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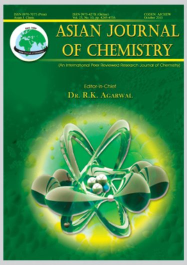

Thermal-Oxidative Stability of Polydimethylsiloxane

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Poly(ferrocenyldimethylsilane) (PFMS) and poly(ferrocenyldiphenylsilane) (PFPS) are employed as additives to enhance the thermal-oxidative stability of PDMS. The thermal-oxidative stability of PDMS, PDMS/PFMS and PDMS/PFPS compounds are characterized as chemical structure (structure of the substituent and the main chain), molecular size (molecular weight and its distribution) and material properties (shear viscosity, gel time and weight loss). The thermal-oxidative stabilities of PDMS/PFMS and PDMS/PFPS compounds at 300 ºC in air are obviously enhanced because PFMS and PFPS restrain the thermal-oxidative degradation of the methyl group and reduce the depolymerization of the main chain. The reduction of the depolymerization of the main chain is a result of the decrease in hydroxyl group formed by oxidation of methyl group. PFPS shows better antioxidation to PDMS than PFMS.

Key Words: Ploy(ferrocenylsilane), Polydimethylsiloxane, Thermal-oxidative stability, Additives.

INTRODUCTION

Since the discovery in the early years of the 20th century, polydimethylsiloxane (PDMS) has been extensively applied in many fields. To date, PDMS is still one of the polymers which have the best thermal-oxidative stability. However, with the rapidly increased demands of industrial developments, it is found that PDMS become inacceptable for many applications in high temperature environment[1]. To enhance the high-temperature stability, bulky groups has been introduced in polysiloxanes to improve the thermal-oxidative stability[2-9]. However, in fact, the industrial applications of these polymers are always restricted by their complicated synthesis processes. Besides designing novel materials, the heat-resistant additive is another candidate that can be employed to improve the thermal-oxidative stability of PDMS, which has attracted many interests because of both the high efficiency and the simple technical process.

Many kinds of heat-resistant additives have already been synthesized and investigated during the past few decades[10-12]. It is found that metal oxides, such as ferric oxide (Fe_2O_3), can obviously improve the thermal-oxidative stability of PDMS by restraining the thermal-oxidative degradation of side groups[13-15]. However, the dispersion of inorganic metal oxides in PDMS is always far from uniform. Therefore, a poor compatibility of inorganic metal oxides with PDMS is also found. Ferrocene and its derivatives are another kind of heat-resistant additives besides metal oxides. Different from inorganic metal oxides, ferrocene and its derivatives have excellent compatibility with the polysiloxane matrix. The thermal-oxidative stability of polysiloxanes is efficiently improved with just a little addition of this kind of heat-resistant additives[16-19]. However, most of these heat-resistant additives reported are of low molecular weight. The high volatility of these low-molecular weight additives shows large impact on the effectiveness in restraining thermal-oxidative degradation[20] and obviously restricts their applications as heat-resistant additives. Poly(ferrocenylsilane) has excellent thermal stability, fine compatibility with PDMS and low volatility and can be used as additive for PDMS.

Here in this paper, two facile synthesized polymers, poly(ferrocenyldimethylsilane) (PFMS) and poly(ferrocenyldiphenylsilane) (PFPS), are employed as heat-resistant additives for PDMS. (The chemical structures of PDMS, PFMS, PFPS and ferrocene have been displayed in Fig. 2a, respectively). The thermal-oxidative stability of PDMS, PDMS/PFMS and PDMS/PFPS compounds are studied in three aspects: molecular structure (structures of the side group and the main chain), molecular size (molecular weight and its distribution) and material properties (shear viscosity, the gel time and weight loss).

EXPERIMENTAL

Ferrocene and *n*-butyllithium (1.6 mol/L in *n*-hexane) are purchased from Acros and used as received. Tetrahydrofuran (THF), *n*-hexane and toluene are dried by refluxing over sodium. Diphenyldichlorosilane (Ph_2SiCl_2), dimethyldichlorosilane (Me_2SiCl_2), tetramethylethylenediamine (TMEDA) and trimethylsilyl terminated polydimethylsiloxane are purchased from Beijing Chemical Reagent Company. Ph_2SiCl_2 and Me_2SiCl_2 are purified with a fractional distillation process before use.

^{29}Si and ^{1}H NMR are recorded on Bruker DMX-300 spectrometer at 300 MHz. Tetramethylsilane is used as an external reference. Solid-state ^{29}Si cross-polarization/magic-angle spinning (CP/MAS) nuclear magnetic resonance is recorded at 79.3 MHz at room temperature, on a Bruker Avance III 400 spectrometer (Bruker instruments, Switzerland). The recycle delay time and the contact time is 3 s and 5 ms, respectively. The excitation pulse is $\Pi/10$ and the probe head is 4 mm.

The molecular weight and molecular weight distribution are determined by gel permeation chromatography (GPC, Waters 515 HPLC) at room temperature. The eluent is toluene and the flow rate is 1 mL/min. The molecular weights and molecular weight distribution is calculated against polystyrene standards. The shear viscosities are recorded at 25 ºC with a Wells-Brookfield cone and plate micro viscometer (programmable DV-II+ viscometer, Brookfield Engineering Laboratories, Stoughton, MA). Shear rate is adjusted by utilizing the spindle (CPE-51: 1-768s1) in the viscometer depending on the required torque. Thermogravimetric analysis (TGA) measurement is carried out with a thermogravimetric analyzer (Perkin-Elmer, Pyris 1 TGA, Boston, MA) in air. The heating rate is 10 ºC/min and the flow rate is 30 mL/min. The weight of each sample is about 5 mg and heating range is 50-800 ºC. The isothermal gravity analysis (IGA) is conducted as follows: 3 mL PDMS is poured into a glass dish and places in an air-circulation oven maintained at 300 ºC. The weigh change and gelling time are determined.

Synthesis

1,1'-Dilithioferrocene-tmeda is prepared according to the literature[21]

Synthesis of poly(ferrocenyldimethylsilane)[22]: The slow addition of dimethyldichlorosilane (5 g, 0.027 mol) in 10 mL THF to a refluxing THF solution of 1,1'-dilithioferrocene-tmeda (0.03 mol) is followed by reflux for 5 h. Trimethylchlorosilane (0.54 g, 0.005 mol) is then added at room temperature and the reaction mixture is stirred for 0.5 h. After removing THF and trimethylchlorosilane under vacuum, the residue is extracted with 50 mL toluene and the extracts are filtered. Then, the extracts is precipitated by addition of *n*-hexane to yield the product to give 0.76 g of the polymer; M_w (GPC) 3.6 kDa, $M_w/M_n = 1.47$. The NMR datas of the sample are in total accordance with published data. ^{1}H NMR (ppm, C_6D_6): 0-0.56 (SiMe), 4.02 (C_5H_5), 4.09-4.26 (C_5H_4). ^{29}Si NMR (ppm): -6.89.

Synthesis of poly(ferrocenyldiphenylsilane)[22]: The slow addition of diphenyldichlorosilane (9.3 g, 0.036 mol) in 10 mL THF to a refluxing THF solution of 1,1'-dilithioferrocene-tmeda (0.038 mol) is followed by reflux for 5 h. Trimethylchlorosilane (0.54 g, 0.005 mol) is then added at room temperature and the reaction mixture is stirred for 0.5 h. After removing THF and trimethylchlorosilane under vacuum, the residue is extracted with 100 mL toluene and the extracts are filtered. Then, the extracts is precipitated by addition of *n*-hexane to yield the product to give 1.3 g of the polymer; M_w (GPC) 4.2 kDa, $M_w/M_n = 1.56$. ^{1}H NMR (ppm, C_6D_6): 4.01 (C_5H_5), 4.08-4.36 (C_5H_4), 7.18-7.66 (C_6H_5). ^{29}Si NMR (ppm): -12.5.

Preparation of PDMS/PFMS and PDMS/PFPS compounds: A 0.05 wt % addition of PFMS or PFPS is added to PDMS at 110 ºC and then stirred for about 1 h.

RESULTS AND DISCUSSION

The high environmental temperature will bring two destructive processes to PDMS: (i) the thermal-oxidative degradation of the side group and (ii) the depolymerization of the main chain (the two processes have been displayed in Fig. 1, respectively). The previous destructive process is the results of reactions of hydrocarbon groups which are bonded to the silicon. This process is accompanied by profound changes in the molecular structure of PDMS. The methyl group is oxidized to hydroxyl group at first and then polycondensation between hydroxyl groups results in long molecular chain, branched structure and cross-linked structure. The latter destructive process is caused by the reactions of siloxane bonds and produces low-molecular weight, usually cyclic, polysiloxanes. These low-molecular weight polysiloxanes are easy to volatize and the volatilization brings the weight loss of PDMS. These destructive processes in PDMS usually result in the changes of molecular weight and shear viscosity.

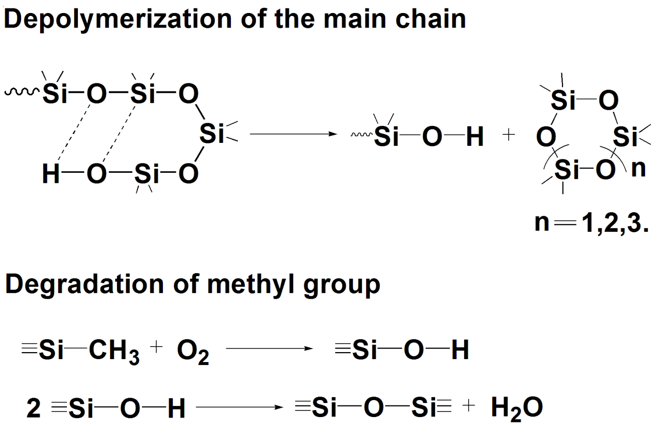


Fig. 1. Main chain depolymerization and side methyl group thermal-oxidative degradation

Thermogravimetric analysis of poly(ferrocenyldimethylsilane) and poly(ferrocenyldiphenylsilane): As displayed in Fig. 2b, an obvious decrease in weight on the weight loss curve of ferrocene has been observed from 100-170 ºC. The temperature of sublimation of ferrocene is 100 ºC and the sharp decrease in the weight of ferrocene is induced by the sublimation. Otherwise, PFMS and PFPS start to lose weight at a temperature beyond 300 ºC. These results suggest that PFMS and PFPS have lower volatility than ferrocene.

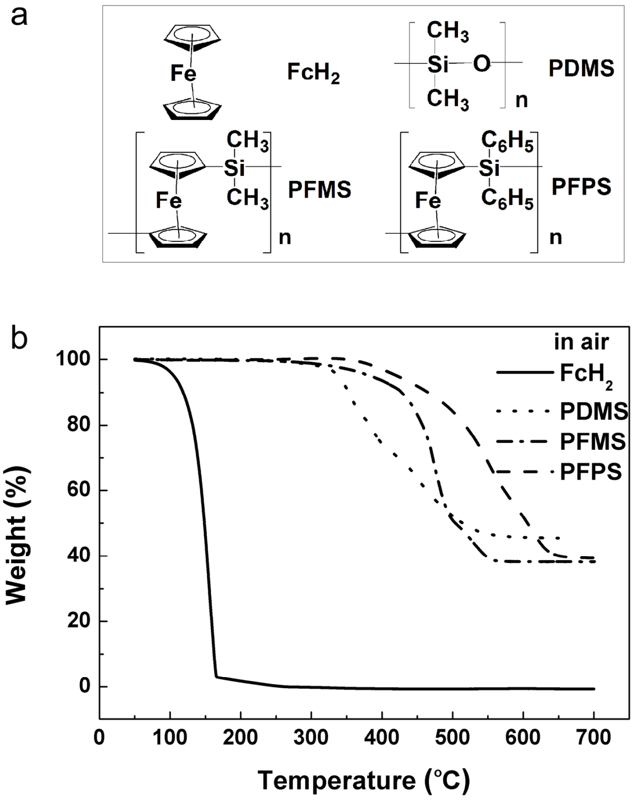


Fig. 2. Structure and TGA curves of ferrocene (FcH_2), PDMS, PFMS and PFPS in air

A well heat-resistant additive should have better thermal stability than the matrix. It is found that the initial loss temperature of PFMS and PFPS are higher than that of PDMS. It indicates that PFMS and PFPS show better thermal stability than PDMS.

Evaluation of molecular structure: The small polarity of the C-H bond causes a high reactiveness when radicals are present. The structure of the substituent of PDMS changes in an environment containing high temperature and oxygen in which radicals are formed. The methyl group is oxidized to hydroxyl group and then polycondensation between hydroxyl groups induces branched and cross-linked structure in PDMS. These changes of the structures are displayed in Fig. 3.

From Fig. 3b, it is found that in PDMS, new peaks at chemical shift 8.9, 12.5, 56.8 and 67.4 ppm, respectively, are observed after ageing for 3 h at 300 ºC. When an end methyl group is oxidized to hydroxyl group, its chemical shift in ^{29}Si NMR is at 8.9 ppm or 12.5 ppm. If a side methyl group is oxidized to hydroxyl, a chemical shift at 56.8 ppm is observed. When a side hydroxyl group reacts with other hydroxyl group, the chemical shift corresponding to the product is at 67.4 ppm. Nearly no evident change of structure has been observed in the curves of PDMS/PFMS or PDMS/PFPS compounds after ageing for 3 h.

From Fig. 3c, it is found that in PDMS, the relative peak intensity of chemical shift at 56.8 and 67.4 ppm are enhanced greatly when the ageing time increased from 3 to 48 h. A new peak of chemical shift at 108.1 ppm, corresponding to silica, is found. In PDMS/PFMS compounds, the peaks of chemical shift at 8.9, 12.5, 56.8 and 67.4 ppm are found and they are similar to that of PDMS after ageing for 3 h. It indicates that the thermal-oxidative degradation of PDMS is restrained by PFMS. In addition, a new peak of chemical shift at 84.6 ppm is observed and its corresponding structure is that a silicon atom is attached by four O-Si bonds. No evident change of molecular structure is observed in PDMS/PFPS compounds.

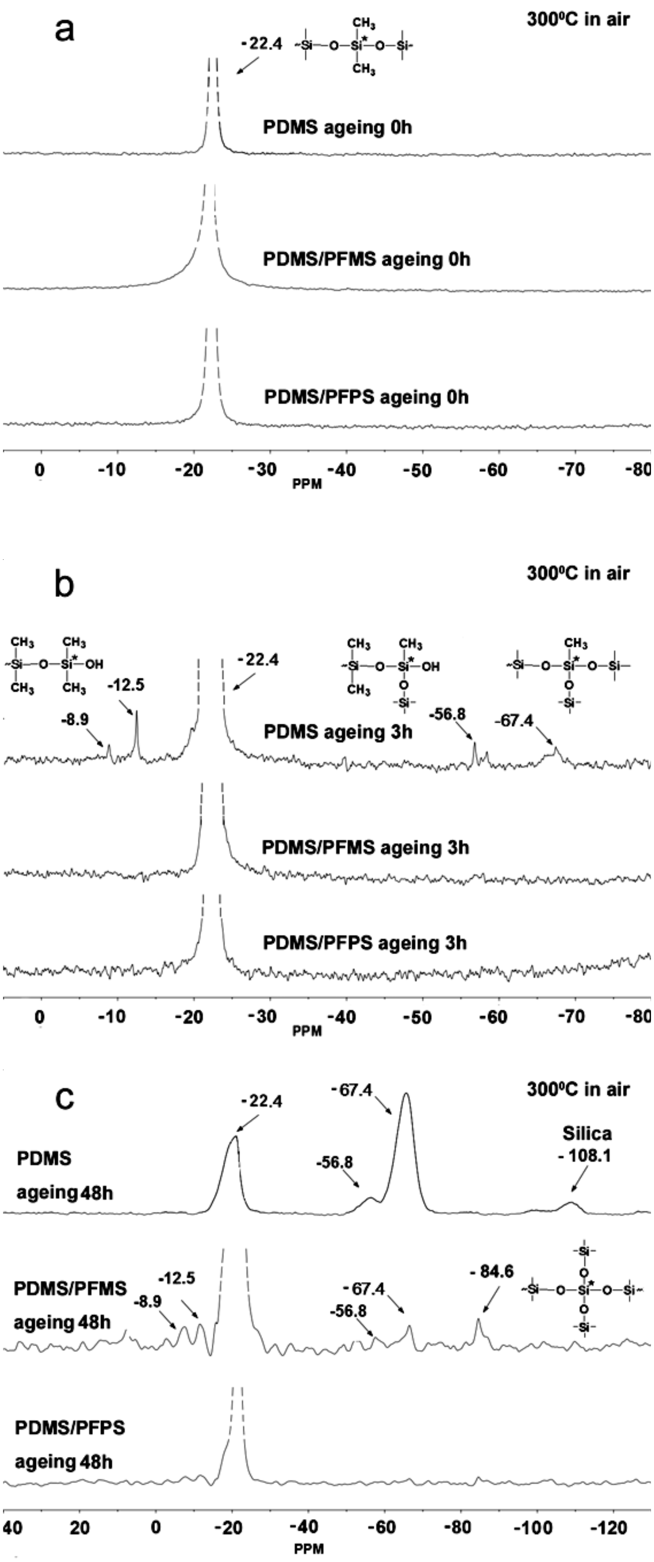
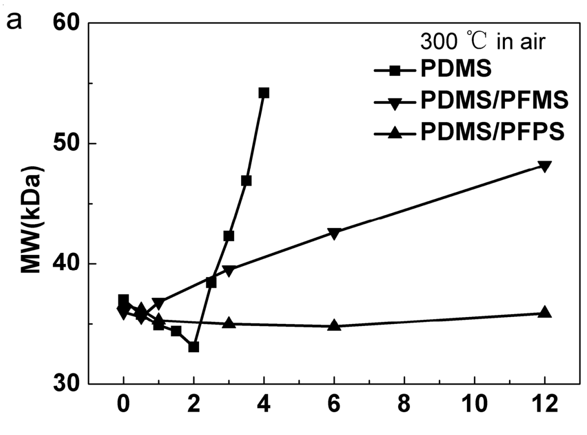


Fig. 3. ^{29}Si NMR spectrum of PDMS, PDMS/PFMS and PDMS/PFPS compounds after ageing for, (a) 0 h, (b) 3 h and (c) 48 h at 300 º in air

From the results above, it is obviously that PFMS and PFPS restrain the produce of hydroxyl group, branched structure and cross-linked structure. The antioxidation of ferrocene to PDMS has been investigated in previous literatures. To date, its mechanism of antioxidation in high temperature is still nknown. Usually, it is considered that the mechanism of antioxidation of ferrocene to PDMS is similar to that of Fe_2O_3. The thermal-oxidative degradation is a process of radical reaction. Ferrocenyl group quenches radical and produces carbocation which can not initiate the thermal-oxidative degradation of methyl group. Therefore, the thermal-oxidative degradation of methyl group is restrained. Phenyl group can also quench radical and restrain the thermal-oxidative degradation. PFPS with both ferrocenyl and phenyl group shows better antioxidation to PDMS than PFMS.

Evaluation of molecular weight and its distribution: The changes of molecular structure usually affect the molecular weight and its distribution. Ageing-time-dependent curves of molecular weight and molecular weight distribution of PDMS, PDMS/PFMS compounds and PDMS/PFPS compounds at 300 °C in air have been displayed in Fig. 4, respectively. From Fig. 4a, a sharp decrease in molecular weight is observed in the curve of PDMS. This decrease in molecular weight is mainly induced by the hydrolysis of the siloxane bonds. After reaching a minimum, the molecular weight of PDMS experiments a sharp increase. The increase of molecular weight is caused by thermal-oxidative degradation of methyl group and the formation of either a branched structure or cross-linked structure[23]. The molecular weight experiences a slight increase in PDMS/PFMS compounds and nearly no change is observed in PDMS/PFPS compounds. The thermal-oxidative degradation rate is determined by the slops of the curves. Following the minimum point, PDMS had the largest rate among the three materials. The thermal-oxidative degradation rate of PDMS/PFPS compounds is less than that of PDMS/PFMS compounds. It indicates that PFMS and PFPS show well antioxidation to PDMS and the effectiveness of PFPS is better that of PFMS.

As shown in Fig. 4b, rapid increase in the molecular weight distribution of PDMS is found. The molecular weight distribution increases slowly in PDMS/PFMS compounds and nearly no change is observed in PDMS/PFPS compounds.



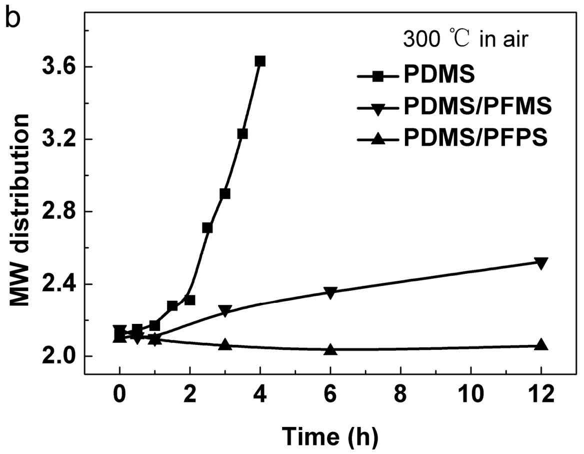


Fig 4. Ageing-time-dependent curves of PDMS, PDMS/PFMS and PDMS/PFPS compounds. (a) molecular weight (weight-average) *versus* the ageing time at 300 °C in air, (b) molecular weight distribution *versus* the ageing time 300 °C in air

Evaluation of shear viscosity and gel time: The shear viscosity, in the majority of cases, changes with the variation of molecular weight and its distribution. Fig. 5 shows the relationship between the shear viscosity of the three materials and the ageing time. The changes of the shear viscosity of the three materials are similar to those of the molecular weight which has been displayed in Fig. 4a. In PDMS, one first observes a very sharp decrease in the shear viscosity and the shear viscosity reaches the minimum 670 mPa s at 2 h. After reaching the minimum, the shear viscosity again increases largely and reaches 1770 mPa s after ageing for 4.5 h. The shear viscosity of PDMS/PFMS compounds increases slowly to 1340 mPa s after ageing for 12 h. A slight decrease in shear viscosity of PDMS/PFPS compounds is observed during 12 h. The small change of shear viscosity of PDMS/PFMS and PDMS/PFPS compounds is a result of a small change of molecular weight.

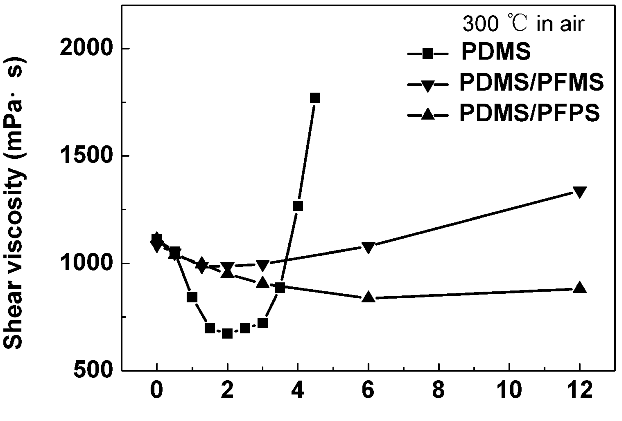


Fig. 5. Effects of ageing time on the shear viscosity. The ageing condition was 300 °C and air atmosphere

The gel time (G_T) is an important parameter to evaluate the antioxidation of PDMS. The G_T of PDMS is just 6.5 h at 300 °C in air. It increases to 48 h with the additive of PFMS. The PDMS/PFPS compounds have shown the best stability and the gel time increases to 312 h with a 0.05 wt % addition of PFPS.

Evaluation of weight loss: Besides the thermal-oxidative degradation of side methyl group of PDMS, the depolymerization of the main chain is the other important aspect that must be considered in the investigation of the thermal-oxidative stability of PDMS. The depolymerization of the main chain produces volatile cyclic siloxanes and induces the weight loss of PDMS. The weight loss of PDMS is evaluated by means of isothermal gravity analysis (IGA) and TGA and the results are shown in Fig. 6.

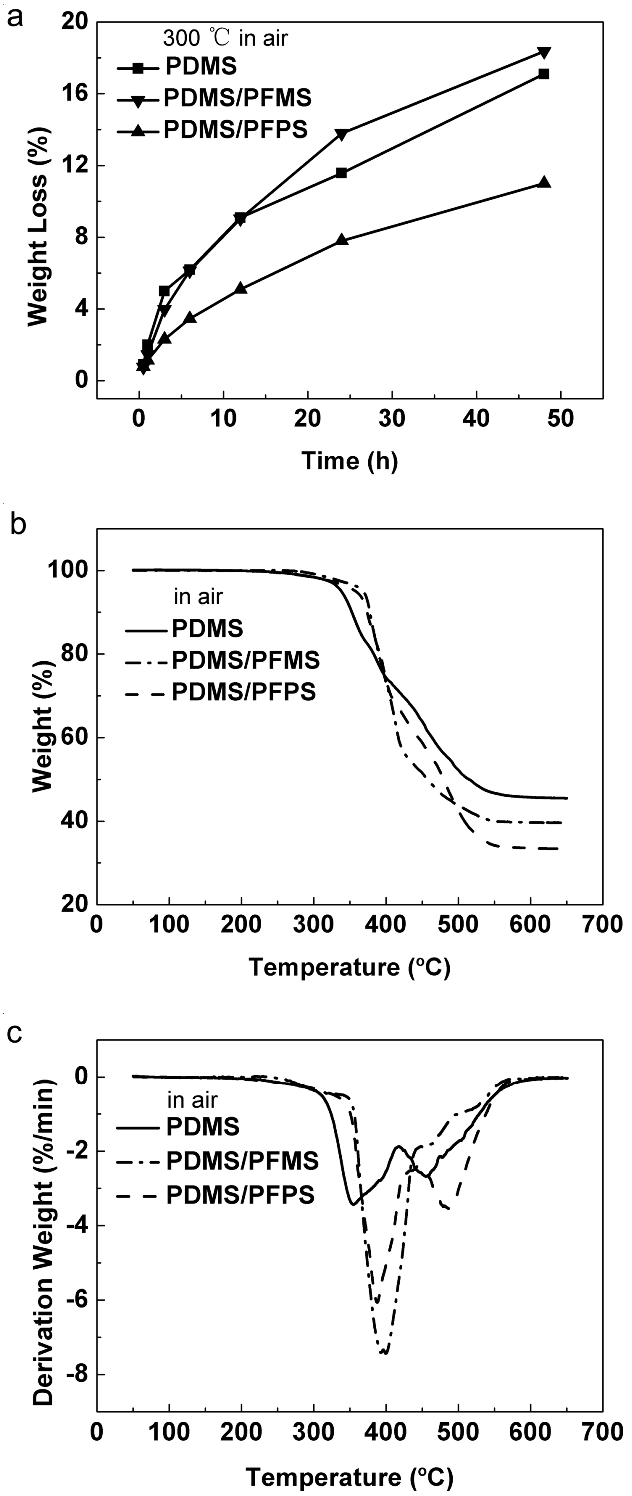


Fig. 6. Weight loss of PDMS, PDMS/PFMS and PDMS/PFPS compounds at 300 °C in air (a) is the IGA; (b) is the TGA and (c) is the DTG

The effects of the ageing time on weight loss of PDMS, PDMS/PFMS compounds and PDMS/PFPS compounds at 300 °C in air are displayed in Fig. 6a. The weight loss of PDMS/PFMS compounds is less than that of PDMS when the ageing time is less than 6 h. Polydimethylsiloxane/poly(ferrocenyldiphenylsilane) compounds show the least weight loss among these three materials during 48 h. The important reason for weight loss of PDMS at high temperature in nitrogen is that the residue Si-OH or the adsorption water in PDMS results in the depolymerization of the main chain by producing low-molecular weight cyclosiloxanes[9]. In air, the hydroxyl group which is formed by the oxidation of methyl group at high temperature also results in the depolymerization of the main chain. When PFMS or PFPS is added, the thermal-oxidative degradation of methyl group is restrained and the number of the hydroxyl group formed by the thermal-oxidative degradation is reduced. This can be proved from the ^{29}Si NMR curves by Fig. 3. Therefore, the depolymerization of the main chain and weight loss of PDMS decrease. Polydimethylsiloxane/poly(ferrocenyldiphenylsilane) compounds show better antioxidation and produce less weight loss at 300 °C in air than PDMS/PFMS compounds.

When the ageing time is more than 6 h, the weight loss of PDMS is less than that of PDMS/PFMS compounds. It is because that PDMS gels after ageing for 6 h. The cross-linked structure suppresses the depolymerization of the main chain and reduces the volatilization of the cyclic low-molecular weight siloxanes.

The thermogravimetric curves and the derivative thermogravimetric analysis (DTG) curves are shown in the Fig. 6b-c, respectively. The initial weight loss temperature and maximum weight loss temperature of PDMS/PFMS and PDMS/PFPS compounds are higher than that of PDMS. It indicates that depolymerization of main chain of PDMS is reduced by adding PFMS or PFPS. The residue of PDMS/PFMS or PDMS/PFPS compounds is less than that of PDMS and its main composition is silica. Polydimethylsiloxane is oxidized more easily and results in more silica which can not volatilize. The best antioxidation of PDMS/PFPS compounds results in the least residue among the three materials.

From results of weight loss above, it is found that the thermal weight loss of PDMS/PFMS and PDMS/PFPS decrease compared with that of PDMS, because PFMS and PFPS enhance the antioxidation of PDMS and reduce the depolymerization of the main chain caused by the hydroxyl group.

Conclusion

Poly(ferrocenyldimethylsilane) and poly(ferrocenyldiphenylsilane) are employed as heat-resistant additives for PDMS. Poly(ferrocenyldimethylsilane) and poly(ferrocenyldiphenylsilane) efficiently restrain the thermal-oxidative degradation of methyl group and reduce the depolymerization of the main chain of PDMS. The decrease in the depolymerization of the main chain is a result of the reduction of hydroxyl group formed by the oxidation of methyl group. Polydimethylsiloxane/poly(ferrocenyldiphenylsilane) compounds show better thermal-oxidative stability than PDMS/PFMS compounds.

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