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Preparation and Properties of Silicon-containing Arylacetylene Resins with Octa(maleimidophenyl)silsesquioxane

Yan Zhou[a], Fuwei Huang[b], *Farong Huang[c], Lei Du[d]

Key Laboratory of Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P R China

[a]zhouyan02@ecust.edu.cn, [b]fweihuang@163.com, *[c]fhuanglab@ecust.edu.cn, [d]leidu@ecust.edu.cn

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Abstract. Modified silicon-containing arylacetylene resins (DMSEPE-OMPS) were prepared from poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE) and Octa(maleimidophenyl)-silsesquioxane (OMPS). The curing reaction of DMSEPE-OMPS resin was studied by FT-IR and DSC techniques. Thermal stability and dielectric properties of cured DMSEPE-OMPS resins were determined. FT-IR and DSC analyses indicate that thermal polymerization of DMSEPE-OMPS resin occurs in the curing process. Thermal stabilities of cured DMSEPE-OMPS resins under N_2 and air atmosphere decrease gradually with the increment of OMPS components. The incorporation of OMPS can obviously reduce dielectric constant of DMSEPE-OMPS resins.

Introduction

In recent years, silicon-containing arylacetylene resins have been developed by Itoh, Buvat, and Huang, et al[1-7]. The silicon-containing arylacetylene resins exhibit good processability, outstanding thermal stability, high mechanical properties and excellent electrical properties.

Polyhedral oligomeric silsesquioxane (POSS) which has an inorganic Si-O-Si cage with eight reactive or non-reactive organic groups has been paid much attention to recently[8-10]. The incorporation of POSS into polymers has led to the enhancement in properties such as thermal and mechanical stability, flammability, oxidative resistance and dielectric property[11-14]. Octa(maleimidophenyl)silsesquioxane(OMPS) has been attracted increasing interest in scientific research and technological innovation. The synthesis of the copolymers of OMPS/N, N'-p-phenylenedimaleimide (OMPS/PPMI) and OMPS/urethane methacrylate (OMPS/UMA) was reported[15]. With the increasing of OMPS content, glass transition temperatures (T_g) and thermal stability of the resins increased, but dielectric constant decreased. The allylated novolac/4, 4'-bismaleimidodiphenylmethane (AN/BDM) resins modified with OMPS were studied and the results showed that the introduction of OMPS enhanced thermal stability[16].

In this work, modified silicon-containing arylacetylene resins (DMSEPE-OMPS) were prepared from poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE) and OMPS. The curing reaction and properties of the DMSEPE-OMPS resins were investigated by FT-IR, DSC, TGA and dielectric analyses.

Experimental

Materials

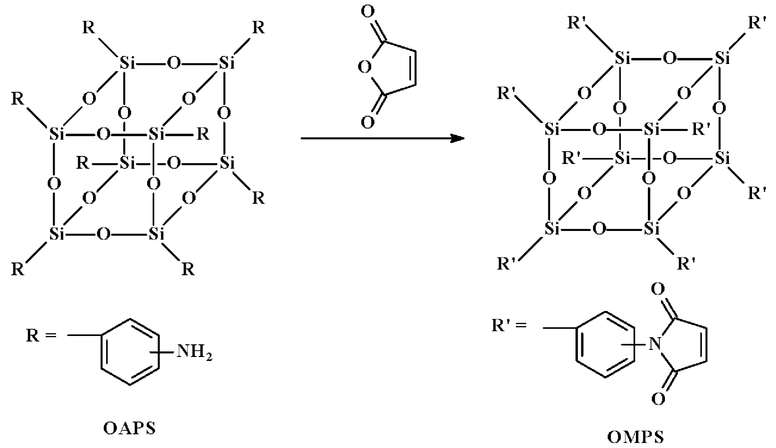
All reagents were purchased and used without further purification unless stated otherwise. Dimethyl formamide (DMF), maleic anhydride, triethyl amine, acetic anhydride, ethyl acetate, anhydrous magnesium sulfate, petroleum ether, and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd. DMSEPE and octa(aminophenyl)silsesquioxane (OAPS) were synthesized in our laboratory[5, 17, 18]. DMF was dried over 4Å molecular sieves before use. Triethyl amine was dried over 4Å molecular sieves and then purified by distillation from Na and benzophenone (as indicator) under nitrogen.

Measurements

FT-IR spectra were determined on a Thermo Nicolet 5700 spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. Differential scanning calorimeter (DSC) measurements were performed on a Netzsch 200 PC modulated system at a heating rate of 10 °C/min from ambient temperature to 350 °C under the nitrogen. Thermogravimetric analysis (TGA) was conducted on a METTLER TGA/SDTA 851 analyzer with a heating rate of 10 °C/min under N_2 and air atmosphere. Dielectric properties were carried out on a Concept 40 (Nococontrol, Ger.) in the range of measuring frequency from 10^1 to 10^6 Hz at room temperature.

Synthesis of octa(maleimidophenyl)silsesquioxane (OMPS)

In a 250 ml flask fitted with a magnetic stirrer, maleic anhydride (1.22 g, 12.5 mmol) dissolved in 5 ml of DMF was added dropwise to a solution of OAPS (1.5 g, 1.3 mmol) in 20 ml DMF. The mixture was continually stirred for 1 h at room temperature under a nitrogen atmosphere. Then triethyl amine (2.5 ml, 26 mmol) was added to the mixture, and subsequently acetic anhydride (3.8 ml, 26 mmol) was added in drops. The mixture was heated and refluxed at 70 °C for another 3 h. Finally, the organic product was extracted by ethyl acetate (90 ml), and the resulting solution was washed with deionized water. The separated organic layer was kept in anhydrous magnesium sulfate overnight. After filtering, the organic layer was precipitated in petroleum ether. The obtained solid (Yield: 70%) was filtered and dried in a vacuum oven at room temperature. ^{1}H-NMR (ppm, DMSO-d_6) δ: 7.1 (br, 2H, protons in C=C of maleimide groups), 7.2-7.8 (br, 4H, aromatic protons). FT-IR (cm^{-1}, v, KBr plate): 3105 (C-H), 1798 (asymmetrical C=O), 1719 (symmetrical C=O), 1381 (C-N), 1129 (Si-O-Si). Synthesis of OMPS is shown in Scheme 1.



Scheme 1. Synthesis of OMPS

Preparation of DMSEPE-OMPS resins

The solutions were obtained through dissolving DMSEPE and OMPS with different proportion in THF. Subsequently, solid DMSEPE-OMPS resins were gained by evaporating the solvent. The resins were cured according to the following procedure: 130 °C /0.5h+140 °C /0.5 h+150 °C /1 h+170 °C /2 h+210 °C /2 h+250 °C /4 h. The formulations of DMSEPE-OMPS resins are listed in Table 1.

Table 1 Formulations of DMSEPE-OMPS resins

Resin sample	OMPS（wt %）	DMSEPE（wt %）
a	5	95
b	10	90
c	15	85
d	20	80

Result and Discussion

The curing behavior of DMSEPE-OMPS resin

DSC curves of DMSEPE and DMSEPE-OMPS resin (Sample b) are shown in Fig. 1. The onset temperature (T_i), top temperature (T_p) and end temperature (T_f) of the curing exothermic peak for DMSEPE are 209 °C, 232 °C and 247 °C, respectively, with a total enthalpy of 467 J/g. DMSEPE-OMPS resin shows two exothermic peaks. T_i, T_p and T_f of the first peak are 145 °C, 173 °C and 191 °C, with an enthalpy of 51 J/g. T_i, T_p and T_f of the second one are 210 °C, 236 °C and 261 °C, with an enthalpy of 149 J/g. The curing mechanism of DMSEPE-OMPS resin is complicated. We deduce that the first peak possibly results from thermal polymerization of OMPS and DMSEPE and the second peak is attributed to the self-polymerization of DMSEPE.

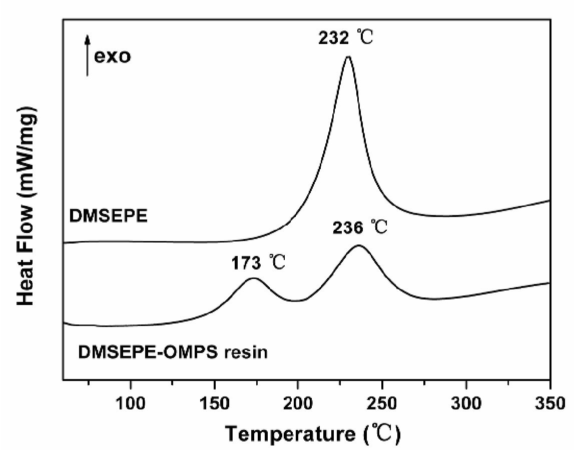


Fig. 1 DSC curves of DMSEPE and DMSEPE-OMPS resin (Sample b)

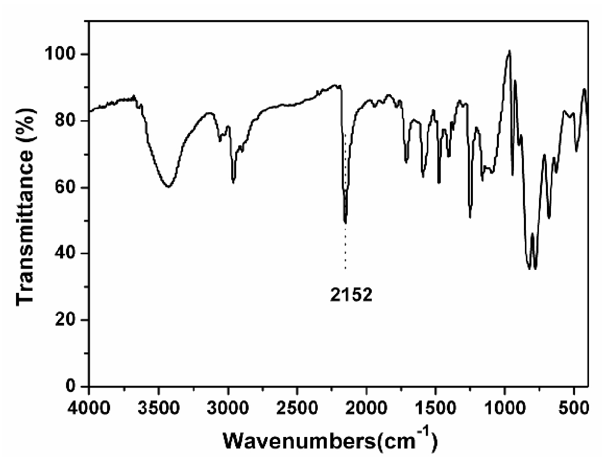
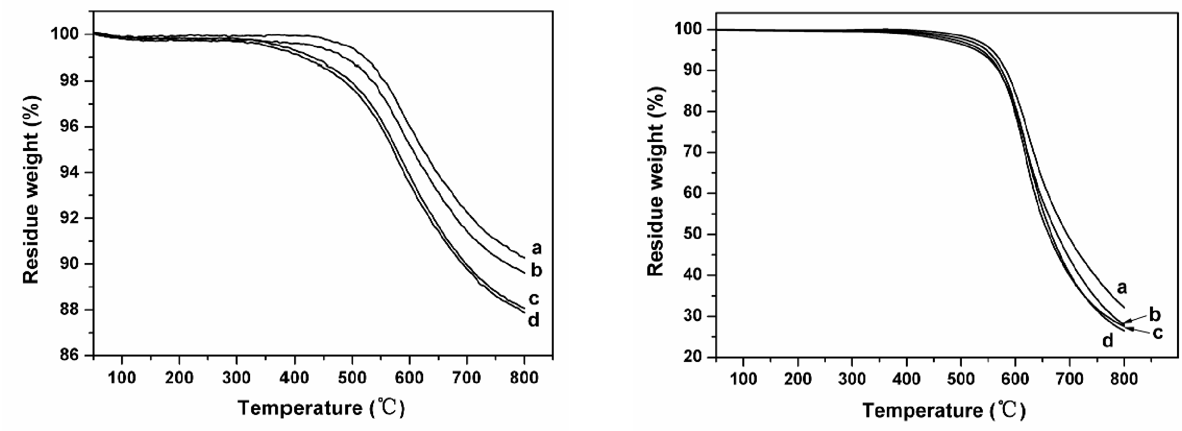


Fig. 2 FT-IR spectrum of cured DMSEPE -OMPS resin (Sample b)

Fig. 2 presents the FT-IR spectrum of cured DMSEPE-OMPS resin (Sample b). The absorption peaks of C=O (1719 cm^{-1}), C-N (1381 cm^{-1}) and Si-O-Si (1129 cm^{-1}) in OMPS are still present in the spectrum of cured DMSEPE-OMPS resin while ethynylene groups(C≡C, 2152 cm^{-1}) in DMSEPE also remain in the spectrum. But the absorption peak of ethynyl groups (≡C-H, 3296 cm^{-1}) in DMSEPE and that of ethenyl groups (=C-H, 3105 cm^{-1}) in OMPS disappear. These analyses indicate thermal polymerization of DMSEPE-OMPS resin occurs in the curing process.

Properties of cured DMSEPE-OMPS resins

Thermal stabilities of cured DMSEPE-OMPS resins (Sample a~d) under N_2 and air atmosphere were determined by TGA analysis. The results are shown in Fig. 3 and Table 2. As seen in the figure, the T_{d5} (temperature of 5% weight loss) and Y_c (char yield at 800 °C) of cured DMSEPE-OMPS resins decrease gradually with the increment of OMPS components both under N_2 and air atmosphere. The low thermal stability of imide rings in OMPS leads to the worse thermal stability of OMPS in comparison of DMSEPE. Thus, thermal stabilities of cured DMSEPE-OMPS resins under N_2 and air atmosphere both decrease with the increment of OMPS components. The oxidation of silicon to silica during thermal degradation can enhance Y_c of cured resins in air atmosphere[15]. Because of the lower silicon content in OMPS than that in DMSEPE, Y_c of cured DMSEPE-OMPS resins in air atmosphere reduces with the increase of OMPS components.

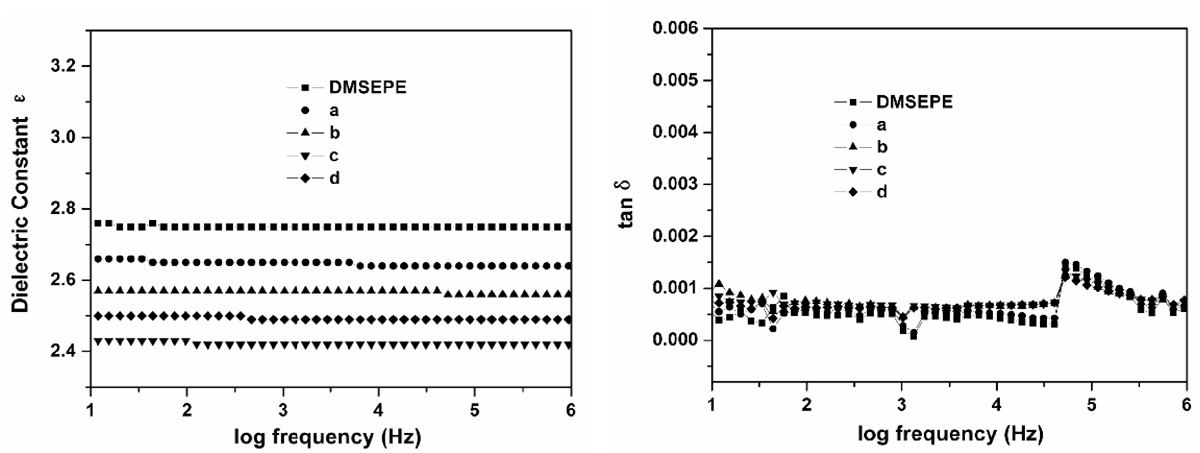


(1) N_2 (2) air

Fig. 3 TGA curves of cured DMSEPE-OMPS resins with different formulation

Table 2 TGA analysis results of cured DMSEPE-OMPS resins

Sample	N_2		Air	
	T_{d5}/ °C	Y_c/%	T_{d5}/°C	Y_c/%
a	623	90.2	557	32.1
b	606	89.6	547	28.0
c	578	88.1	537	27.6
d	571	87.9	528	26.5



(1) dielectric constant (2) dielectric loss

Fig. 4 Frequency dependences of dielectric properties of cured DMSEPE and cured DMSEPE-OMPS resins (Sample a~d)

The frequency dependences of dielectric properties of cured DMSEPE and cured DMSEPE-OMPS resins (Sample a~d) are shown in Fig. 4. Dielectric constants of the cured resins descend obviously with the increment of OMPS components while dielectric losses keep at the same level, which is attributed to Si-O-Si linkages and the nanoporosity in the core of the POSS molecules[15].

Conclusions

Modified silicon-containing arylacetylene resins (DMSEPE-OMPS) were prepared and investigated in this paper. FT-IR and DSC analyses indicate that thermal polymerization of DMSEPE-OMPS resin occurs in the curing process. Thermal stabilities of cured DMSEPE-OMPS resins under N_2 and air atmosphere decrease gradually with the increment of OMPS components. Dielectric constants of the cured resins descend obviously with the increment of OMPS components while dielectric losses keep at the same level.

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