}$  from room temperature to  $700^\circ\text{C}$  in  $\text{N}_2$  atmosphere. The thermogravimetry/Fourier transform infrared coupling investigation (TGA-FTIR) (TG/DSC1, METTLER TOLEDO, Switzerland; Nicolet IS50, Thermo Scientific, USA) was done to analyze the thermal degradation mechanism of composite fibers.

RD of MF resin was measured by miscibility index (MI). The test procedure was as follows: About  $5\text{ g}$  of MF resin solution ( $m_1$ ) was weighed out and kept at  $80^\circ\text{C}$ , then  $80^\circ\text{C}$   $5\text{ wt}\%$  DMSO aqueous solution was added dropwise into MF resin solution until mixed solution became turbid. The turbidness of the mixed solution should be last for at least  $30\text{ s}$ . The weight of the added DMSO aqueous solution was recorded as  $m_2$ . MI was defined as  $m_2/m_1$ .

## RESULT AND DISCUSSION

### Structure and Properties of MF Resins with Different RD

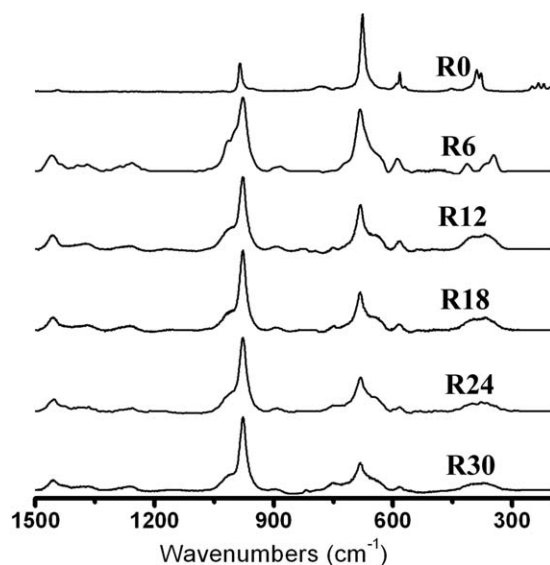
The reactions of MF resin are too complex to be characterized clearly. But with the prolonging of reaction time, the apparent viscosity of MF resin solution would increase, and its compatibility with DMSO solution might deteriorate. So both the MI and the apparent viscosity can be considered as evaluation criteria for the RD of MF resin, and related results are shown in Figure 1.

Since the RD will affect vibration of the triazine ring in MF resin, Raman spectrum also can be considered as a suitable solution to characterize the RD of MF resin. In the Raman spectra of melamine resins, as shown in Figure 2, sharp bands at  $676\text{ cm}^{-1}$  and  $975\text{ cm}^{-1}$  are observed. Both these two bands are ascribed to the deformations of the triazine ring. Obviously, with the increase of RD, the band at  $676\text{ cm}^{-1}$  decreases while the band at  $975\text{ cm}^{-1}$  increases.<sup>21</sup> The ratio between the area of the band at  $676\text{ cm}^{-1}$  ( $A_{676}$ ) and the area of the band at  $975\text{ cm}^{-1}$  ( $A_{975}$ ) can also be used to represent the RD of MF resin.

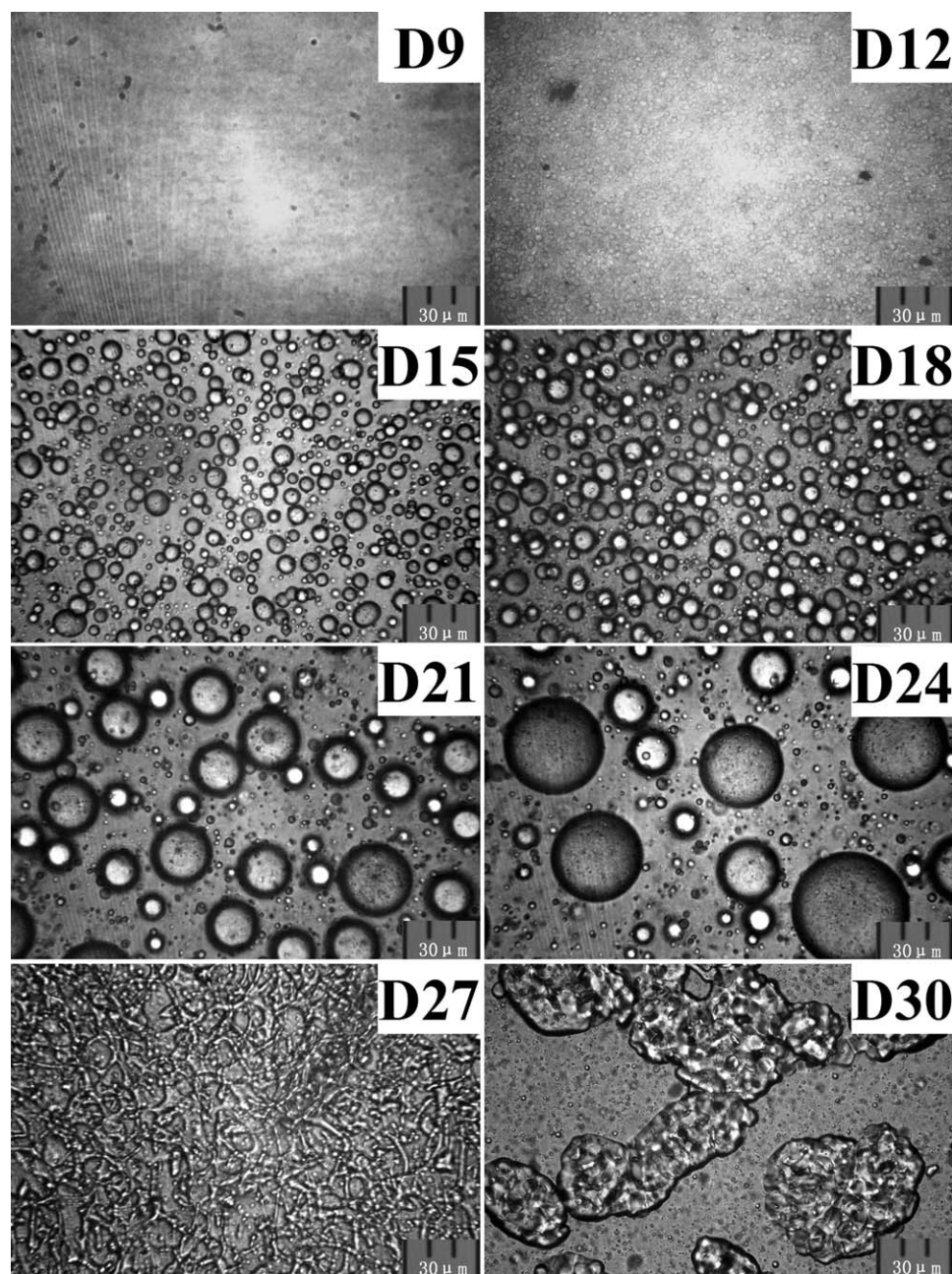
### Phase Structures and Properties of MF/PVA Composite

#### Spinning Dopes

Figure 3 shows the OM images of MF/PVA spinning dopes prepared from MF resins with different RD. It can be seen that when the RD of MF resin is at low level, the MF resin and PVA solution are mutually soluble and the spinning dope is homogeneous, as shown in Figure 3 (D9). Sample D0, D3, and D6 are also homogeneous which are not shown in Figure 3. With the RD of MF resin increasing, the compatibility between MF resin and PVA solution worsens gradually; the interface between MF resin and PVA solution becomes clear and the size of MF resin phase region increases, which can be seen from Figure 3 (D12~D24). When the MI of MF resin decreases to  $0.86$ , a bicontinuous structure can be found in the composite dope, as shown in Figure 3 (D27). With a further increase of RD, the MF resin will be hard to disperse in the PVA solution, as shown in Figure 3 (D30), which makes the dope lose its spinnability.



**Figure 2.** Raman spectra of MF resins with different reaction time.



**Figure 3.** Optical microscope images of spinning dopes made from MF resins with different reaction degree.

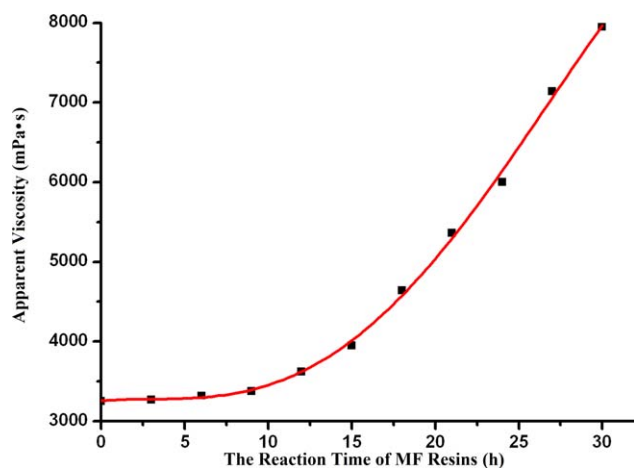
These results suggest that when the RD of MF resin increases, the phase separation occurs in the MF/PVA composite spinning dope where the PVA solution forms continuous phase and the MF resin forms dispersed phase, but when the RD of MF resin is too high, it will lead to a bicontinuous phase structure or even bad dispersion of MF resin in spinning dope, which is not suitable for spinning.

Apparent viscosities of spinning dopes prepared from MF resins with different RD are shown in Figure 4. Combining with above OM results, it can be seen that when the blended spinning dopes are homogeneous the viscosity of the dopes goes up slightly with the increase of reaction time of MF resin. When

the phase separation occurs, the viscosity of the spinning dopes grows rapidly with the increase of reaction time. Similar phenomena have already been found in some studies of the phase separation process in TS/TP toughening systems.<sup>16</sup> In practice, the MI was used to detect and character the RD of MF resins.

#### Phase Structures and Properties of MF/PVA Composite Fibers

In the wet spinning experiments, the spinning dopes made from MF resins with low RD (D0, D3, and D6) failed to coagulate in the coagulation bath, and sample D30 cannot be spun because of the bad dispersion of MF resin. Only the dopes made from MF resin D9~D27 can be spun successfully. Figure 5 shows the SEM photos of the cross-sections of the composite fibers after

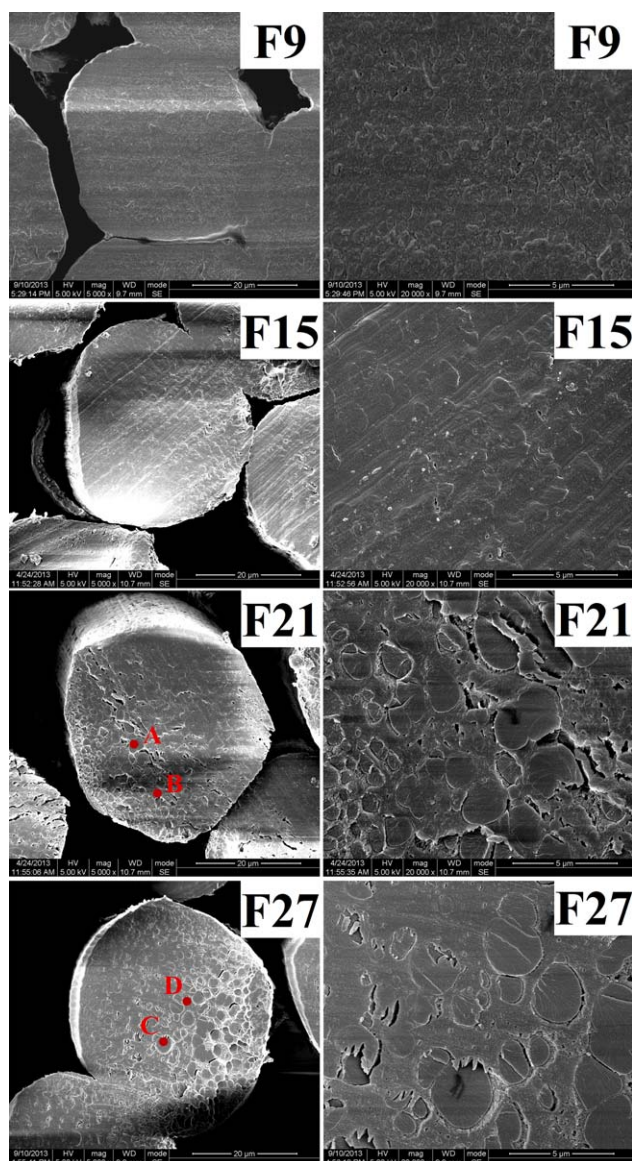


**Figure 4.** Apparent viscosity of the spinning dopes made from MF resins with different reaction degree. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

heat treatment. Although the sample D9 can be spun, it is hard to be coagulated in coagulation bath entirely. So the composite fibers made from it adhere to each other badly, as shown in Figure 5(F9). This phenomenon hardly appears in the composite fibers made from higher RD MF resins. It also can be seen that a higher RD of MF resin causes a more obvious phase separation. With the RD of MF resin increasing, the interface between MF resin and PVA becomes clearer and the size of MF resin phase region gets larger. In order to discriminate the regions of MF resin and PVA, energy-dispersive X-ray spectroscopy (EDS) test was conducted in the SEM observation process. Since the smallest test size of EDS is  $1.5 \times 1.5 \mu\text{m}$ , no independent separated phase zones in sample F9 and F12 are big enough to be distinguished. The EDS test results are presented in Table I. The EDS test results prove that the MF resin is the dispersed phase in the composite fiber and the higher RD of MF resin lead to the deeper phase separation between PVA and MF resin in fiber matrix.

#### Nitrogen Loss of MF/PVA Composite Fibers

The  $\text{Na}_2\text{SO}_4$  coagulation bath can only coagulate PVA, but cannot coagulate MF resin, so MF resin would partly be dissolved in the coagulation bath during wet spinning of MF/PVA composite fiber, which causes that the nitrogen content in fiber is less than expected. As the MF resin is the only nitrogenous substance in composite fiber, the nitrogen loss can be used to characterize the loss of MF resin during the spinning process. Nitrogen loss of MF/PVA composite fibers made from MF resins with different RD can be seen in Table II. It is obvious that nitrogen loss show a downtrend when the RD of MF resin increases. Since the degree of the phase separation becomes higher as the RD of MF resin grows, PVA can be coagulated in  $\text{Na}_2\text{SO}_4$  coagulation bath more effectively and wrap the MF resins more thoroughly which could reduce the loss of MF resin during the spinning process. However, when the RD of MF resin is too high, and the composite spinning dope has a bicontinuous phase structure (the sample D27), MF resin fails to be wrapped by PVA entirely and contacts with the coagulating bath



**Figure 5.** SEM images of composite fibers made from MF resins with different reaction degree. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

directly, which cause a rebound of nitrogen loss. The LOI of different MF fibers are in good coincidence with the nitrogen contents of composite fiber and are all above 42%, which proves these composite fibers have outstanding flame retardancy.

**Table I.** Relative Elemental Composition of Different Regions in the Composite Fibers Measured by EDS

Element	Relative mass percentage (%)			
	Area A	Area B	Area C	Area D
C	71.45	86.53	61.94	88.10
N	20.34	4.44	27.47	1.89
O	8.21	9.03	10.58	10.01

**Table II.** Nitrogen Loss of MF/PVA Composite Fibers

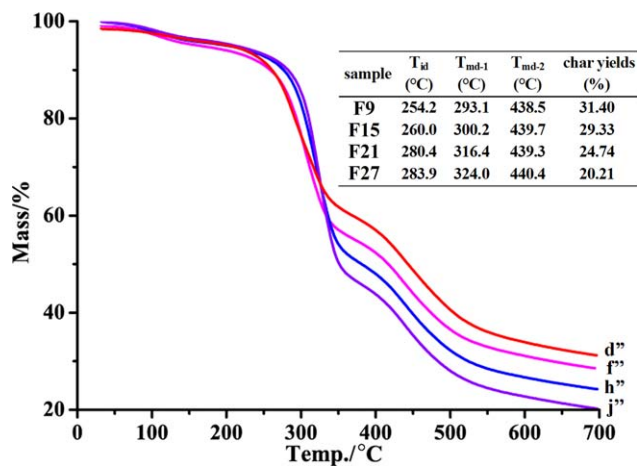
Sample	Nitrogen contents (%)		Nitrogen loss (%)	LOI
	Cast films	Fibers		
F9	29.79	26.88	9.77	42.2
F12	29.90	29.11	2.63	42.3
F15	30.15	29.90	0.82	42.5
F18	30.52	30.39	0.41	42.9
F21	28.91	28.81	0.35	43.1
F24	29.99	29.93	0.21	43.3
F27	31.64	30.15	4.72	42.3

### Properties of MF/PVA Composite Fibers

The mechanical properties of MF/PVA composite fibers are shown in Table III. The results show that the fibers mechanical properties are dramatically affected by the RD of MF resin. The fibers made from MF resins with low RD have high tensile strength but low breaking elongation and low rupture work. With the RD of MF resin increasing, the breaking strength of fibers decreases first, then increases, and then decreases again; the breaking elongation of sample F18 has a highest value of 16.20% and the rupture work of sample F21 has a peak value of  $8.46 \times 10^{-5}$  J/dtex. The mechanical properties of MF/PVA fiber are determined by their structures. In the fibers made from low RD MF resin, the good compatibility between PVA and MF resin contributes to reducing the flaws and enhancing the cross-link density, which lead to higher breaking strength and lower breaking elongation of composite fiber. From the breaking elongations and rupture works of composite fibers, it can be observed that the toughness of composite fiber is improved when the RD of MF resin increases to some extent. This proves that the phase separation between MF resin and PVA is helpful to enhance the toughening effect of PVA in composite fiber. But when the RD of MF resin is too high, and the MF resin cannot be well dispersed in PVA solution, more defects would be generated in composite fiber, which do harm to the mechanical properties of composite fiber. The sample F21 has the best comprehensive mechanical properties (breaking strength: 4.29 cN/dtex, breaking elongation: 13.55% and rupture work:  $8.46 \times 10^{-5}$  J/dtex). For comparison, the breaking strength, breaking

**Table III.** Mechanical Properties of MF/PVA Composite Fibers

Sample	Breaking strength (cN/dtex)	Breaking elongation (%)	Rupture work (10 <sup>-5</sup> J/dtex)
F9	4.46 ± 0.21	7.21 ± 0.69	3.31 ± 0.25
F12	3.72 ± 0.18	9.32 ± 0.83	4.27 ± 0.31
F15	3.37 ± 0.16	13.15 ± 1.02	7.02 ± 0.46
F18	3.74 ± 0.23	16.20 ± 1.47	7.93 ± 0.51
F21	4.29 ± 0.29	13.55 ± 1.06	8.46 ± 0.67
F24	3.29 ± 0.20	12.00 ± 0.93	6.88 ± 0.39
F27	2.94 ± 0.14	11.65 ± 0.88	6.64 ± 0.41

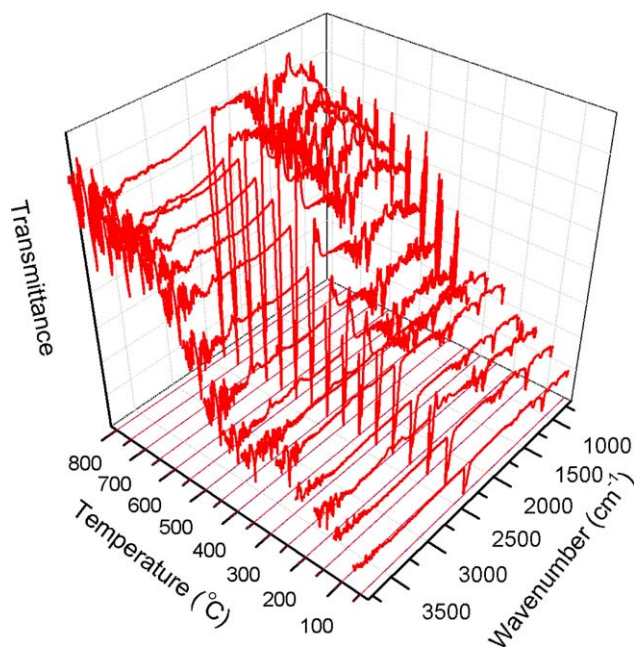


**Figure 6.** TGA curves of MF/PVA fibers made from MF resins with different reaction degree. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elongation and rupture work of “Basofil” are 1.85 cN/dtex, 6.21% and  $1.74 \times 10^{-5}$  J/dtex, respectively.

The TGA curves of composite fibers are shown in Figure 6. There exist two weight loss stages during the thermal decomposition of composite fibers. With the RD of MF resin increasing, the initial thermal decomposition temperature (5% weight loss) ( $T_{id}$ ) and the first maximum thermal decomposition temperature ( $T_{md-1}$ ) of composite fiber both have a increasing trend, and no obvious changes has been observed among the second maximum thermal decomposition temperatures ( $T_{md-2}$ ), while the char yield of composite fiber at 700°C decreases from 31.40% to 20.21%.

For common understanding, the thermal stability of PVA is inferior to that of MF resin, so the first weight loss stage maybe due to the decomposition of PVA and second belongs to the decomposition of MF resin. However, the weight losses at the first stages in TGA curves are much higher than 30% (the weight percentage of PVA in composite fibers), which proves that not only PVA decomposes at the first stage. TGA-FTIR was adopted to clarify the decomposition mechanism of the composite fiber. Figure 7 shows the FTIR spectra collected at different temperatures during the thermal decomposition of sample F21. The absorption peaks at  $966 \text{ cm}^{-1}$  and  $892 \text{ cm}^{-1}$  all belong to  $\text{NH}_3$ , and the vibrations band at  $1372\sim 1854 \text{ cm}^{-1}$



**Figure 7.** FTIR spectra of sample F21 collected at different temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

belongs to amines, which mean that MF resin would thermal degrade at the first weight loss stage. The MF resins with higher RD have better thermostability than those with low RD, so the fibers made from MF resins with higher RD have higher  $T_{id}$  and  $T_{md-1}$ . But the higher RD of MF resins leads to the deeper phase separation between PVA and MF resin, as a result, less hydroxyl groups of PVA will participate in the crosslinking reaction with the hydroxymethyl groups of MF resin, which makes MF resins fail to protect PVA at high temperature, so the fibers made from MF resins with higher RD have lower char yields.

## CONCLUSIONS

In this study, a new kind of MF/PVA composite fibers with the potential to be applied in most flame retardant textiles was prepared by wet spinning process. The phase structures of these composite fibers were controlled by changing the RD of MF resins. With the RD of MF resins increasing, the compatibility between MF resin and PVA became worse, and the phase structure of composite fibers changed from sea-island structure to bicontinuous structure. The composite fibers' phase structures greatly impacted fibers' mechanical properties. A certain degree of phase separation between MF and PVA benefits the improvement of the toughness of the composite fiber. Through this study, the toughening effect of PVA in MF/PVA composite fiber was strengthened, the spinnability of composite spinning dope with a low PVA content was improved, and MF/PVA flame retardant filament fibers with satisfactory comprehensive properties were successfully prepared.

## ACKNOWLEDGMENTS

The financial support of this study was from the youth science foundation of Natural Science Foundation of China (NSFC) (Subject No. 51103088). The authors wish to thank all the testers of State Key Laboratory of Polymer Materials Engineering (Sichuan University) for their help and efforts in completing this research.

## REFERENCES

- Devallencourt, C.; Saiter, J. M.; Fafet, A.; Ubirch, E. *Thermochim. Acta* **1995**, *259*, 143.
- Hans, E. In *High-Performance Fibres*; Hearle, J. W. S. Ed.; Woodhead: Abington, **2001**; Vol. 1, Chapter 9, p 282.
- Bann, B.; Miller, S. A. *Chem. Rev.* **1958**, *58*, 131.
- Kandelbauer, A.; Wuzella, G.; Mahendran, A.; Taudesb, I.; Widsten, P. *Chem. Eng. J.* **2009**, *152*, 556.
- Shishoo, R. *Int. J. Cloth. Sci. Tech.* **2002**, *14*, 201.
- Kent, G. M.; Gadoury, D. R.; Burlone, D. A.; Johnson, K. L. (BASF Co.) U.S. Patent 5,849,648, **1998**.
- Berbner, H.; Eichhorn, H. D.; Ott, K. (KINZEBACH Werner) WO Patent 1,997,042,365, **1997**.
- Kent, G. M.; Ott, K. (BASF Co.) U.S. Patent 5,853,880, **1998**.
- Kent, G. M.; Ott, K. (BASF Co.) U.S. Patent 5,918,453, **1999**.
- Kent, G. M.; Ott, K. (BASF Co.) U.S. Patent 6,013,366, **2000**.
- Lilani, H. N. (Norfab Co.) U.S. Patent 5,496,625, **1996**.
- Nihongi, Y.; Yasuhira, N. (Kuraray Co.) Patent 4,088,620, **1978**.
- Zheng, H.; Du, Y.; Yu, J.; Huang, R.; Zhang, L. *J. Appl. Polym. Sci.* **2001**, *80*, 2558.
- Mouritz, A. P.; Gibson, A. G. In *Fire Properties of Polymer Composite Materials*; Gladwell, G. M. L., Ed.; Solid Mechanics and Its Applications Series 143; Springer: Dordrecht, **2006**; p 241.
- Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. *Macromolecules* **1999**, *32*, 8517.
- Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. *Macromolecules* **1999**, *32*, 8524.
- Naffakh, M.; Dumon, M.; Gérard, J. F. *Compos. Sci. Technol.* **2006**, *66*, 1376.
- Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 119.
- Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. In *Polymer Analysis Polymer Physics*; Pasch H., Ed.; Advances in Polymer Science Series 128; Springer: Berlin Heidelberg, **1997**, p 95.
- Woo, E. M.; Shimp, D. A.; Seferis, J. C. *Polymer* **1994**, *35*, 1658.
- Scheepers, M. L.; Meier, R. J.; Markwort, L.; Gelan, J. M.; Vanderzande, D. J.; Kip, B. J. D. *Vib. Spectrosc.* **1995**, *9*, 139.