Journal of Hazardous Materials 179 (2010) 373–381

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Experimental study on the fire protection properties of PVC sheath for old and new cables

Qiyuan Xie*, Heping Zhang, Lin Tong

State Key Laboratory of Fire Science, USTC, Hefei, 230027, PR China

ARTICLE INFO

Article history:
Received 13 November 2009
Received in revised form 4 March 2010
Accepted 4 March 2010
Available online 10 March 2010

Keywords:
Fire protection property
Old cable
Atmosphere
TG–FTIR
MCC

ABSTRACT

The objective of the present study is to analyze the fire protection properties of old and new cables through TG, FTIR and MCC experiments. The results show that the mass loss of old cable sheath is clearly larger than the new one when the temperature is higher than 550 K in air or nitrogen atmosphere. It suggests that the old cable sheath starts to pyrolyze generally at the same temperature based on the analysis of the onset temperatures of mass loss. The results also show that there is a main peak DTG for the old and new cable sheath under each condition. However, the main peak DTG of old cable sheath is larger than that of the new cable sheath, especially in air atmosphere. The FTIR experiments show that the HCl is released by the new cable later but more quickly than the old cable. The MCC experiments suggest that compared with the new one, the peak heat release rate is larger for the old cable. It illustrates that the old cable sheath generally pyrolyzes and combusts more strongly and completely than the new one. Namely, the fire protection properties of the old cable in old buildings are relatively weak.

1. Introduction

The fire statistics in the past several years illustrate that the use of electrical appliances is one of the most common fire reasons, especially for those old buildings [1–6]. The present work was motivated by officers of the Fire Department in China, who found that in old buildings, there were much more electric fires than in new buildings. The cable false is one of the most important reasons for the electric fires. China is a big developing country with a long history and large population. In the past three decades, the economy developed fast in China. The living standard of Chinese people has also improved fast. In addition, the prices for those typical household electrical appliances, such as TV sets, refrigerators, personal computers, air conditions, etc., have decreased a lot since the development of the science and technology. In this case, lots of new household electrical appliances are introduced for common people. However, in many old buildings in China, the electrical power systems were designed and installed long time ago. The load carrying capacity of the old electric power system does not fit the electrical power requirements for many old buildings, in which lots of powerful electrical appliances are added. In addition, the cables in the old buildings have been used for a long time. These cables were the products manufactured long ago, fire protection properties of which were limited by the fire retardant technology at that time. Therefore, will the fire-resistant properties of the old cables in those old buildings change after being used for so long time? In addition, what is the difference of fire properties between the old cables and new cables? This would be the important and necessary knowledge for officers of the Fire Department to design the modification program for the electrical cable system in those old buildings.

As the outer sheath is the main combustible part of the cable, the analysis of its pyrolysis and combustion processes of the cable sheath is key to the research of fire protection properties of cables. Ma et al. [7], Henrist et al. [8], Cheng et al. [9], and Gao [10] have studied the thermal degradation characteristics of typical PVC cable, which is widely used in China. However, little work was done to analyze the fire protection properties of the old cable. Therefore, in this study, TG and FTIR experiments were carried out for the pyrolysis properties of old cables, which have been in use for more than 10 years. In addition, TG and FTIR experiments were also conducted for the new cable, which represents the typical PVC cable manufacture technology at present. In addition, the combustion behaviors of both were experimentally analyzed through the microscale combustion calorimeter. Finally a comparison of the fire protection properties between the old and new cable sheath was made.

2. Experimental

As addressed above, the outer PVC sheath is the main combustible material of cable, thus its pyrolysis characteristics play

---

* Corresponding author. Tel.: +86 551 3607329; fax: +86 551 3606981.
E-mail address: xqy@ustc.edu.cn (Q. Xie).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.03.015

a key role in analyzing the fire resistance of cable systems. The degradation of PVC sheath of cable involves complex chemical and physical changes. In studying the chemical reactivity of a solid material being heated, the thermogravimetry method is one of the most popular ways [11,12]. While TG experiments are being conducted, the changing weight of a small solid material is recorded as it is heated inside an oven under controlled temperature and a certain atmosphere. Providing qualitative and quantitative information for the different reactions taking place in the heated solid, the method is widely used to study solid thermal degradation. Therefore, based on a thermal analyses apparatus (DTG-60H of Shimadze), thermogravimetric experiments were carried out in this work for an old cable, which has been in use for more than 10 years. At air atmosphere, a series of TG experiments was conducted with the temperature rising rates of 5, 15, 25 and 35 K/min, respectively. In order to analyze the degradation behavior of the old cable sheath at different atmospheres, similar series of experiments were done at nitrogen atmosphere. The same TG experiments were also carried out for a new cable sheath at air and nitrogen atmospheres. Then a comparison was made on the pyrolysis difference between the old and new cable sheath at both atmospheres. The PVC sheath was cut into small pieces before putting into the heating oven. About 8 mg of sheath was used for each test. The corresponding flow rate inside the oven was 50 mL/min. From the room temperature, the thermogravimetric experiments were carried out with different temperature rising rates until more than 1000 K.

In order to analyze the gaseous release during the thermal degradation behavior of old and new cables, some other experiments were further carried out with the Nicolet 6700 FTIR spectrophotometer equipped with a ventilated oven having a heating device. The transition mode was used and the wavenumber range was set as 4000–500 cm^{-1} with the resolution of 4 cm^{-1}. The investigations were carried out under nitrogen atmosphere with the heating rate of 15 K/min.

As addressed above, the main objective of the present work is to test the fire protection properties of the old and new cables. The detail composition of the cables is very helpful for the analyses of the different pyrolysis properties of old and new cables. But it seems that it is difficult to achieve such information from the cable manufacturers, especially for the old cable. In order to get more detailed information about the fire protection properties for the old and new cables, experiments were carried out based on the microscale combustion calorimeter (Govmark MCC-1) with the heating rate of 60 K/min. The heat release rates and the oxygen consumptions of the old and new cables were experimentally analyzed and compared.

3. Results and discussions

The thermal degradation of PVC is generally considered to be a two-step process. The first step involves dehydrochlorination of the polymer, resulting in the formation of conjugated double bonds that break during the second step. The main labile sites for dehydrochlorination are the tertiary chlorines. In the second step, the degradation of the polymer continues with cracking and pyrolysis to low hydrocarbons of linear or cyclic structure. Loss of HCl leaves a residue with a conjugated polyene structure. The degradation is related to the presence of some weak points along the PVC chains, since the bond dissociation energies for C–C, C–H and C–Cl were 435, 347 and 326 kJ/mol, respectively [13].

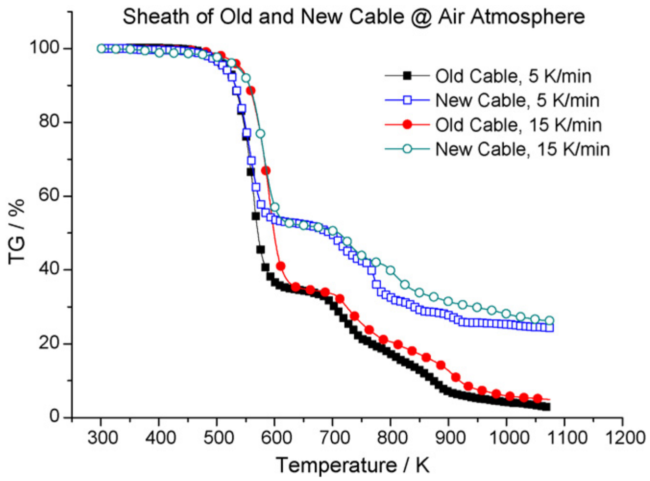


Fig. 1. Comparison of TG of PVC sheath for old and new cable in air atmosphere (5, 15 K/min).

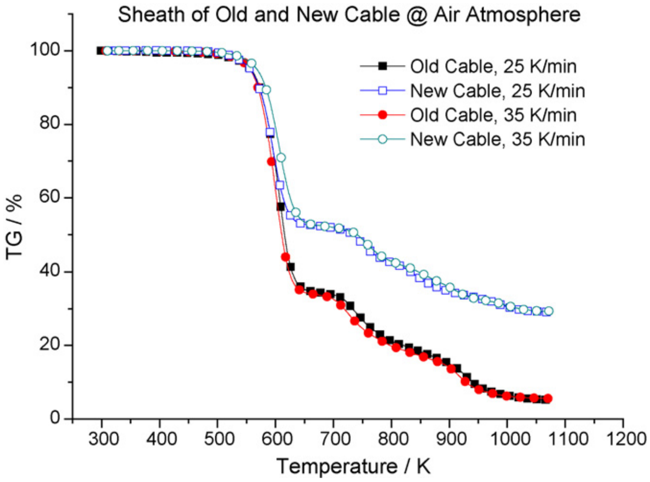


Fig. 2. Comparison of TG of PVC sheath for old and new cable in air atmosphere (25, 35 K/min).

Fig. 1 shows the relative mass loss for the PVC sheath of old and new cables in air atmosphere with the temperature rising rates of 5 and 15 K/min. It is shown that the mass loss curves of the old and new cables are clearly different under each heating rate. With the temperature rising rate 5 K/min, the mass loss curve of old cable sheath is similar to that of new cable sheath when the temperature is less than 550 K. However, the mass loss of the old cable sheath is faster than that of the new one as soon as the temperature is higher than 550 K. In this case, the final remaining mass of the old cable sheath is clearly less than that of the new one. Fig. 2 gives the corresponding results with the temperature rising rate 25 and 35 K/min. In a word, as is shown in Figs. 1 and 2 that, when the temperature rising rates are 5, 15, 25 and 35 K/min, the pyrolysis differences between the old and new cable sheaths are all similar.

Figs. 3 and 4 give the DTG of old and new cable sheath in air atmosphere with different heating rates. It is shown that there is a main peak DTG for each curve in Figs. 3 and 4. It should be noted that the onset temperature of mass loss is an important variable for polymer pyrolysis analysis. This parameter suggests the ignition time of the cables in fire. As shown in Figs. 1–4, the onset temperature of mass loss between the old and new cables for all heating rates in air atmosphere is practically the same, except at 35 K/min. Figs. 2 and 4 illustrate that the onset temperature shift slightly to lower temperature at 35 K/min. It is suggested that the old and new cable start to pyrolyze at nearly the same temperature although the old cable is pyrolyzed more strongly and completely than the new one.

Table 1 gives the typical pyrolysis parameters of sheath for old and new cable in air atmosphere with different heating rates.

Table 1
Pyrolysis parameters of sheath for old and new cable in air atmosphere.

Heating rate (K/min)	DTG_{peak} (%/min)		$Ratio_{old-new}$[a] (%)	$T_{DTG\text{-}peak}$ (K)		$Mass_{remaining}$ (%)	
	Old	New		Old	New	Old	New
5	−7.45	−4.63	60.91	563.38	560.48	2.69	24.32
15	−19.43	−14.78	31.47	590.57	580.70	4.95	26.23
25	−32.03	−22.85	40.18	605.97	595.93	5.11	29.03
35	−42.91	−31.64	35.62	599.40	606.00	5.59	29.31

[a] $Ratio_{old-new} = (DTG_{peak\text{-}old} - DTG_{peak\text{-}new})/DTG_{peak\text{-}new} \times 100\%$.

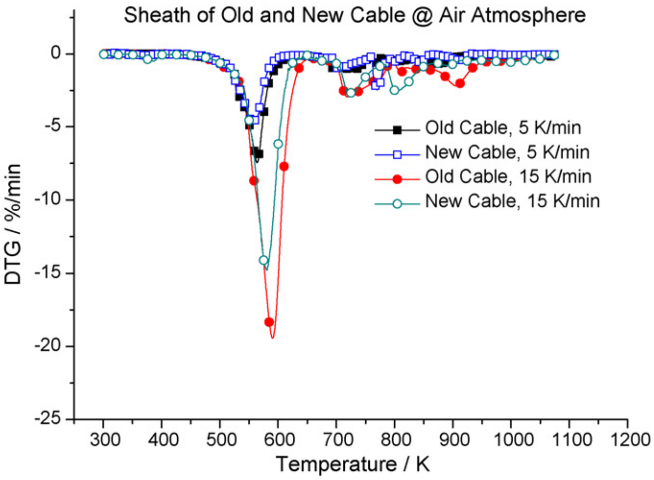


Fig. 3. Comparison of DTG of PVC sheath for old and new cable in air atmosphere (5, 15 K/min).

As shown in Table 1 and Figs. 3 and 4, for the old cable sheath, the peak DTGs increase with the heating rates. The corresponding temperature for each peak DTG generally increases with the increasing of the heating rate, except with the heating rate 35 K/min. In addition, the larger heating rate, the more final remaining mass. For the pyrolysis properties of new cable in air atmosphere, the effect of heating rates on the peak DTG, the temperature for peak DTG and the final remaining mass are all similar to that of the old cable sheath.

For the pyrolysis difference between the old and new cable sheath, it is shown in Table 1 and Figs. 3 and 4 that the peak DTG of old cable sheath is clearly larger than that of new cable sheath for each heating rate. The defined $Ratio_{old-new}$ in Table 1 describes the relative difference of peak DTG between the old and new cable sheath at each heating rate. As shown in Table 1, the $Ratio_{old-new}$ is the largest (60.91%) when the heating rate is as slow as 5 K/min. However, the $Ratio_{old-new}$ is the smallest (31.47%) when the heating rate is 15 K/min. The final remaining mass for the old cable sheath is much less than that of the new cable sheath at each heating rate.

Based on the above analysis, it is suggested that the old cable sheath is pyrolyzed more strongly and completely than the new cable sheath under the same heating condition, namely, at either slow or fast heating rate. Therefore, the fire protection properties of the old cable in old buildings are weaker than the new cable. In addition, as mentioned above, the current in the old cable in some old buildings may be too large since more and more new electrical appliances are introduced in recent years. This may be another reason for the more frequent electrical fire in those old buildings.

There may be two main reasons for the pyrolysis difference of the outer sheath between the old and new cables. As mentioned above, the old cable, which is tested here, has been used for more than 10 years. The temperature of the cable core would increase a little once the power loading is applied. After a long-time use and heating, the sheath of the old cable aged, the fire protection ability of the old cable decreased. The other reason may be the development of the science and technology of the flame retardant materials. The old cable tested was made more than 10 years ago, while the new cable, a new kind of product, represents the up-to-date manufactory technology of fire resistance of cables.

Figs. 5 and 6 give the mass loss of old and new cable sheath in nitrogen atmosphere with the temperature rising rates 5, 15, 25 and 35 K/min. It is also shown that the old cable sheath was pyrolyzed faster than the new one at nitrogen atmosphere at each heating rate. In addition, the old cable sheath was pyrolyzed more completely than the new one in nitrogen atmosphere, similar to the results at air atmosphere.

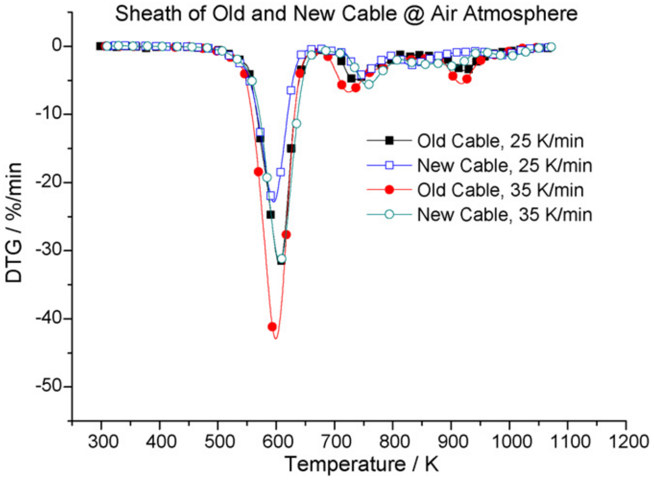


Fig. 4. Comparison of DTG of PVC sheath for old and new cable in air atmosphere (25, 35 K/min).

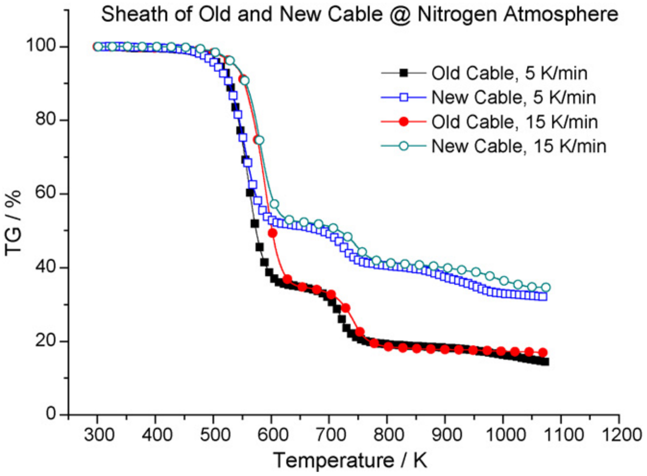


Fig. 5. Comparison of TG of PVC sheath for old and new cable @ nitrogen atmosphere (5, 15 K/min).

Table 2
Pyrolysis parameters of sheath for old and new cable at nitrogen atmosphere.

Heating rate (K/min)	DTG_{peak} (%/min)		$Ratio_{old-new}$[a] (%)	$T_{DTG\text{-}peak}$ (K)		$Mass_{remaining}$ (%)	
	Old	New		Old	New	Old	New
5	−5.482	−4.16	31.78	561.91	552.15	14.44	32.11
15	−16.32	−13.41	21.70	590.18	580.79	19.95	34.66
25	−27.52	−22.18	24.08	604.13	595.30	16.30	34.14
35	−37.01	−30.04	23.20	612.85	606.02	12.46	34.27

[a] $Ratio_{old-new} = (DTG_{peak\text{-}old} - DTG_{peak\text{-}new})/DTG_{peak\text{-}new} \times 100\%$.

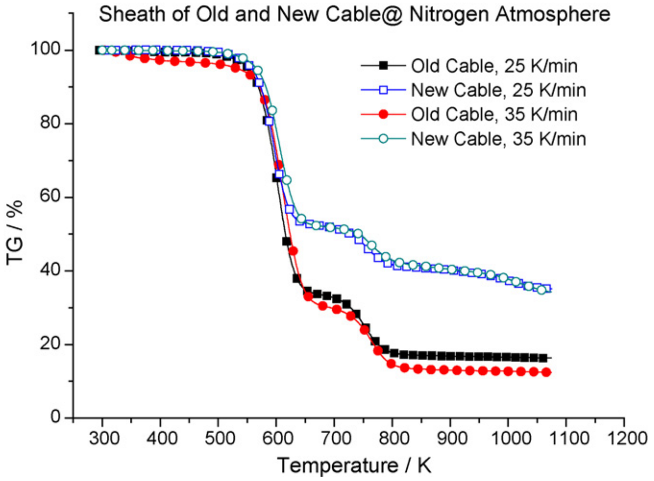


Fig. 6. Comparison of TG of PVC sheath for old and new cable @ nitrogen atmosphere (25, 35 K/min).

Figs. 7 and 8 give the comparison of the DTG for old and new cable sheath in nitrogen atmosphere at different heating rates. It is also shown that there is an obvious main peak DTG at each heating rate. With the increasing of the heating rate, a second small peak DTG appears after the main peak DTG in nitrogen atmosphere. As shown in Figs. 5–8, the onset temperature of mass loss of the old and new cables for all heating rates in nitrogen atmosphere is also the same. Table 2 gives the typical pyrolysis parameters of the sheath for old and new cables in nitrogen atmosphere at different heating rates.

As shown in Table 2 and Figures 7 and 8, the main peak DTG of old cable sheath is also much larger than that of the new cable sheath in nitrogen atmosphere, similar to the results in air atmosphere. However, the $Ratio_{old-new}$ in Table 2 indicate that the difference of main peak DTG between old and new cable sheath in nitrogen atmosphere is smaller than that in air atmosphere. With the heating rate 5 K/min in nitrogen atmosphere, there appears the largest $Ratio_{old-new}$ (31.78%), which is much less than the largest one (60.91%) in air atmosphere. Also, with heating rate 15 K/min in nitrogen atmosphere, there appears the smallest $Ratio_{old-new}$ (21.70%), which is less than the smallest one (31.47%) in air atmosphere. Table 2 shows that the temperature for the peak DTG increases with the heating rates in nitrogen atmosphere for both old and new cables. The temperature for the peak DTG of old cable sheath is relatively larger than that of the new cable sheath at each heating rate. The final remaining mass for old cable sheath is also much less than that of the new cable sheath at each heating rate in nitrogen atmosphere. The final remaining mass for the old cable sheath is relatively different at the different heating rates. However, the effect of the heating rate on the final remaining mass of new cable sheath is smaller in nitrogen atmosphere.

In order to further analyze the effects of the atmosphere (air or nitrogen) on the pyrolysis of cables at different heating rates, the corresponding pyrolysis curves at air and nitrogen atmospheres were drawn together for each case (shown in Appendix A). It is suggested that the main effects of atmosphere on the pyrolysis are similar for old and new cables. Namely, there is little difference in the early stage of the pyrolysis process of cables in air and nitrogen atmospheres. However, when it comes to the late stage, the cable sheath keeps degrading in air atmosphere, which is not the case in nitrogen atmosphere. Therefore, there was more final remaining mass for the cable sheath pyrolysis in nitrogen atmosphere.

Fig. 9 gives the FTIR spectra of old and new cable sheaths at 561 K (10.391 min). It shows that HCl, CO_2 and H_2O are released at this stage for old cable sheath. However, as shown in Fig. 9, only CO_2 and H_2O are released for the new cable sheath. Fig. 10 gives the FTIR spectra of old and new cable sheaths at 638 K (13.509 min). At this stage, HCl, CO_2 and H_2O are released both from the old and new

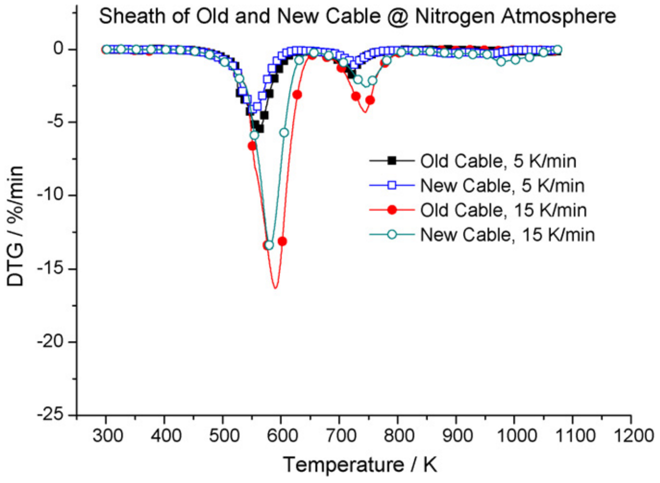


Fig. 7. Comparison of DTG of PVC sheath for old and new cable @ nitrogen atmosphere (5, 15 K/min).

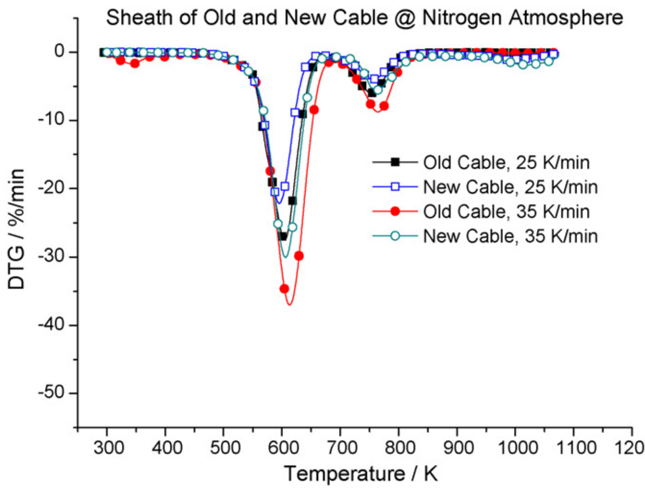


Fig. 8. Comparison of DTG of PVC sheath for old and new cable @ nitrogen atmosphere (25, 35 K/min).

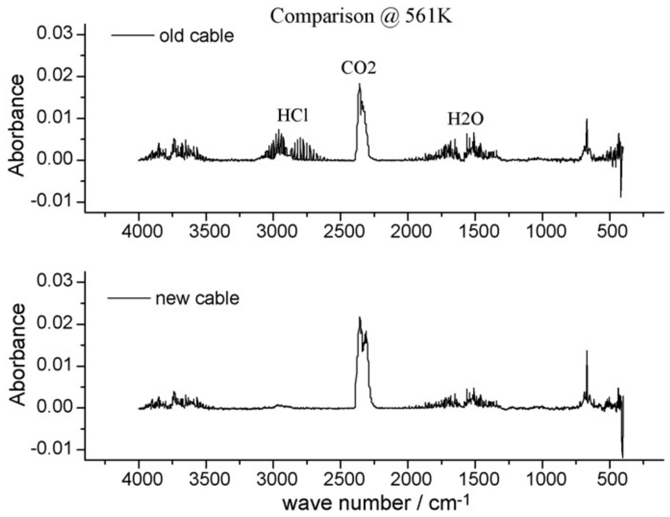


Fig. 9. Comparison of FTIR spectra of the gas released from old and new cable sheaths.

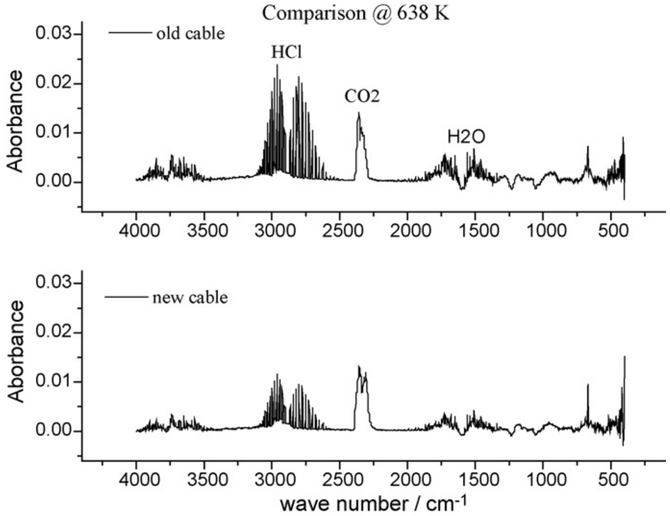


Fig. 10. Comparison of FTIR spectra of the gas released from old and new cable sheaths.

cable sheath. It suggests that compared with the new one, the HCl gas is released earlier from the old cable sheath.

Figs. 11 and 12 give the 3D surface for the FTIR spectra of the released gas by old and new cable sheaths, respectively. It is clearly shown that the HCl gas is released from old cable much earlier than the new one. It takes a rather long time for the HCl gas to be released completely for the old cable, as shown in Fig. 11. However, as can be seen in Fig. 12, there is a clear tall absorption peak for HCl near the wavenumber range of 3100–2600 cm^{-1} for the new cable. It shows that the HCl is released by the new cable later but more quickly than by the old cable.

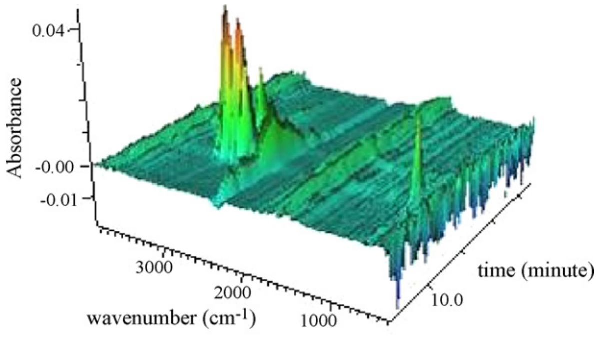


Fig. 11. The 3D surface for the FTIR spectra of the released gas by old cable sheath.

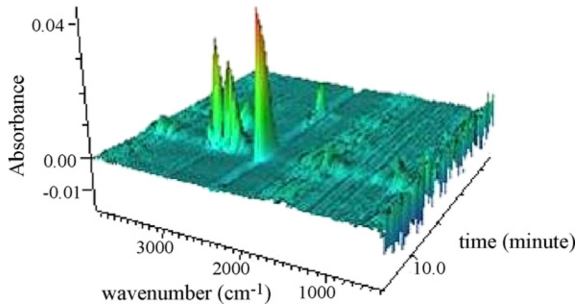


Fig. 12. The 3D surface for the FTIR spectra of the released gas by new cable sheath.

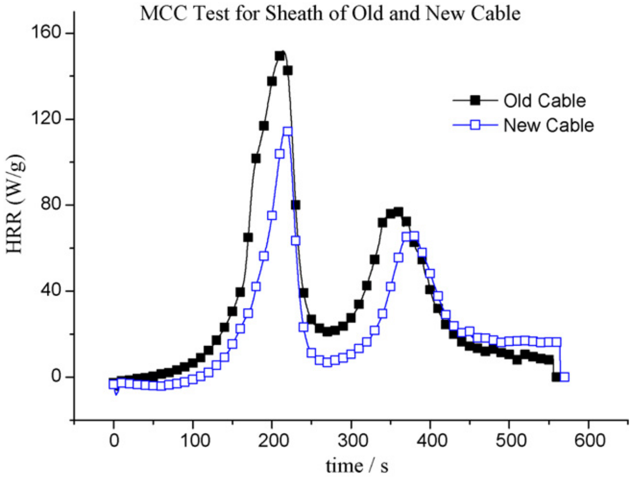


Fig. 13. Heat release rate of old and new cable sheath by MCC test (60 K/min).

Fig. 13 gives the heat release rate per unit mass for the old and new cable sheath through the MCC test with the heating rate 60 K/min. It is shown that there are two peak heat release rates for both old and new cables. The peak heat release rates for the old cable sheath are larger than those of the new one, either for the first or second peak. It suggests again that the old cable sheath would combust more strongly and completely, which agrees well with the above analyses of the mass loss in Figs. 1–8. Additionally,

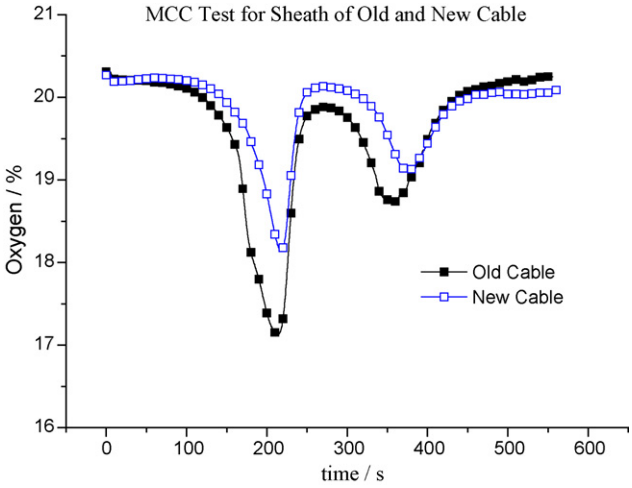


Fig. 14. Oxygen concentration of old and new cable sheath by MCC test (60 K/min).

Fig. 14 shows the oxygen consumption during the combustion for the old and new cable sheaths in the MCC test. It illustrates that more oxygen was consumed for the old cable sheath. As a result, the old cable sheath is pyrolyzed and combusted more strongly than the new cable.

4. Conclusions

In the present study, thermogravimetric experiments were conducted for old and new cables with different heating rates in air and nitrogen atmospheres. In addition, the gas release of cables during pyrolysis was analyzed with FTIR experiments. The results illustrate that the pyrolysis behavior of the old cable sheath is rather different with that of the new cable sheath in either air or nitrogen atmosphere. The mass loss of the old cable sheath is clearly larger than that of the new one when the temperature is higher than 550 K at air or nitrogen atmosphere. The final remaining mass of old cable is much less than that of the new cable. In addition, the onset temperatures of mass loss of the old and new cables for all heating rates in air or nitrogen atmosphere are generally the same. It illustrates that the old and new cable start to pyrolyze at nearly the same temperature although the old cable would pyrolyze more strongly and completely than the new one. The results also show that there is a main peak DTG for the old and new cable sheath under each condition. However, the main peak DTG of old cable sheath is clearly larger than that of the new cable sheath, especially at air atmosphere. In consequence, the fire protection properties of the old cable in those old buildings are weaker than the new cable, which suggests that the modification of the electrical power system is important for the fire protection improvement of the old buildings. The measured FTIR spectra illustrates that the HCl release was different for the old and new cable sheaths. The experiments in the microscale combustion calorimeter show that the old cable sheath combusts more strongly than the new one. More heat is released by the old cable sheath combustion than the new one for unit mass. Finally, different pyrolysis properties of the old and new cables may be attributed to the aging of cable and the fast development of fire retardant materials.

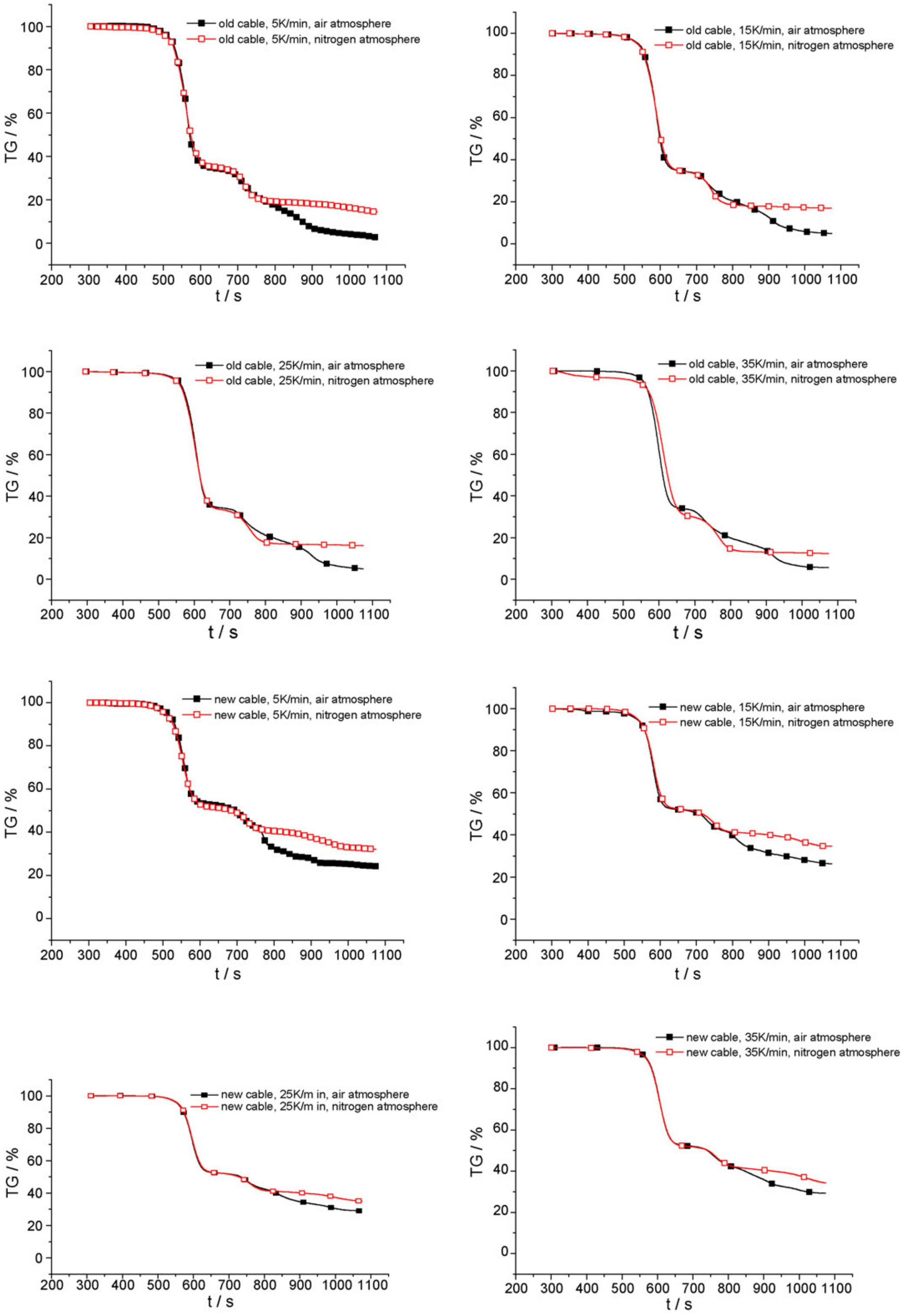
Acknowledgements

This work was supported by the China Postdoctoral Science Foundation (no. 20070410220) and the Young Teachers Foundation in Anhui Province (no. 2009SQRZ006ZD). The authors thankfully acknowledge the supports. Also many thanks for the good comments of the two reviewers.

Appendix A.

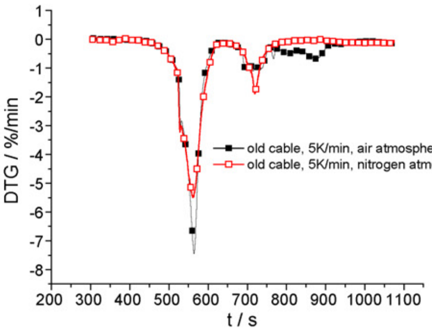
Figures for the analyses of the effects of atmosphere (air or nitrogen).
(1) TG comparison.

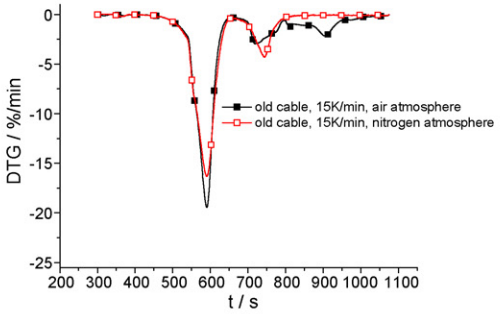
(1) TG comparison

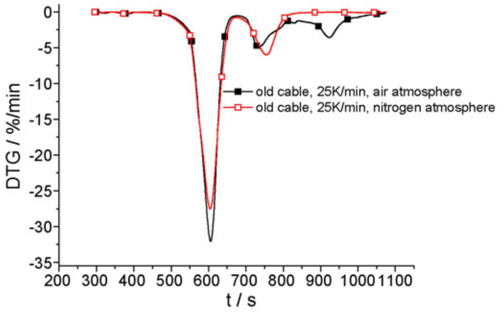


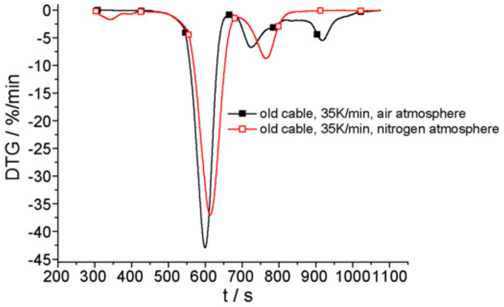
(2) DTG comparison.

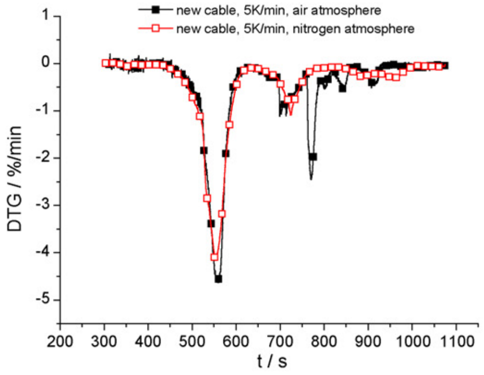
(2) **DTG comparison**

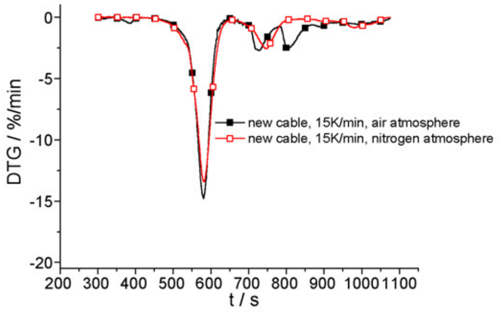


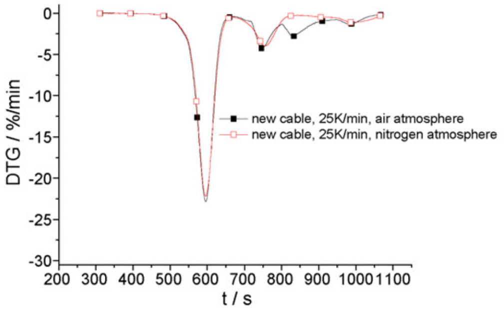


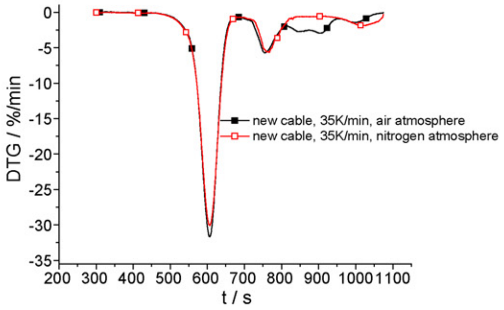












References

[1] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2003, The Personnel Press of China, Beijing, 2006.

[2] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2004, The Personnel Press of China, Beijing, 2005.

[3] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2005, The Personnel Press of China, Beijing, 2006.

[4] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2006, The Personnel Press of China, Beijing, 2007.

[5] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2007, The Personnel Press of China, Beijing, 2008.

[6] The Fire Bureau of the Ministry of Public Security, Fire Statistical Yearbook of China-2008, The Personnel Press of China, Beijing, 2009.

[7] R.H. Ma, Y.C. Lin, C.P. Kuo, The study of thermal pyrolysis mechanisms for chloro organic compounds in electric cable and medical wastes, J. Anal. Appl. Pyrolysis 75 (2) (2006) 245–251.

[8] C. Henrist, A. Rulmont, R. Cloots, et al., Toward the understanding of the thermal degradation of commercially available fire-resistant cable, Mater. Lett. 46 (2–3) (2000) 160–168.

[9] J.Q. Cheng, W.N. Jia, Z.J. Shu, et al., Experimental research on rules of releasing of the halogen gas of PVC cable under hydrogenation condition, Fire Sci. Tech. 26 (4) (2007) 383–386.

[10] Y.P. Gao, Study on pyrolysis characteristics of insulative PVC material used for fire retardant cable, Eng. Plast Appl. 35 (3) (2007) 44–47.

[11] H.M. Zhu, J.H. Yan, X.G. Jiang, et al., Study on pyrolysis of typical medical waste materials by using TG–FTIR analysis, J. Hazard Mater. 153 (1–2) (2008) 670–676.

[12] M. Benes, N. Milanov, G.G. Matuschek, et al., Thermal degradation of PVC cable insulation studied by simultaneous TG–FTIR and TG–EGA methods, J. Therm. Anal. Calorim. 78 (2) (2004) 621–630.

[13] H.M. Zhu, X.G. Jiang, J.H. Yan, et al., TG–FTIR analysis of PVC thermal degradation and HCl removal, J. Anal. Appl. Pyrolysis 82 (2008) 1–9.