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EFFECTS OF FULLERENES ON THERMAL BEHAVIORS OF POLYETHYLENE GLYCOL

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Effects of fullerenes including FS, EFS and pure C_{60} on thermal behaviors of polyethylene glycol (PEG) have been studied by employing thermogravimetry-differential thermogravimetry (TG-DTG), differential scanning calorimeter (DSC) and off-line furnace-type pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The products were collected by Cambridge filter pad which was widely used in analyzing the combustion products of cigarette. The results showed that the addition of fullerenes obviously restrained the thermal decomposition of PEG. The initial decomposition temperatures (IDT) and maximum decomposition peak temperatures (MDT) were evidently postponed by the addition of fullerenes. Pyrolysis products with one or two hydroxyl end groups obviously increased with the addition of 10% C_{60}. The reasons of the changes were discussed from the aspects of reaction mechanisms.

Keywords: *fullerenes, polyethylene glycol, Py-GC/MS, thermal pyrolysis*

Introduction

PEG is one of the most widely used polymeric binders in solid rocket propellants. It serves to hold the raw materials of propellants together having the general formula of $HO(CH_2CH_2O)_nH$. With the different values of n, PEG has many useful applications in packaging, cosmetics, biotechnology, pharmaceutics and minimum-smoke solid propellants [1, 2]. Carbon black (CB) is one of the most useful catalysts in solid rocket propellants and the effect of CB on the thermal behavior and electric properties of PEG is widely reported [3–5]. Fullerenes which are discovered in 1985 [6] and mass produced in 1990 [7] are one kind of allotropes of CB. They have many characteristics such as their high feasibilities as a new kind of functional materials [8], spherical closed carbon and π-electron conjugated system delocalized over the entire surface of the molecule. Fullerenes can obviously improved the decomposition process of AP [9], but the addition of fullerenes restrained the decomposition process of pure PEG. Although the thermal pyrolysis of PEG has been studied, the effects of fullerenes and the processing additives on the overall pyrolysis scheme of PEG have not been investigated.

Madorsky and Straus [10] reported that the pyrolysis products of PEG were aldehydes, ketones, and ethers. They supposed two types of molecular cleavages to explain the product formations. In first type, cleavage involved homolytic cleavage of the C–O and C–C bonds with an intramolecular transfer of hydrogen. In second type, cleavage did not involve intramolecular transfer of hydrogen, but homolytic cleavage of the polymer backbone produce new radicals. These radicals were then ruptured to form smaller molecules and monomer products. The Madorsky–Straus mechanism did not present an adequate discussion of the termination reactions associated with the decomposition. In this article, we discuss the effects of fullerenes on the termination reactions due to the decomposition, and a hydrolysis mechanism is supposed to explain the lack of aldehydes and ketones products.

Experimental

Materials

The average molecular mass of PEG is 10000–12000. FS (fullerene soot, comprised of 10% fullerenes and 90% carbon black) is the primary product of electric arc evaporation of graphite under helium atmosphere. EFS (extracted fullerene soot) contains about 80% C_{60} and 20% C_{70}, and the purity of C_{60} is 99.9%. Mixtures of fullerenes and PEG were prepared by carefully mixing of the two components in a polished baker at a constant temperature of 80°C in order to disperse the fullerenes uniformly into PEG. Care was taken to preheat PEG for only a briefest period of time because slow decomposition reportedly occurs even at these relatively low temperatures [11]. Dichloromethane (CH_2Cl_2) used in the experiments is analytical reagent.

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Instrumental

TG-DTG data were obtained on a TA TGA2950 instrument in the temperature range of 20–550°C. Thermal decomposition patterns of the mixtures were studied thermogravimetrically at a heating rate of 10°C min^{-1} in pure nitrogen atmosphere. The sample mass was about 1~2 mg and the sample was placed in aluminum oxide crucible.

DSC data were obtained on a model Netzsch DSC 204 in the temperature range of 20–550°C with a heating rate of 10°C min^{-1} in 0.1 MPa pure nitrogen atmosphere. The sample mass was about 1.0 mg and the sample was placed in aluminum oxide crucible with cover.

The credibility of apparatus used in the thermal pyrolysis experiments was proved by our previous work [12]. A 450°C pyrolysis temperature was chosen because TG and DSC results showed that this temperature was above the maximum pyrolysis temperature of PEG. Pure nitrogen was used as carrier gas. The pyrolysis products were collected by CH_2Cl_2 and Cambridge filter pad, and then analyzed by GC-MS.

Analysis of the pyrolysis products was accomplished by a GC-MS (Agilent Techn. Inc., 6890GC/5973MSD) using a HP-5MS capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness), with the following temperature programming: initial oven temperature was 40°C, held for 2 min and then raised to 250°C at 4°C min^{-1} and held for 10 min. Helium was used as carrier gas with a flow rate of 1.5 mL min^{-1} (constant flow). Programming temperature vaporizer (PTV) injector temperature was 250°C, and the amount of injection was 1.0 μL at split mode (split ratio, 20:1). The temperature of the GC-MS transfer line was 280°C. The ion source temperature was 230°C and the electron energy was 70 eV. The mass range from m/z 35 to 500 was scanned.

Results and discussion

Thermal analysis of PEG-fullerene mixtures

The TG-DTG results of PEG with 10% fullerene additives were shown in Table 1.

From the TG-DTG data of pure PEG, one can see there was a rapid mass loss process beginning at about 168°C and was completed at about 380°C. The maximum decomposition temperature was 286°C. The mass loss was 99.5% from 168 to 380°C with about 0.5% residual. This process was corresponding to the reactions of oxidation and cleavage of PEG backbone.

The initial decomposition temperature (IDT) for PEG with 10% FS was not as early as that of pure PEG. Thermal decomposition of PEG with 10% FS started at 340°C, about 172°C higher than pure PEG. Maximum decomposition peak temperature (MDT) of this sample was at 399°C which was 113°C higher than that of PEG. With the addition of 10% EFS and 10% C_{60}, the same results were found that the IDT of the two samples were 360°C and 365°C which were 192 and 197°C higher than that of pure PEG. MDT of PEG with 10% EFS and PEG with 10% C_{60} were about 129 and 123°C higher than that of PEG. These facts were clearly indicative of the difference in the thermal decomposition mechanism for pure PEG and PEG with fullerenes. The addition of fullerenes could postpone the decomposition temperature of PEG. This was possibly because the spherical structure of the fullerenes could absorb the decomposition products which resulted in the higher decomposition temperature of PEG with fullerenes.

Table 1 Thermal analysis data of PEG and PEG-fullerene mixtures

Sample	IDT./ °C	MDT./ °C	Final temp./ °C
PEG	168	286	380
PEG+10% FS	340	399	423
PEG+10% EFS	360	415	453
PEG+10% C_{60}	365	409	436

The DSC data for PEG and PEG with fullerenes recorded in nitrogen atmosphere were given in Table 2. The DSC data were in good agreement with the TG-DTG data. This also proved the credibility of the thermal analysis data.

From the DSC data above, firstly, there was an endothermic peak at about 63°C which was consistent with the melting point of the PEG. The melting points of the different samples were almost the same which showed that the addition of fullerenes didn’t affect the melting temperature of PEG. But the MDT of PEG was evidently postponed by the addition of fullerenes. TG-DTG and DSC results showed that the thermal decomposition mechanism of PEG with fullerenes were obviously different with that of pure PEG.

GC-MS analysis of the pyrolysis products of PEG and PEG with 10% C_{60}

Gas chromatography can be used to separate the mixture of stable pyrolysis gases. Pyrolysis GC/MS

Table 2 DSC data for PEG and PEG-additive mixtures in nitrogen atmosphere

Sample	Melt. temp./°C	MDT./°C
PEG	63	288
PEG+10% FS	63	399
PEG+10% EFS	65	413
PEG+10% C_{60}	64	414

(Py-GC/MS) or simple GC/MS researches are available to help identify the products of pure PEG [13, 14]. In order to investigate the effect of fullerenes on the pyrolysis mechanism of PEG, pure PEG and PEG with 10% C_{60} were used to carry out the pyrolysis experiments.

Pyrolysis products firstly collected by CH_2Cl_2 and Cambridge filter pad which was widely used in analyzing the combustion products of cigarette, and it was also a suitable material for collecting long-chain and macrocyclic compounds [15, 16]. Then the products was extracted from the Cambridge filter pad by CH_2Cl_2 and analyzed by GC-MS. For each sample, three replicate runs were done to ensure the reliability of experimental results. Figure 1 showed the total ion chromatograms of the pyrolysis products of PEG with 10% C_{60} in comparison with that of pure PEG sample. By comparing to the NIST02 mass spectral library, the mass spectral identifications were identified.

30 main products and their yields acquired by the internal standard method were listed in Table 3. Because the products were collected by Cambridge filter pad and analyzed by off-line GC/MS, the aldehyde end products were hydrolyzed to hydroxyl end products, also the addition of fullerenes increased the probability of aldehyde products hydrolyzed to hydroxyl products [17]. So the products with low molecular mass ($<C_4$) and aldehyde end products (expect benzaldehyde) were missed in the 30 main products of pyrolysis of pure PEG and PEG with 10% C_{60}. Consequently, we only discussed the effects of fullerenes on the hydroxyl products of PEG.

The products could be classified into four groups according to the molecular structure: compounds having benzene ring, polymer of glycol, long-chain alkanes and crown ether.

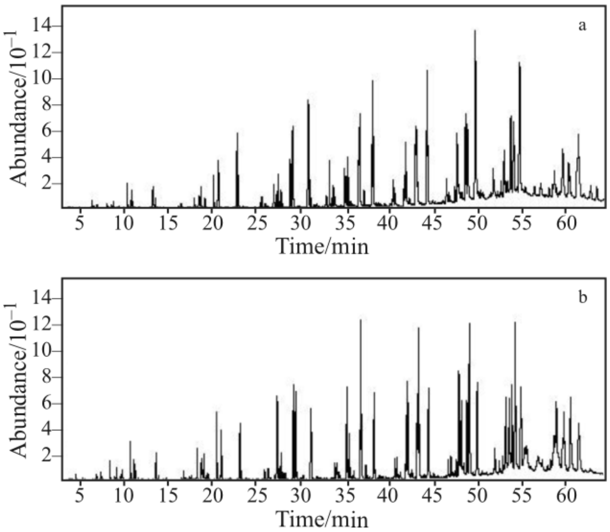


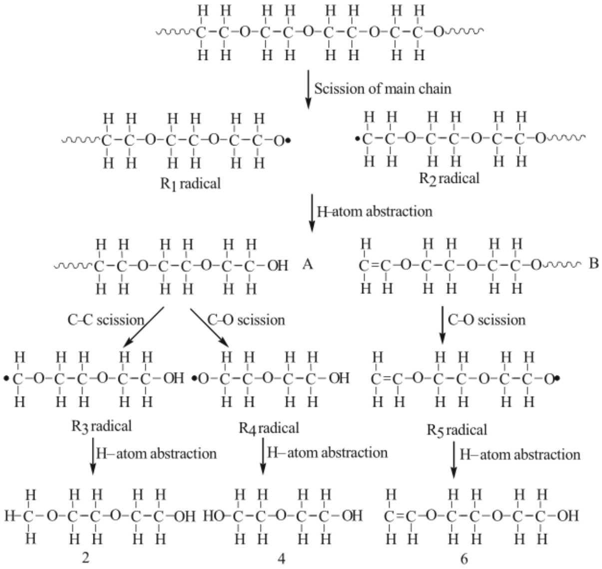
Fig. 1 Pyrolysis total ion chromatograms of a – PEG and b – PEG with 10% C_{60}

These products included oligomers of various chain lengths and terminal groups, long-chain alkanes and cyclized products. The major products were PEG monoether oligomers ($CH_3CH_2O[CH_2CH_2O]_nH$+ $CH_3O[CH_2CH_2O]_nH$), PEG diether oligomers ($CH_3CH_2O[CH_2CH_2O]_nOCH_2CH_3$+ $CH_3O[CH_2CH_2O]_nOCH_3$), crown ether and oligomers of glycol.

Most researchers considered that the pyrolysis mechanism of PEG was through a random homolysis of the C–C and C–O bonds by a radical chain mechanism [14, 18]. The possible pyrolysis mechanisms of PEG and PEG with 10% C_{60} were shown in Schemes 1–7. Firstly, scission of PEG backbone occurred through a C–O homolysis mechanism to form the R_1 radical and R_2 radical, then the R_1 radical and R_2 radical formed polymer A and B through a H-atom abstraction reaction respectively. The compounds 2 and 4 were produced through C–C scission and C–O scission of hydroxyl terminal compound A, respectively. The compound 6 was formed through the C–O scission and H-atom abstraction reaction of the vinyl terminal compound B.

Hydroxyl terminal compounds 5, 9, 12, 13 and 15 were also produced through C–C scission and H-atom abstraction reactions of compound A. The mechanism was shown in Scheme 2.

The compounds 7 and 17 were formed in the following way as Scheme 3. Firstly, the ethyl terminal compound was formed through a H-atom abstraction of R_2, then C–C homolysis reaction and H-atom abstraction reactions occurred, consequently, compounds 7 and 17 formed. The compound 8 was formed by C–O scission and H-atom abstraction reactions of compound B.



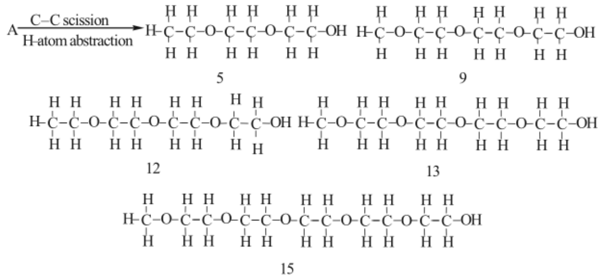
Scheme 1

Grassie [19] reported that the H-atom abstraction and radical recombination reactions also contained in the pyrolysis process of PEG. The R_6 radical was formed through a radical recombination of R_2 radical and a following C–O scission of the combination product. The compound 23 was formed through a series C–O scission and radical recombination reactions. This process was shown in Scheme 4.

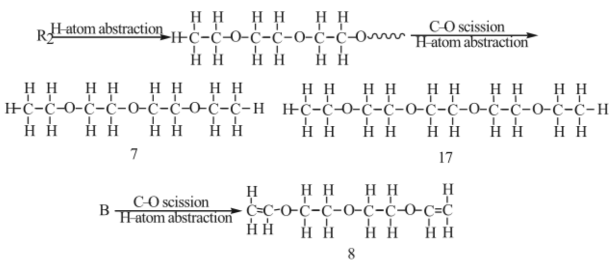
R_7 radical was formed through a C–O scission of the R_6 and R_3 recombination product. The formation

Table 3 Principal products released from pyrolysis of pure PEG and PEG with 10% C_{60}

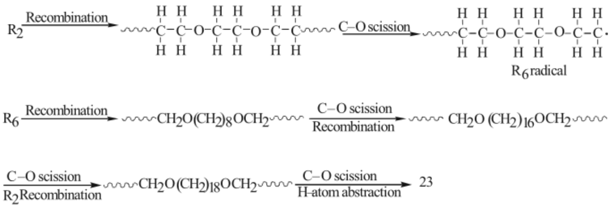
Compounds	Peak number	t_R/min	Concentration/%	
			PEG	PEG/10% C_{60}
Styrene	1	6.32	0.10	0.00
2-(2-methoxyethoxy)-ethanol	2	7.95	0.12	0.22
Benzaldehyde	3	8.60	0.05	0.04
2,2'-oxyethanol	4	9.38	0.00	0.30
2-(2-ethoxyethoxy)-ethanol	5	10.30	0.42	0.54
2-[2-(ethenyloxy)ethoxy]-ethanol	6	10.70	0.14	0.24
1,1'-oxybis[2-ethoxy]-ethane	7	13.21	0.23	0.19
1,1'-[oxybis(2,1-ethanediyloxy)]bis-ethene	8	13.51	0.66	0.06
2-[2-(2-methoxyethoxy)ethoxy]-ethanol	9	17.91	0.29	0.46
Mequinol	10	18.42	0.11	0.53
2,5,8,11,14-Pentaoxapentadecane	11	18.50	0.24	0.23
2-[2-(2-ethoxyethoxy)ethoxy]-ethanol	12	20.16	0.66	1.13
Tetraethyleneglycol monomethylether	13	20.76	2.11	0.00
12-Crown-4	14	26.81	1.05	1.82
2,5,8,11,14-Pentaoxahexadecan-16-ol	15	27.00	0.69	3.76
Hexaethylene glycol dimethyl ether	16	27.34	2.10	2.91
Tetraethylene glycol diethyl ether	17	30.86	0.83	0.69
1,1'-(1,3-propanediyl)bis-benzene	18	31.24	0.17	0.00
Hexanedioic acid, bis(2-methylpropyl)ester	19	32.30	0.02	0.04
15-Crown-5	20	35.59	2.83	1.39
Pentaethylene glycol	21	36.59	0.04	1.37
18-Crown-6	22	37.48	2.70	3.90
Octadecane	23	48.39	0.11	0.00
Tetracosane	24	52.53	0.15	0.00
Heptaethylene glycol	25	53.41	0.00	1.89
Heptaethylene glycol monododecyl ether	26	54.09	1.27	6.21
Heptacosane	27	54.42	0.68	0.00
Nonacosane	28	54.54	0.00	0.17
Hexacosane	29	55.85	0.00	0.38
Triacontane	30	62.09	0.30	0.00



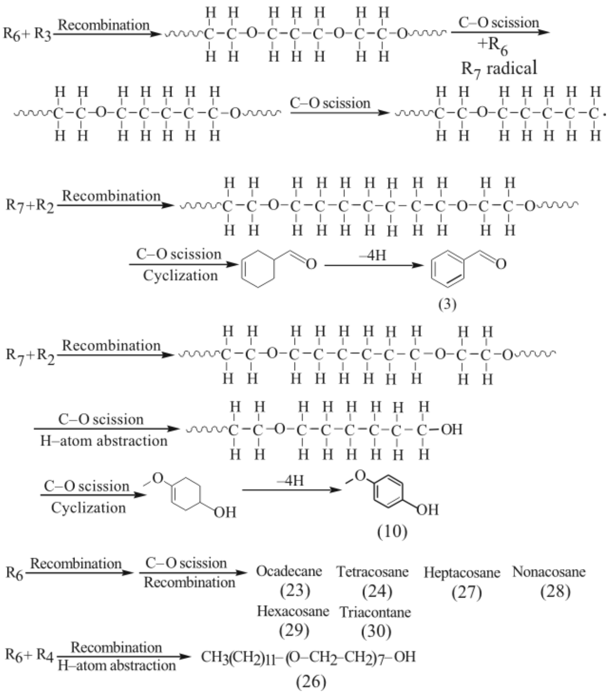
Scheme 2



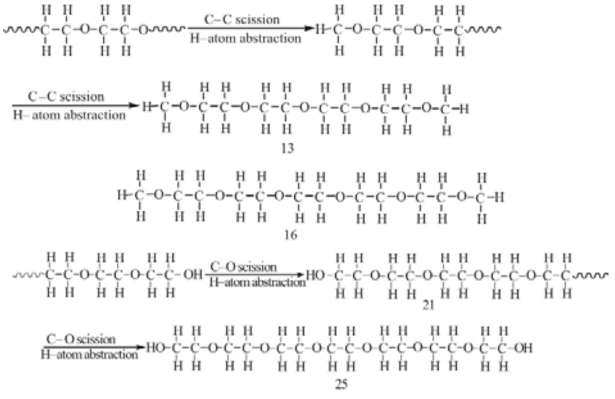
Scheme 3



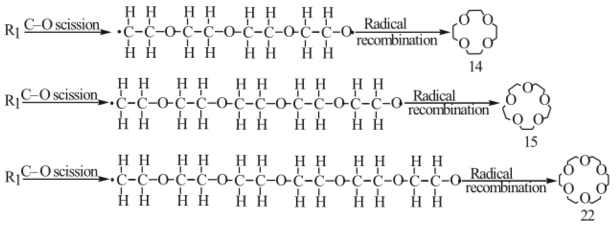
Scheme 4



Scheme 5



Scheme 6



Scheme 7

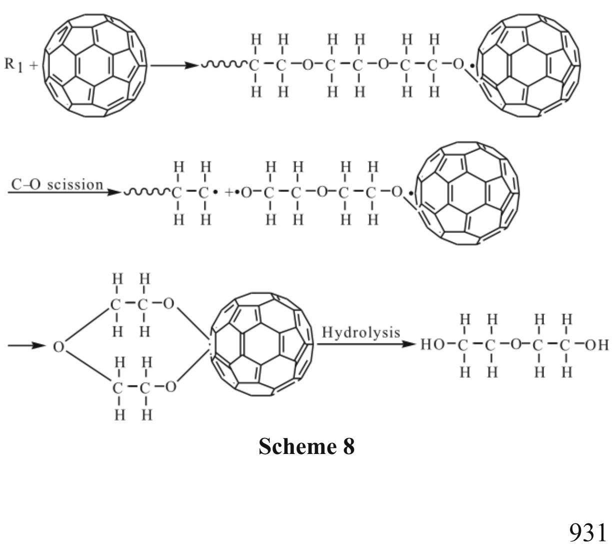
of phenyl ring compounds 3 and 10 was shown in Scheme 5. The long-chain alkanes compounds 23, 24, 26, 27, 28, 29, 30 were formed through a series of different C–O scission and radical recombination reactions of R_6 radical.

The formation process of compounds 13, 16, 21 and 25 were shown in Scheme 6. The dimethyl and dihydroxyl end group products were also reported by Lattimer [20].

The formation of crown esters was shown in Scheme 7. Three crown esters were produced during pyrolysis of pure PEG and PEG with 10% C_{60}.

Figure 1 and Table 3 revealed that with the addition of 10% C_{60}, the kinds of pyrolysis products were not so different to that of pure PEG, but the yields were highly different. With the addition of 10% C_{60}, the yields of monohydroxyl and dihydroxyl end groups oligomers were obviously increased. The fact that oligomers with monohydroxyl and dihydroxyl end groups appeared in high abundance was obviously consistent with the conclusion that C–O homolysis dominates over C–C homolysis in this pyrolysis circumstance. This suggested that the addition of fullerenes increased the probabilities of C–O homolysis and promoted the formation of the oligomers with monohydroxyl and dihydroxyl end groups. Also hydrolysis reaction was one of the significant origins to form hydroxyl group products, and the effect of fullerenes on hydrolysis of aldehyde terminal products was another origin to form hydroxyl group products. The off-line analysis of the pyrolysis products was another reason for the formation of hydroxyl group products.

Scharff *et al.* [21] and Hamwi *et al.* [22] reported that the fullerene could react with oxygen and hydroxyl group to form oxidized fullerene derivatives. The approximate double bond structure in



Scheme 8

fullerenes C_{60} and C_{70} molecules could possibly react with the oxygen radical in R_1, R_4 or R_5, also the hydroxyl end group compounds could react with fullerenes through double bond to give the cyclic ether compounds like complex (c). The cyclic ether compounds can further hydrolysis to hydroxyl group products resulted in the high abundance of hydroxyl end group compounds with the addition of 10% C_{60}.

Conclusions

This paper indicated that the effects of fullerenes on thermal behaviors of PEG were quite significant. The existence of fullerenes were obviously restrained the initial decomposition temperature and the maximum decomposition peak temperature of PEG. The pyrolysis products with one or two hydroxyl end groups evidently increased with the addition of 10% C_{60}. This was possibly because of hydrolysis reaction of aldehyde terminal products to form hydroxyl group products, and the addition of fullerenes increased the probability of aldehyde products hydrolyzed to hydroxyl products, also the off-line analysis of the pyrolysis products was another reason for the formation of hydroxyl group products.

Acknowledgements

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Nomenclature

PEG	poly(ethylene glycol)
TG-DTG	thermogravimetry-differential thermogravimetry
DSC	differential scanning calorimeter
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
IDT	initial decomposition temperatures
MDT	maximum decomposition peak temperatures
CB	carbon black
FS	fullerene soot
EFS	extracted fullerene soot

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