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Effects of collagen fiber addition on the combustion and thermal stability of natural rubber

Weixing Xu¹, Xintao Wu², Qilin Wen¹, Shuangyang Li¹, Yongjiao Song³ and Bi Shi^{1,4*}

Abstract

Collagen fiber (CF) and silane coupling agent-modified collagen fiber (MCF) were used as flame retardant filler for natural rubber (NR) modification. The combustion phenomena and properties of composites blended with different dosages of CF or MCF were compared to elucidate the flame retardant mechanism of the composites. The flame retardancy of NR can be enhanced effectively by increasing nitrogen content (the nitrogen content of CF is about 18%), creating air pockets, and structuring the flame retardant network in the composites. MCF failed to structure a flame retardant network in the composite, indicating that its modification effects of MCF are weaker than those of CF. When CF dosage was 30 wt%, the composite can achieve the best flame retardancy, with limited oxygen index of 29.4% and without smoke and dripping during burning. This study demonstrated a new method for the flame retardant modification of NR.

1 Introduction

Natural rubber (NR) is an important chemical materials in the modern industry. It can be used as a “commodity polymer”, and as an “engineering elastomer” [1]. NR has some unique properties in applications, such as excellent toughness and elasticity, and good alkali resistance. Given these advantages, NR, one of the earliest natural polymers used by mankind, still attracts great attention in material science. However, the inherently high flammability of NR limits its application [1–4].

In general, the flammability of polymer materials can be decreased in two ways. One way is through chemical modification using reagents or monomers containing fire retardant elements [5–7]. Chlorine- or bromine-containing monomers can enhance the flame resistance of NR effectively [8, 9]. However, addition of halogens triggers the release of toxic gases during combustion

[10, 11]. Another way is to introduce a flame-retardant additive (FRA) [2, 4, 12–18]. Many FRAs have been developed to increase the flame retardancy of polymer material. Previous researchers have successfully improved the flame retardancy of NR by using proper FRAs, such as montmorillonite, aluminium hydroxides, and melamine–formaldehyde resin [2, 4, 19]. Most of these works focused on making NR resistant to ignition. The high flammability of NR is reflected in two aspects: NR is easy to ignition; flame spreads quickly across the material following the dripping. Thus, understanding the flame propagation in NR is important.

Flame propagation of polymers during burning can be affected by two methods of flame retardant modification corresponding to two types of carbon residues formed by FRAs in composites. One type is the dense carbon layer covered on the composite surface, which improves the flame retardancy of composites by cutting off air contact (blocking effects) [20–23]. The other type is the continuous porous carbon layer, which improves the flame retardancy of composite by blocking heat propagation (intumescent effects) [15, 24–27]. However, little is known about the blocking effects applied on the flame

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retardant modification of NR. The FRAs used in the flame retardant modification of NR with intumescent effects can be divided into two groups: hyperbranched molecule [3, 4, 28, 29] and microcapsule [2, 30–32]. However, the synthesis cost of these two FRAs is relatively high, which seriously affects their practicability.

Our previous study proved that collagen fiber (CF) has some advantages in preparing efficacious flame retardant filler [33]. In addition, the multilevel structure [34] of CF is similar to the structure of hyperbranched molecule, which is well-designed to achieve a better modification effect. This structure may contribute to the formation of a porous carbon layer that blocks the energy transmission of a combustion flame [35]. As such, CF is expected to be processed into a type of FRA for NR. Moreover, CF is a renewable biomass resource [35–38]. Our previous study also proved that blending with CF does not impair the mechanical properties of NR [39]. Thus, the practicability of CF-based FRA can be guaranteed.

In the present study, we used CF to construct a flame retardant network in NR. We hoped this method could enhance the flame retardancy of NR by blocking the dripping. To achieve this goal, we prepared a series of CF/NR composites. The limited oxygen indexes (LOIs) of these composites were tested. The flame retardant mechanism of NR modified by CF was studied by morphologic characterization and thermogravimetric analysis (TGA).

2 Experimental

2.1 Materials

Wet-blue splits with an average thickness of 1.6 mm were obtained from a local tannery in China. Surfactant (FG-B) was commercial grade and supplied by Sichuan Dowell Science & Technology Inc. (Sichuan, China). Formic acid (HCOOH), acetic acid (CH₃COOH), aluminum sulfate octadecahydrate (Al₂(SO₄)₃·18H₂O),

magnesium oxide (MgO), sulfur (S) and isopropyl alcohol were all analytical pure and purchased from Kelong Chemical Reagent Corporation (Sichuan, China). Natural rubber was commercial grade and supplied by Sinopec Group (China). Silane coupling agent (KH-550) was commercial grade and supplied by Nanjing Xiangqian Chemical Co., LTD (Jiangsu, China).

2.2 Preparation of collagen fiber powder

Wet-blue splits were washed and wrung, and then processed as in Table 1 in a drum (Ø 30 cm) commonly used in leather processing. After drying, splits were smashed by an Ultra Centrifugal Mill (ZM 200, Retsch, Germany) to obtain collagen fiber powder. The sieve size is 0.08 mm with trapezoid holes.

2.3 Preparation of modified collagen fiber powder

Silane coupling agent, isopropyl alcohol and water were mixed in the ratio of 1:90:10 (w/w/w) to get the modification solution. Ten grams collagen fiber powder was impregnated in 60 g modification solution for 3 h at 40 °C. During this progress, pH was checked every 10 min and kept at 6.0 ~ 6.5 by adding acetic acid. After filtration, collagen fiber powder was heated at 105 °C for 6 h. After washing and re-smashing, modified collagen fiber (MCF) powder was obtained.

2.4 Preparation of the CF/NR and the MCF/NR composites

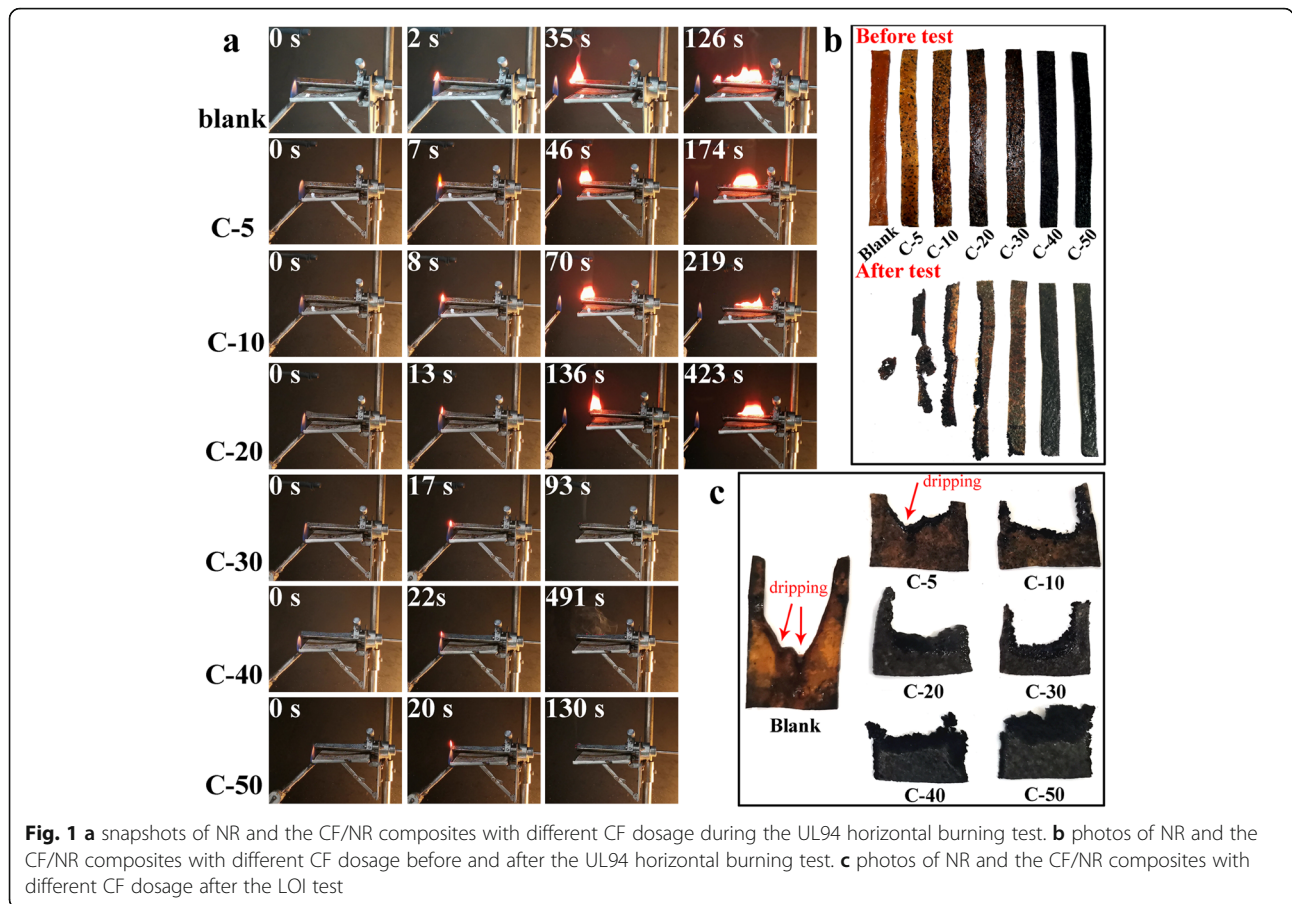
CF or MCF was mixed with NR by a torque rheometer (RM-200C, Harp, China) at 150 °C for 20 min. 5 wt% sulfur (based on the weight of NR) was added as sulfurizing reagent. Then the CF/NR and MCF/NR composite were prepared by a vulcanizing press (QLB-25 T, Junyu, China) at 150 °C with a pressure of 1.5 MPa for 15 min.

Table 1 Pretreatment processes of wet-blue split

Step	Material	Dosage ^a (%)	Temperature (°C)	Time (min)	pH
Rewetting	water	400	35	40	
	Surfactant (FG-B)	0.4			
Washing	water	400	35	10	
Retanning	water	200	35		3.0
	HCOOH (1:10) ^b	0.2 × n			
	Al ₂ (SO ₄) ₃ ·18H ₂ O	13			
	Al ₂ (SO ₄) ₃ ·18H ₂ O	13			
Run 50 min per hour for 5 times					
Basification	MgO	0.1 × n	25	10 × n + 30	pH = 4.0 ~ 4.2
Washing	water	100 × 3	25	15 × 3	

^a: All the quantities were based on the weight of wet-blue splits

^b: Formic acid was diluted ten times before addition



2.5 Characterizations

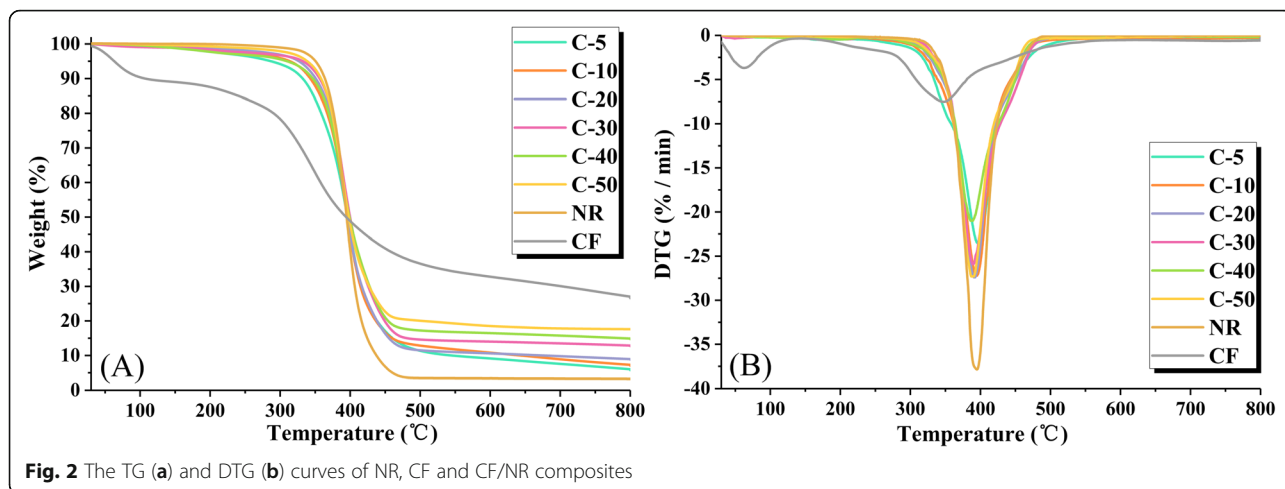
The morphology of CF and MCF was observed by a stereo microscope (SM, DFC550, Leica, Germany). The morphology of the CF/NR and the MCF/NR composite was observed by a scanning electron microscopy (SEM, SU3500, JEOL, Japan) with an accelerating voltage of 15.0 kV. The combustion behavior of NR and the composites was determined using a horizontal and vertical combustion tester (CZF-5CD, Jiangning, China) according to UL 94. The samples for horizontal and vertical combustion test were cut to 130 mm long, 13 mm wide and less than 3 mm thick. The LOI of NR and the

composites was determined using an oxygen index meter (JF-3, Jiangning, China) according to ASTM D2863. The samples for LOI test were cut to 140 mm long, 52 mm wide and less than 5 mm thick. The thermal stabilities of CF, MCF, NR and the composites were carried out on a thermogravimetric analyzer (TGA, TGA 8000, PerkinElmer, America) at a heating rate of 10 °C/min under air atmosphere. The thermal conductivities of NR and the composites were determined using a thermal constant analyzer (TPS 2500S, Hot Disk, Sweden) according to ISO 22007-2:2015. The nitrogen contents of the CF/NR and the MCF/NR composites

Table 2 The LOI and combustion phenomena of NR and the CF/NR composites

Sample	CF dosage (wt%)	LOI (%)	Smoke	Dripping	Flying Spark	horizontal burning rate (mm/min)
NR	0	17.9 ± 0.4	(+)	(+)	(-)	49.45 ± 3.44
C-5	5	19.2 ± 0.4	(+)	(+)	(-)	35.16 ± 2.84
C-10	10	21.9 ± 0.4	(-)	(±)	(-)	30.20 ± 1.34
C-20	20	25.6 ± 0.6	(-)	(-)	(-)	15.68 ± 0.94
C-30	30	29.4 ± 0.3	(-)	(-)	(-)	self-extinguishing
C-40	40	27.2 ± 0.6	(-)	(-)	(+)	self-extinguishing
C-50	50	25.6 ± 0.7	(-)	(-)	(+)	self-extinguishing

(+): positive; (-): negative; (±): sometimes positive, sometimes negative



were detected by a total organic carbon and protein-nitrogen analyzer (Primacs^{SNC-100}, SKALAR, Netherlands).

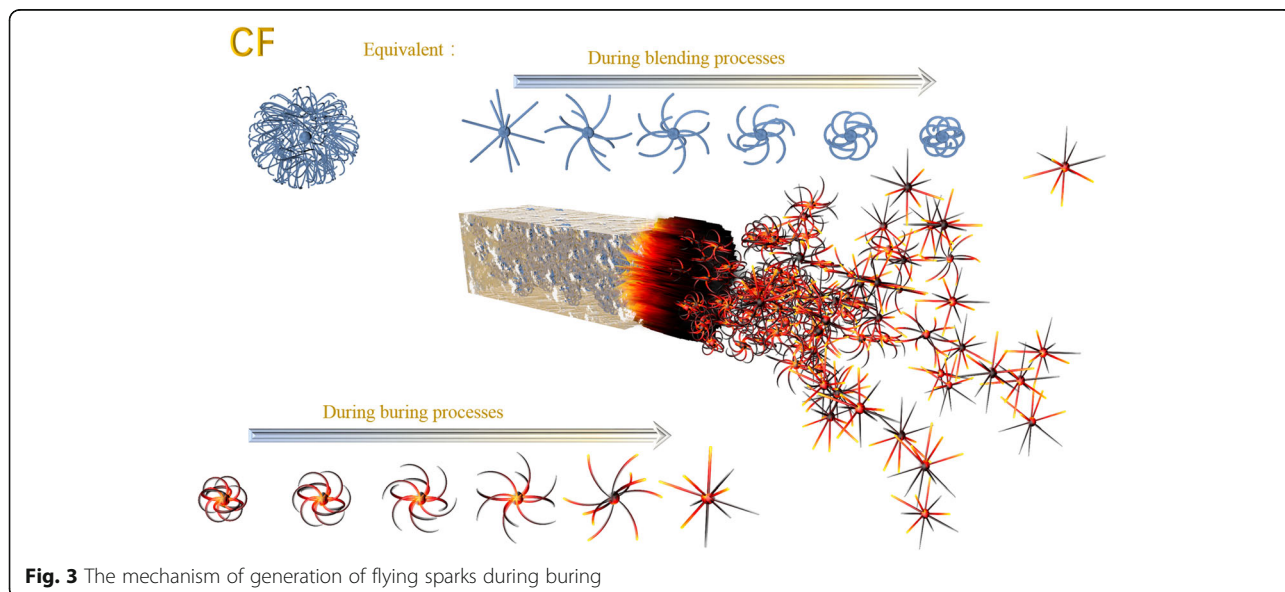
3 Results and discussion

3.1 Effect of CF dosage on the flammability of CF/NR composites

The flame retardancy of the different NR and CF/NR composites with different CF dosage was estimated by UL94 horizontal/vertical burning test and LOI test (Fig. 1 and Table 2). The flammability of NR obviously reduced with the addition of CF. Figure 1a shows that the time to ignition of the CF/NR composites was prolonged with the addition of CF. In addition, the horizontal burning rate decreased rapidly. When the dosage of CF was higher than 10 wt%, burning smoke can be suppressed. When the CF dosage was 30 wt%, self-extinguishing phenomenon was

observed. However, all these samples failed to reach UL94-V2 level (supporting 1). Figure 1b shows the NR and CF/NR composites before and after the horizontal burning test. When the CF dosage exceeded 10 wt%, combustion occurred only in the upper layer of the sample. In addition, the CF/NR composites did not contract violently due to combustion. Figure 1c illustrates the NR and CF/NR composites after the LOI test. When the CF dosage exceeded 10 wt%, dripping can be suppressed significantly. These results proved that CF is a feasible filler for the flame retardant modification of NR.

LOI and the combustion phenomena missed by snapshots are also listed in Table 2. The LOI of the composites initially increased then decreased with increasing CF dosage. However, flying sparks appeared when the CF dosage exceeded 40 wt%. This phenomenon has two possible reasons. First, the active groups (e.g. -COOH,



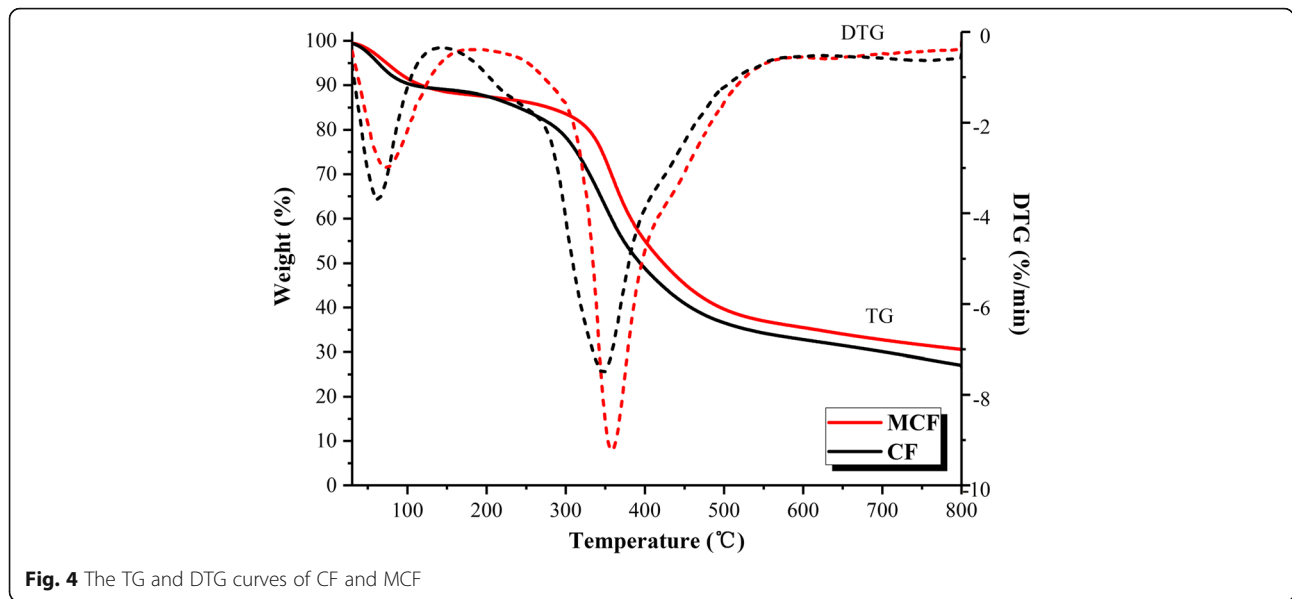


Fig. 4 The TG and DTG curves of CF and MCF

-NH₂ and -OH) on the collagen molecule may decompose during combustion [40], leading to the release of gases, such as CO₂ and H₂O. These gases can blow some residues. Second, a large amount of energy is stored in the composites during mixing and hot-pressing. When NR, as the continuous phase, melts and burns, the energy stored in CF is released. Both reasons explain why the ignited CF scatters in all directions. With the loss of CF, the CF/NR composite becomes easier to burn, while flying sparks can ignite other parts of the sample. When 50 wt% CF was added in the composite, this phenomenon became more obvious and LOI was further decreased. The composite with 30 wt% CF (C-30) presented the best flame retardancy, where the highest LOI was achieved, and smoke, dripping, and flying spark were suppressed.

The thermal decomposition behaviors of NR, CF, and CF/NR composites with different CF dosages were characterized by TGA, as shown in Fig. 2. Except water evaporation (0 ~ 160 °C), only one region of decomposition appeared in the temperature range of 160 ~ 800 °C for

all these samples [41, 42]. The onset decomposition temperature (T_{onset}) and char yield at 800 °C increased with the increase in CF dosage. Although the temperature corresponding maximum decomposition rate (T_{max}) of CF was lower than that of NR, no significant decrease in the T_{max} of CF/NR composites was found. These phenomena indicate that the addition of CF enhanced the thermal stability of NR. The change regularity of the thermal decomposition characteristics of the CF/NR composites was inconsistent with the LOI test results. Because the thermal decomposition reaction in TGA was not as violent as burning. CF did not burn and scatter rapidly during heating in TGA. Thus, the modification result was not affected.

The labile groups on the collagen molecule decomposed into gases during TGA. No unexpected mass change was observed. The flying sparks observed in the LOI tests were caused by the dramatic release of energy. CF has a good compressibility. When the movement of CF is no longer restricted, the tight CFs become loose immediately, whereas the lithe CFs are blown away by

Table 3 The LOI and combustion phenomena of the MCF/NR composites

Sample	MCF dosage (wt%)	LOI (%)	Smoke	Dripping	Flying Spark
NR	0	17.9 ± 0.4	(+)	(+)	(-)
C-30	30 (CF)	29.4 ± 0.3	(-)	(-)	(-)
MC-5	5	20.4 ± 0.3	(-)	(+)	(-)
MC-10	10	22.3 ± 0.4	(-)	(+)	(-)
MC-20	20	23.2 ± 0.9	(-)	(+)	(-)
MC-30	30	24.5 ± 1.4	(-)	(+)	(-)
MC-40	40	25.1 ± 0.8	(-)	(+)	(-)
MC-50	50	25.7 ± 0.8	(-)	(+)	(-)

(+): positive, (-): negative

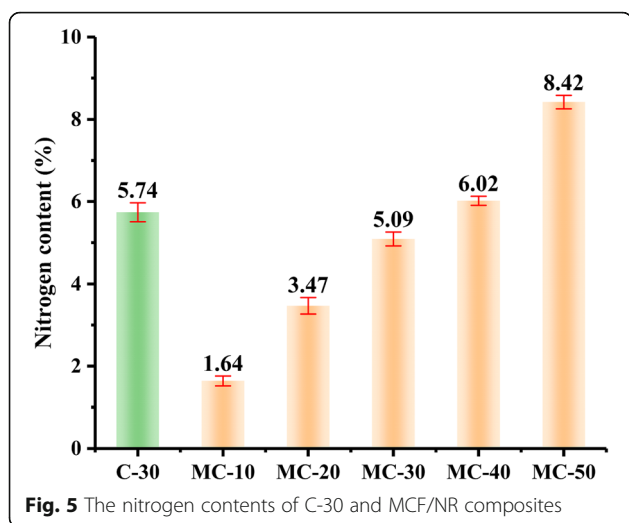


Fig. 5 The nitrogen contents of C-30 and MCF/NR composites

the air easily. This phenomenon explains the flying sparks in the LOI test when the CF dosage was more than 30 wt%. A schematic of the generation of flying sparks during burning is shown in Fig. 3.

3.2 Effect of MCF dosage on the flammability of MCF/NR composites

The results above prove that although the addition of CF can enhance the flame retardancy of NR, the energy stored in the composite can affect the modification results. Given that a high pressure is needed to force NR to become a continuous phase (supporting 2), a practical solution is to change the interfacial force between NR and CF. A silane coupling agent was used to improve the interaction between CF and NR to eliminate the negative influence. Moreover, the introduction of silicon is considered beneficial to the improvement of flame retardancy [43–45]. The TGA curves of CF and MCF are shown in Fig. 4. The T_{onset} , T_{max} , and char yield at 800 °C of MCF were obviously higher than those of CF. LOI tests showed that the LOIs of MCF and CF were 68.1% and 60.7%, respectively. These results prove that MCF has a better flame retardancy than CF, implying that MCF has the

potential to modify the flame retardancy of NR more effectively than CF.

The LOI test results of the MCF/NR composites with different MCF dosages are shown in Table 3. The LOI obviously increased with increasing MCF Amount. No smoke and flying sparks were found during the test. However, compared with C-30 in Table 2, the MCF/NR composites did not achieve a higher LOI and better flame retardancy. In fact, dripping always occurred during the LOI test of the MCF/NR composites. Flame and energy can travel quickly with the droplets.

The TGA test results (supporting 3) showed that the T_{onset} , T_{max} and char yield at 800 °C of MC-30 were all higher than those of C-30, indicating that the thermal stability of MC-30 was better than that of C-30. These results were inconsistent with the LOI test results possibly because dripping did not occur in the TGA test.

Given that the flame retardancy and thermal stability of MCF were all better than those of CF, the lower LOI of MCF/NR should be caused by the structural change during modification and mixing. After all, LOI is a more important indicator for flame retardant material than char yield. The use of a silane coupling agent to improve the interaction between CF and NR is not a feasible plan to enhance enhancing flame retardant effects in the CF/NR composite.

3.3 Flame retardant mechanism of NR modified with CF

For most flame retardant modifications of polymers, increasing the nitrogen content of the blended system is an effective method [46–48]. In the present study, the addition of CF or MCF can increase the nitrogen content of the blended system. However, it is not a decisive factor. The nitrogen contents of the CF/NR (C-30) and MCF/NR composites are shown in Fig. 5. Even the nitrogen content of MC-50 was much higher than that of C-30, and the LOI of the former was still lower than that of the latter.

The special structure of CF may play an important role in the modification. Figure 6 illustrates the SM photos of CF and MCF. Obviously, these two fibers have different structures. CF is much fluffier than MCF. Similar

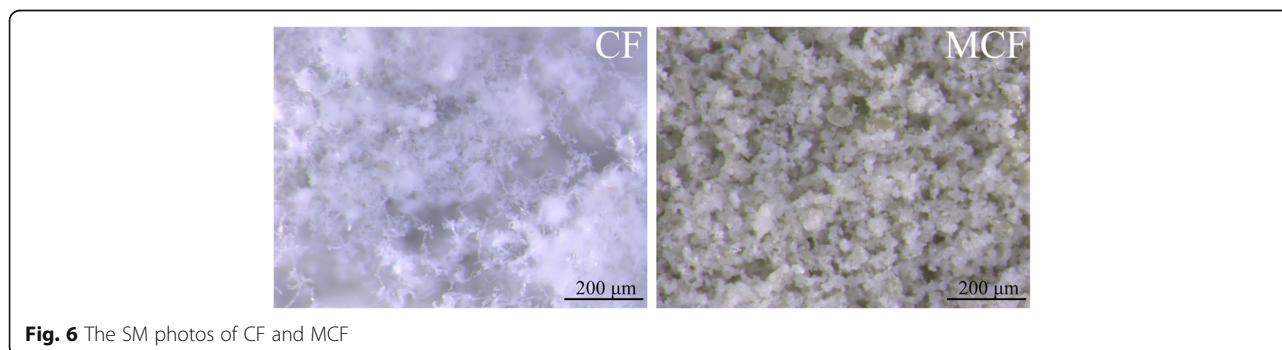


Fig. 6 The SM photos of CF and MCF

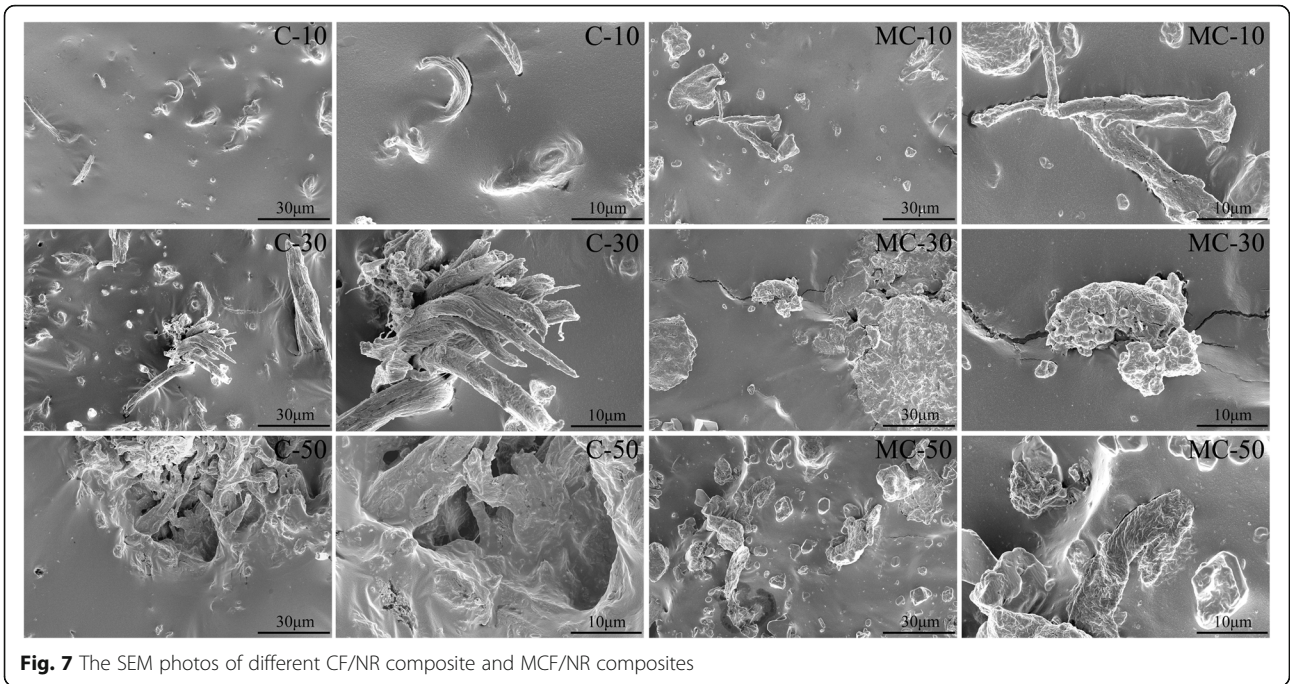


Fig. 7 The SEM photos of different CF/NR composite and MCF/NR composites

phenomena can be also found in the SEM photos of the composites in Fig. 7. The multilevel structure of CF can still be observed in the CF/NR composites. Meanwhile the MCF added in the composite was coated with a dense film, which covers the open-framework structure of CF. Because of this dense structure, a network

structure is hard to build, even when the dosage of MCF is 50 wt%. Hence, a semi-interpenetrating network (semi-IPN) of CF is important for the flame retardancy modification of NR. This network can block the spread of flame, and has a great anti-dripping effect [49–52]. The action mechanism and effects of CF and MCF in

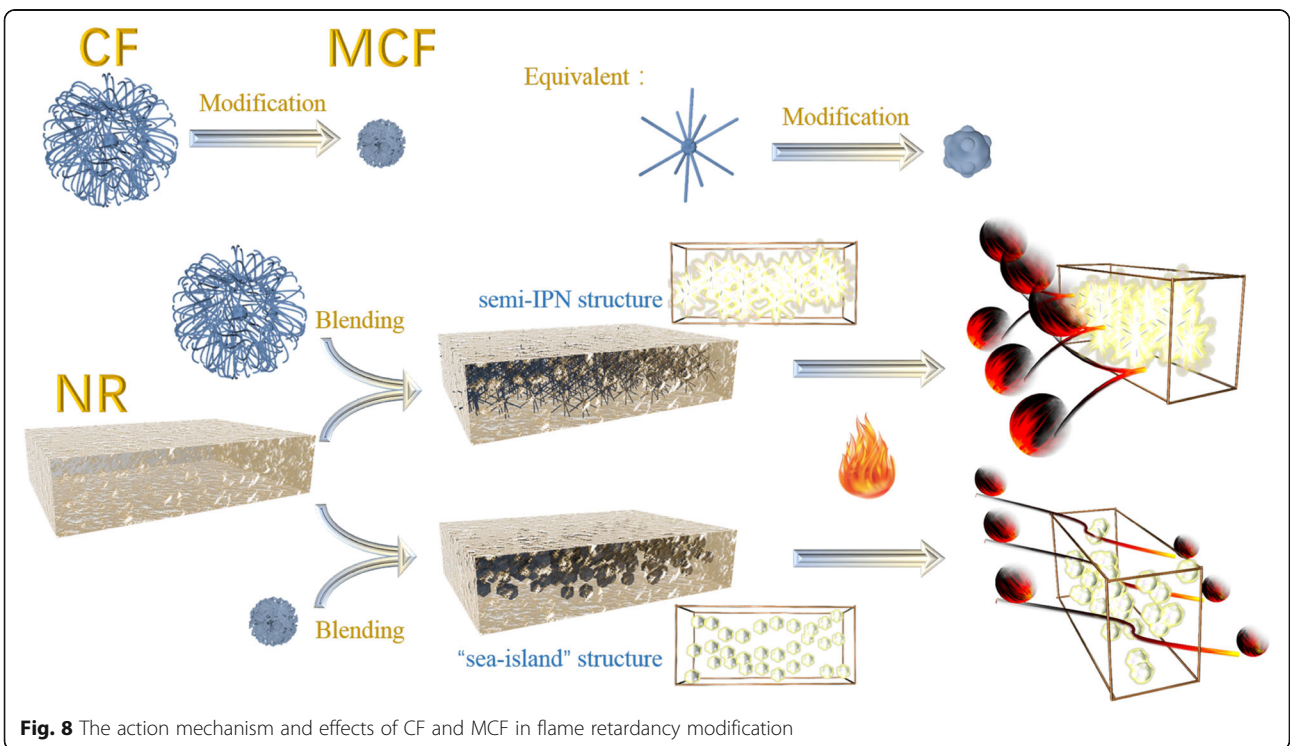


Fig. 8 The action mechanism and effects of CF and MCF in flame retardancy modification

Table 4 The thermal conductivity of NR, C-30 and MC-30

Sample	NR	C-30	MC-30
Thermal conductivity (W/mK)	0.1733	0.1457	0.1629

flame retardancy modification of NR are shown in Fig. 8. The fluffy CF can entangle with each other and tends to be semi-interpenetrating in the blend system. While, the MCF can only form the “sea-island” structure in the blend system, which may fail to block the flame propagation effectively.

Table 4 shows the thermal conductivities of NR, C-30 and MC-30. Results showed that the thermal conductivity of C-30 was lower than those of NR and MC-30, indicating that the heat flow propagation in C-30 was more difficult than those in NR and MC-30. A fully dispersed structure of CF can form a certain amount of air pockets in the composite to block heat propagation. By contrast, the unsatisfactory modification result of MCF is caused by the fact that these air pockets are filled up by the silane coupling agent.

Combining with all the above results, the flame retardant mechanism of NR modified with CF has three aspects. First, the nitrogen content of the composite increased. Second, the network structure containing CF formed firebreaks in the composite, which helped impede flame and dripping. Third, the multilevel structure of CF created air pockets in the composite to block heat propagation.

4 Conclusion

The flame retardancy of NR can be improved by blending with CF. The addition of CF suppressed smoke and dripping during burning. A flame retardant network and enough air pockets must be structured to ensure the modification effect. As such, CF should be remain fluffy and polyporous. With 30 wt% dosage of CF, the LOI of modified NR was as high as 29.4%. This composite also had satisfactory T_{onset} and char yield at 800 °C. With these properties, the usage of NR can be extended to highly demanding applications.

The practicability of this flame-retardancy modification method should be further investigated. The problem of flying sparks should be solved to improve the flame retardancy of NR. We speculate another compound may be needed to replace the silane coupling agent to enhance compatibility between NR and CF. The improvement of the blending system should also be considered. All these works are undertaken.

5 Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s42825-020-00040-1>.

Additional file 1 Supporting 1: Figure S1 snapshots of C-30 during UL94 vertical burning test. **Figure S1** shows the C-30 during vertical burning test. Results show that even with the highest LOI, C-30 still failed to reach the UL94-V2 level.

Additional file 2 Supporting 2: Figure S2 The SM photos of the CF/NR composite. **Figure S2** shows the SM photos of the CF/NR composite, when the input quantity in the torque rheometer is only 2/3 of normal samples. NR is covered by CF, and the whole structure is discontinuous.

Additional file 3 Supporting 3: Figure S3 The TGA curves of C-30 and MC-30. **Figure S3** displays TGA curves of C-30 and MC-30. The T_{onset} , T_{max} and char yield at 800 °C of MC-30 are all higher than those of C-30, as shown in Table S1.

Additional file 4 Table S1 The results of TGA of C-30 and MC-30.

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Authors' contributions

Weixing Xu: conception of the work, preparation of MCF/NR composite, morphological observation of composite, analysis and interpretation of data, drafting the manuscript. Xintao Wu: characterization of the LOI of materials. Qilin Wen: characterization of the thermostability of materials. Shuangyang Li: Preparation of modified collagen fiber powder. Yongjiao Song: Preparation of CF/NR composite. Bi Shi: conception of the work, substantively revision of the manuscript. All authors have read and approved the submitted version (and any substantially modified version that involves the author's contribution to the study). All authors have agreed both to be personally accountable for the author's own contributions and to ensure that questions related to the accuracy or integrity of any part of the work, even ones in which the author was not personally involved, are appropriately investigated, resolved, and the resolution documented in the literature.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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