Thermal properties of polycarbonate containing potassium perfluorobutane sulfonate

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Abstract: Potassium perfluorobutane sulfonate (PPFBS) was used to impart flame retardancy to polycarbonate (PC). The thermal properties of of the PC/PPFBS composites were studied by limiting oxygen index (LOI), vertical burning test (UL-94), TG, and scanning electron microscopy (SEM). The results showed that PC/1wt.% PPFBS composites passed UL-94V-0 rating, and its LOI values were 30.6%. Compared with PC, for the PC/PPFBS composites, the thermal stability and the char yield are increased. Scanning electron microscopy revealed that the char properties had crucial effects on the flame retardancy.

Introduction

Organic halogen compounds have been commonly used as flame retardants (FR) for polymeric materials because of their extremely high flame retardancy [1]. However, these compounds might generate highly toxic and potentially carcinogenic substance during combustion [2,3]. For this reason, Various halogen-free flame retardants have been tried to use for polymers , such as triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP) [4]. However, these phosphates usually bring some proceeding problems such as the high processing temperatures and their different resin state. In addition, the use of organosulfonates in low concentration (no less than 1wt.%) was found to be effective in flame-retarding polycarbonate (PC) as a special case, such as potassium perfluorobutane sulfonate (PPFBS), potassium diphenysufonesulfonate[5]. However, the thermal degradation of PC/PPFBS composites was not found.

So in this work, PPFBS was applied to PC, and its thermal degradation of PC/PPFBS composites was discussed.

Experimental

Materials

PC was received from Jinhzhou Wanghan Fine Chemical Engineering Limited Company (China). Potassium perfluorobutane sulfonate (PPFBS) was purchased from Sa En Chemical Technology Co., Ltd.

Preparation of PC samples

PC samples were prepared by mixing PC with different amounts of PPFBS as shown in Table 1, then blending them in a two-roll mill at 210°C for 10 min and compressing them at 210°C to form sheets of 130mm ×50mm × 3mm. The test specimens were cut from the molded sheets.

Limiting oxygen index test

The limiting oxygen index (LOI) test was performed with a JF-3 oxygen index test instrument (Jiangning, China) in terms of the standard LOI test, ASTM D 2863-97. The specimen size for the LOI measurement was 130mm×6.5mm×3mm.

Vertical burning tests

The vertical burning test was conducted by a CZF-II horizontal and vertical burning tester (Jiang Ning Analysis Instrument Company, China). The specimens used were 127 ×12.7× 3 mm^3 according to UL94 test ASTM D3801 standard.

Thermogravimetry analysis

Thermogravimetry (TG) was carried out on a HCT-2 thermal analyzer (Beijing Hengjiu Scientific Instrument Factory) under a dynamic nitrogen (dried) atmosphere at a heating rate of 10°C min^{-1}, PC samples were heated from room temperature to 750°C.

Scanning electron microscope analysis

The char residues after LOI test were studied with a scanning electron microscope (KYKYEM-3200, China) scanning electron microscope (SEM). The samples were gold-coated before scanning to provide an electrically conductive surface. An accelerating voltage of 22 kV and 60mA of electric current were used while we recorded the scanning electron micrograms.

Results and discussion

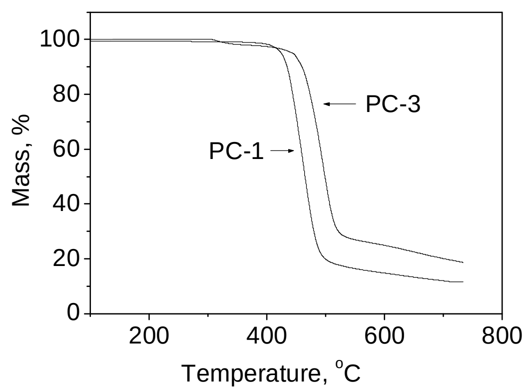
Flame retardant behavior

Table 1 Flame retardant properties of PC samples

Samples	PC (g)	PPFBS (g)	(g)	LOI (%)	UL 94 rating
PC-1	100	0	-	22.7	V-2
PC -2	99.5	0.5	-	26.9	V-1
PC -3	99.0	1.0	-	30.6	V-0
PC -4	98.5	1.5	-	33.4	V-0

Table 1 presents the LOI values and UL-94 testing results of and PC/PPFBS composites. From Table 1 we can see that the LOI values of PC are increased to 26.9% when PPFBS is added by a 0.5g. In general an LOI value of at least 26% is needed for a realistic degree of flame retardancy [6]. However, the UL-94 rating of the flame retardant systems did not exceed V-0, indicating an inadequate level. When 1g dosage is added, the LOI values reached 30.6%, and UL-94 rating changed from V-1 to V-0. The LOI of PC/1.5g PPFBS composites is 33.4%, which shows very good flame retardancy of PPFBS.

Degradation of polycarbonates



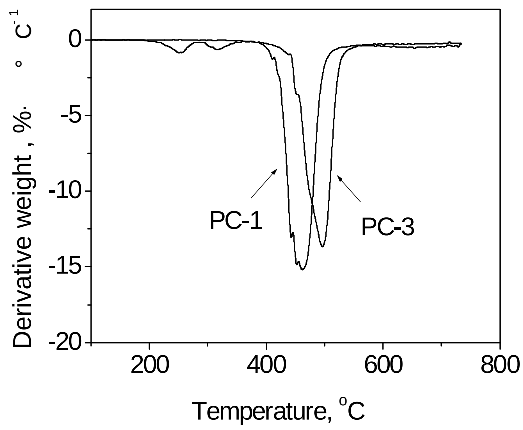


Figure 1 TG curves of PC samples.   Figure 2 DTG curves of PC samples.

The TG and DTG curves of PC-1 and PC-3 were carried out in dynamic nitrogen from ambient temperature to 750°C and are shown in Fig. 1 and Fig. 2. The initial decomposition temperature (IDT) determined by 5% of mass loss, showing samples begin to degrade, and indicates the apparent thermal stability of the samples. Integral procedure decomposition temperature (IPDT) determined by 50% of weight loss, exhibits the sample inherent thermal stability. The char yield at 700°C, temperatures at the maximum mass loss rate (T_m) and the value of the maximum weight loss rate (R_{max}) were measured, list in Table 2.

Table 2 Thermal data of the PC samples from TG and DTG

Samples	IDT (°C)	T_m (°C)	IPDT (°C)	R_{max} (%/°C)	Char yield (%)	Ea (kJ/mol)
PC -1	420	460	470	15.0	12.0	185.0
PC -3	440	500	500	14.0	20.0	205.0

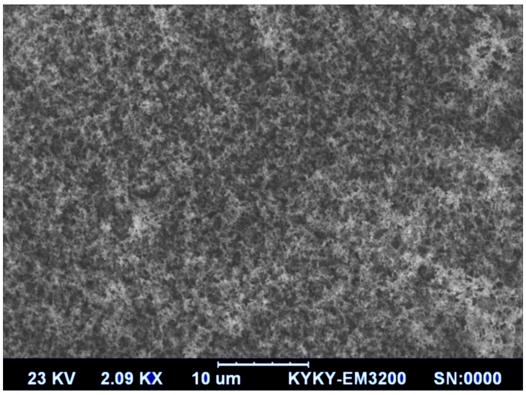
Generally, the function of flame retardant in materials is to increase the char at the cost of flammable volatile products [7]. From the Fig. 1, Fig. 2 and Table 2, it can be seen that there is a main and quick decomposition stage, and the mass loss behavior of PC containing PPFBS is found to follow the patterns discussed above.

The results indicate that pure PC is thermally stable below 400°C, and IDT is 420°C. It has a small amount of volatile until the temperature rises to 430°C, and it has a mass loss of less than 10% at 430°C. When the temperature further increases, mass loss increases rapidly and a quantity of volatile is produced until almost exhaust at 490°C, and char yields at 700°C are 12.0%. TG and DTG curves of PC/PPFBS composites are different. It is noted that R_{max} (14.0%/°C) are decreased while char yields (20.0%) is increased. The decrease of the mass loss significantly reduces the release of combustible products from the PC decomposition, consequently depressing the flammability.

Thermal stability of polycarbonates

From Table 3, it can be seen that PC/PPFBS composites shows relatively higher IDT (440°C) than that of PC (420°C). Meanwhile, PC-3 exhibits higher IPDT (500°C) than that of PC-1 (460°C), and PPFBS in PC-3 retards the mass loss rate of the polymers at high temperatures. The high IDT and IPDT imply the PC/PPFBS composites potential application in highly anti-thermal coatings and thermal insulating materials. The temperatures at the maximum mass loss rate (T_m) are also increased.

Morphology of polycarbonates chars



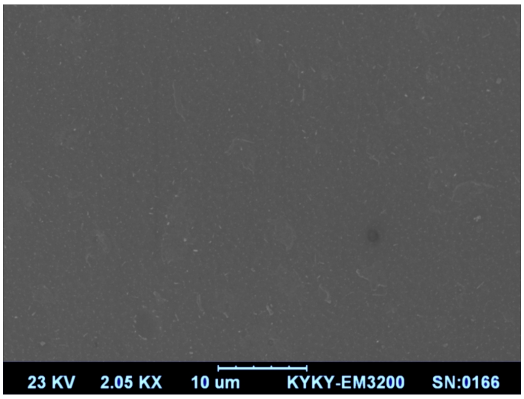


Figure 3 SEM micrographs of the char of PC-1 Figure 4 SEM micrographs of the char of PC-3.

As we know, when flame retardants are exposed to a fire, they will form a non-flammable, multicellular char layer on the surface of polymers. This layer provides an efficient shield and insulation for the underlying material against direct contact with fire, oxygen, and heat [9]. As a result, the structure and formation of the char layer are a critical factor for the flame retardancy of PPFBS. Figs. 3-4 present the SEM photographs of the surface of char of PC and PC/PPFBS composites. From Fig. 3 it can be observed that the char of PC is very porous, fragile and fragmentary, which could not effectively protect the underlying material from fire. From Fig. 4, we can see that the surface of the PC/PPFBS char is continuous and compact, which retards the overflow of the flammable volatiles at high temperature, and improves the flame retardancy of PC.

Conclusions

PPFBS was applied to PC to get good flame retardancy. 1% of PPFBS were added into PC to get 30.6% of LOI and UL 94 V-0. The rate of heat release (RHR), total heat release (THR) of the PC/PPFBS composites are much decreased compared with that of pure PC. Incorporating PPFBS into PC alters degradation characteristics. For the PC/PPFBS composites, compared with PC, the IDT, IPDT, T_m, char yield and activation energy are increased, mass loss is decreased. *Ea* for the decomposition of UP is 185.0 $kJmol^{-1}$ while it becomes 205.0 $kJmol^{-1}$ for PC containing PPFBS, increased by 20 $kJmol^{-1}$. In the thermal degradation of the PC/PPFBS composites, PPFBS increases the stability of PC, make it decompose at relatively low temperature, increasing the char at the cost of flammable volatile products, forming a continuous and compact char which retards the mass loss rate of the PC at high temperatures, protecting the underlying combustible substrate to improve the flame retardancy of PC.

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