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Fluorosilicone resins with perfluorocyclobutylaryloxyethane structure：synthesis, curing and properties

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Abstract: Fluorosilicone resins possess the advantages of both organic silicon materials and organic fluorine materials, and have attracted extensive attention from researchers. In this papepr, a series of fluorosilicone resins with the structure of perfluorocyclobutylaryloxyethane (PFCB) were designed and prepared. Different PFCB contents of fluorosilicone resins were prepared through hydrolysis condensation under acidic conditions by using perfluorocyclobutylaryloxyethane siloxane monomer as the raw material, methylphenyldimethoxysilane (MPMS) as the quantitative component, and phenyltrimethoxysilane (PTMS) as the co-condensate monomer. and the fluorosilicone resins with PFCB structure located in the main chain were obtained through thermal curing. The thermal stability, hydrophobicity, and dielectric properties of these resins were studied. The results show that the T_{10} of the fluorosilicone resins containing the PFCB structure is around 400 ^{o}C; as the content of PFCB groups increases, the water contact angle of the fluorosilicone resins increases from 88^{o} to 113^{o}; when the PFCB content is the maximum, the average dielectric constant within the frequency range of 1.5-30 MHz is 2.55.

Key words: fluorosilicone resin, perfluorocyclobutylaryloxyethane, curing, properties

1 Introduction

Organic silicon materials have a Si-O-Si framework structure. The silicon-oxygen

bonds have high bond energy and large bond angles, and the chain segments have good flexibility. Therefore, they have a lower glass transition temperature (*Tg*), excellent thermal oxidative stability, and good resistance to high and low temperatures[1]. In addition, organic silicon materials also have good low dielectric properties, weather resistance, hydrophobicity, and film-forming properties. Thus, they have broad application prospects in electronic packaging, heat-resistant coatings, protective materials, and aerospace fields [2-5]. Among them, organic silicon resins, as an important type of thermosetting polysiloxane materials, usually have excellent resistance to high and low temperatures and weather resistance, and are widely used in aerospace, electronic packaging, construction, and other fields. However, pure organic silicon resins have relatively weak intermolecular bond forces, and are prone to chain segment breakage and the formation of volatile small molecules at high temperatures, resulting in a decrease in structural stability. They also have the disadvantages of long curing time and poor adhesion. Therefore, modifying organic silicon resins to improve their performance has become an important approach.

Fluorinated materials possess unique molecular structural characteristics. Due to the high bond energy and low polarization rate of the C-F bond, fluorinated polymers usually exhibit excellent low dielectric constant, thermal stability, chemical stability, and photostability[6]. Therefore, fluorinated polymers have significant application value in waterproof coatings, dielectric insulation, functional materials, and other fields [7-9]. Introducing fluorine into organic silicon resins can provide materials with good hydrophobicity, oleophobicity, and anti-pollution properties while maintaining the flexibility, weather resistance, and processability of the silicon-oxygen chain segments[10], combining the advantages of both fluorine and silicon materials. Wu[11] used fluorinated polyphenyl bis-siloxane (F-PPSS) and urea-based MQ siloxane resin (U-MQ) in combination with functional fillers to prepare modified addition-type liquid silicone rubber (with a main chain of polysiloxane structure), which enhanced the electrical insulation cracking resistance and thermal stability of the silicone rubber. Wu[12] used a self-made siloxane resin containing trifluoropropyl MTQ as reinforcing filler to prepare high ultraviolet transmission addition-type liquid silicone rubber, which

improved the mechanical strength and ultraviolet transmission performance of the silicone rubber, and also slightly improved the thermal stability of the material. Ke[13] used cyclic hydrogen-fluorinated silicone oil and tetramethyltetraethenyl ring tetrasiloxane to form a bond through silicon-hydrogen addition, to prepare high ultraviolet transmission fluorosiloxane resin, which simultaneously optimized the light transmission, mechanical strength and hydrophobicity of the resin. Huang[14] used a trifluorovinyl ether (TFVE) fluorosilane monomer and methylalkoxy silane for copolymerization to prepare fluorosiloxane resin with a perfluorocyclobutane structure, significantly enhancing the thermal stability and hydrophobicity of the resin. Wang[15] used various alkoxysilanes and perfluoroalkyl triethoxysilane (FTEOS) to conduct hydrolysis and copolymerization to prepare fluorosilicon resins. These resins were then chemically grafted with polyesters to obtain fluorosilicon-modified polyester resins, significantly enhancing the heat resistance, hydrophobicity, oleophobicity, and anti-sticking properties of the polyester. Previous studies have shown that the fluorosilicon synergistic structure not only can significantly reduce the surface energy of the material, improve hydrophobicity and anti-pollution performance, but also can improve the thermal stability and structural stability of the material. However, current systematic research on specific structure fluorosilicon resins is still relatively limited. Therefore, developing functional units that simultaneously possess fluorine characteristics and structural rigidity and effectively introducing them into the siloxane network is an important direction for achieving high-performance fluorosilicon resins.

Perfluorocyclobutyl aryl ether (PFCB) polymers are a new type of semi-fluorine-containing polymers. The perfluorocyclobutyl structure is usually formed by the [2π+2π] ring addition reaction of trifluorovinyl aromatic ethers under the induction of heat. Its uniqueness lies in the simultaneous presence of PFCB groups and aromatic groups. In existing studies, it has been shown that introducing the PFCB structure into the polymer system can endow the material with a series of excellent properties. Not only does it possess the hydrophobicity and chemical stability typical of fluorine-containing materials, but also due to the stable tetra-ring structure and the presence of the pyridine group, the thermal stability of the material is enhanced[16-18]. Therefore,

introducing the PFCB structure into organosilicon resins is expected to show good potential. In this study, we used phenyl trimethoxysilane, methyl phenyl dimethoxysilane, and the prepared perfluorocyclobutyl aryl ether siloxane monomer as raw materials, and carried out a hydrolysis condensation reaction under acidic conditions to synthesize a fluorosilicon resin prepolymer with PFCB structure. Then, the fluorosilicon resin prepolymer was cured by the condensation curing method, and the structure and properties of the cured fluorosilicon resin were characterized and tested. The influence of different PFCB contents on the properties of the fluorosilicon resin was studied.

2 Experimental

2.1 Materials

The perfluorocyclobutylaryloxyalkoxysilane monomer was prepared according to the literature [19] . Phenyltrimethoxysilane and methylphenyldimethoxysilane were purchased from Tianjin Xishen Biochemical Technology Co., Ltd. Toluene and hydrochloric acid were purchased from Yantai Sanhe Chemical Reagent Co., Ltd.

2.2 Characterization and Measurements

The infrared spectrum of the sample was determined using an infrared spectrometer (IRAffinity). DSC was measured by Netzsch Instrument (DSC 200F3). TGA was measured by TG 209F1 instrument under nitrogen. The lap shear test (GB/T 7124-2008) was conducted on the UTM4103 electronic universal testing machine. Water contact angle was determined by contact angle measuring instrument (OCA 25). The transmittance was measured using an ultraviolet spectrophotometer (UV-1900i). The dielectric property was determined by a precise impedance analyzer (4294A).

2.3 Synthesis of fluorosilicone resin containing PFCB

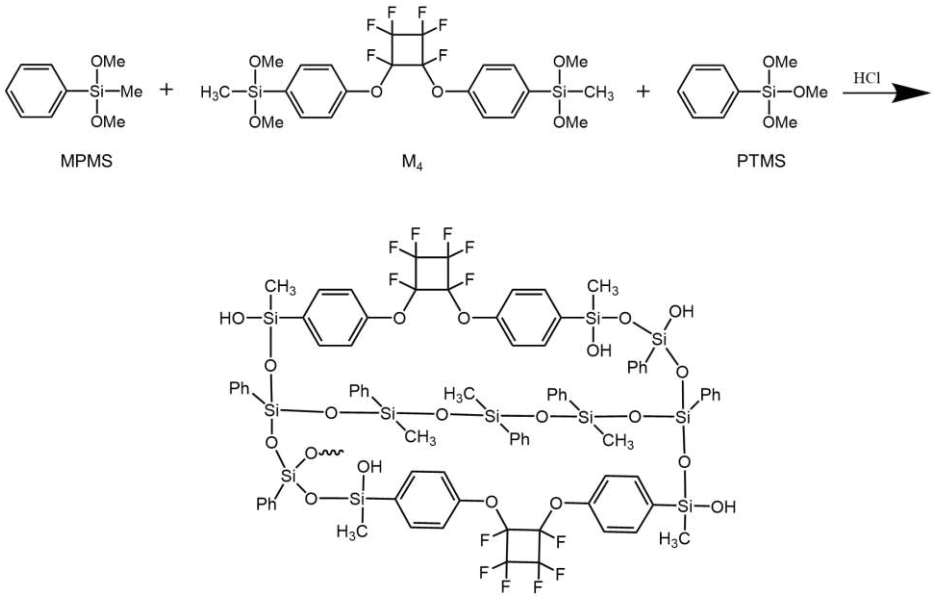


Figure 1 The synthesis of fluorinated silicone containing PFCB

The fluorosilicon resin with PFCB structure was synthesized by the hydrolysis condensation method. With MPMS as the quantitative standard, four fluorosilicon resins (FSRx) were synthesized by adjusting the molar ratio of M_4 to PTMS. The ratio of the organic group (R) to the silicon atom (Si) in these four resins was 3/2. Taking the synthesis process of FSR2 as an example for illustration: dilute hydrochloric acid solution was added to a three-necked flask to make the system react under acidic conditions (pH = 1). Then M4 (16 mmol, 8.91 g), MPMS (48 mmol, 8.75 g), PTMS (16 mmol, 3.17 g), and toluene (40 mL) were added to form a mixed system. the mixed system was dripped slowly into the three-necked flask by using a constant pressure dropwise funnel, and the system was kept to react at room temperature for 16 h. After the reaction, the mixed solution with toluene solution was washed with saturated sodium chloride solution until neutral. The solution was dried with anhydrous sodium sulfate for 12 hours, and was performed on the rotary evaporation to obtain the pre-polymer of silicon resin with the fluorinated cyclobutylaryloxy ether structure. The synthesis route is shown in Figure 1, and the composition and dosage of synthesis are shown in Table 1.

Table 1 The composition and dosage of fluorosilicone resin containing PFCB

Sample	MPMS（mmol）	M_4（mmol）	PTMS（mmol）	R/Si
FSR0	48	0	48	3/2
FSR1	48	8	32	3/2
FSR2	48	16	16	3/2
FSR3	48	24	0	3/2

2.4 Curing of fluorosilicone resin

The prepared fluorosilicone resin prepolymer was poured into a polytetrafluoroethylene mold and placed in an oven for gradual temperature increase and curing. The entire curing process: first, the temperature was set to 80 ºC for a duration of 4 hours; then, the temperature was set to 120 ºC for 4 hours; followed by setting the temperature to 150 ºC for 4 hours; finally, the temperature was set to 180 ºC for 2 hours and 200 ºC for 1 hour for complete curing. The curing mechanism of the fluorosilicone resin is shown in Figure 2.

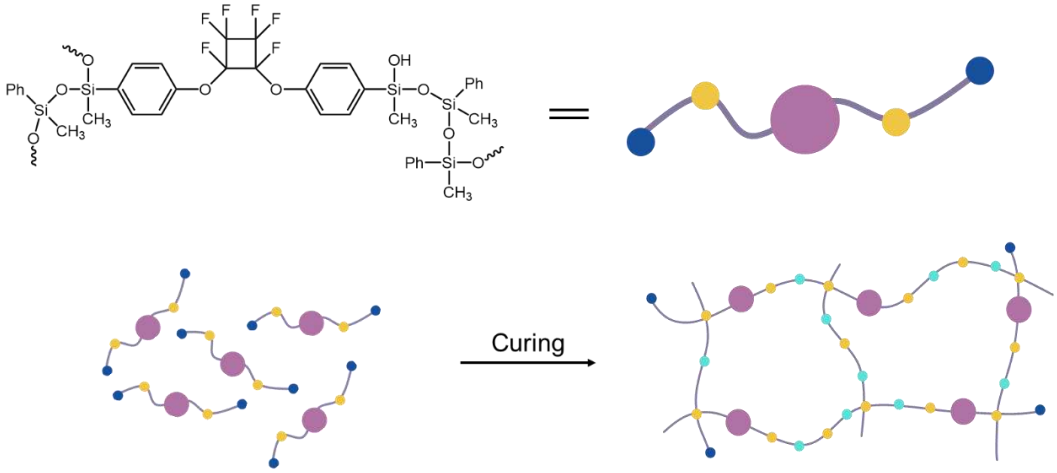


Figure 2 The curing mechanism of condensation type PFCB fluorosilicone resin

3. Results and Discussion

3.1 Fourier infrared spectroscopy analysis

The FTIR spectrum of the samples is shown in Figure 3. The peak at 1590 cm^{-1} is the stretching vibration peak of the aromatic ring skeleton (C=C), the characteristic peak at 1500 cm^{-1} belongs to the stretching vibration of Si-C in Si-Ar (aromatic group), the absorption peak at 1415 cm^{-1} is the asymmetric deformation vibration of -CH_3 in

Si-CH_3, the absorption peak at 1275 cm^{-1} is the symmetric vibration of the methyl group, and the absorption peaks at 1080~1030 cm^{-1} are the vibration absorption peaks of Si-O-Si, indicating the formation of the main chain structure of resin Si-O-Si. Except for sample FSR0, the other samples all show the characteristic peak of the perfluorocyclobutyl aromatic ether group at 960 cm^{-1}. The result indicates the successful introduction of the perfluorocyclobutyl aromatic ether silane monomer.

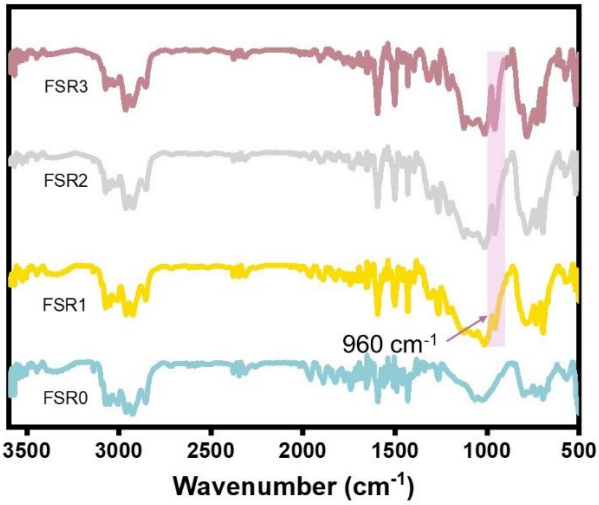


Figure 3 FTIR spectrum of condensation type PFCB fluorosilicone resin

3.2 Thermogravimetric analysis

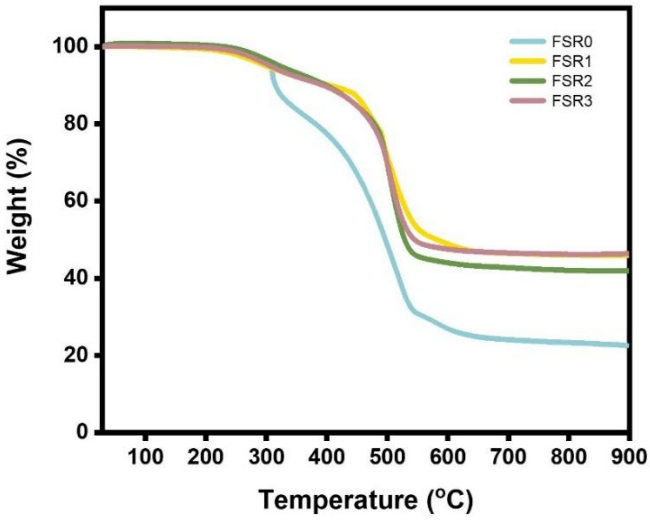


Figure 4 The TG curve of condensation type PFCB fluorosilicone resin

Due to the extremely high bond energy of the C-F bond in perfluorocyclobutyl,

which is higher than that of C-C and C-O bonds, and also both the perfluorocyclobutyl structure and the aromatic ring structure are rigid structures, they are difficult to be disrupted under high-temperature conditions. In order to verify the impact of introducing the PFCB structure into the silicone resin on the thermal stability of the silicone resin, performance tests were conducted on the fluorosilicone resin (Figure 4). The thermal performance data of the samples are shown in Table 2.

Table 2 The thermal properties of condensation type PFCB fluorosilicone resin

Sample	T_5[a] (°C)	T_{10}[a] (°C)
FSR0	306	313
FSR1	300	404
FSR2	323	399
FSR3	306	393

a: T_5, the 5% weight loss temperature; T_{10}, the 10% weight loss temperature

As can be seen from Table 2, the silicon resin T_{10} without the PFCB structure modification has the lowest value, indicating the poorest thermal stability. As the content of the PFCB structure increases, the modified resins T_5 and T_{10} generally show an increasing trend. Especially for FSR1, FSR2, and FSR3, the T_{10} values are around 400 °C. Due to the four-ringed structure of the PFCB having good rigidity and spatial stability, the introduction of PFCB into the silicon resin reduces the thermal vibration and rearrangement of the modified silicon resin molecular chains affected by high temperatures, thereby helping to improve the thermal stability and aging resistance of the material.

3.3 DSC analysis

The curing behavior of fluorosilicone resins was studied using a differential scanning calorimeter (Figure 5). As can be seen from the figure, after curing, all the silicone resins did not show any exothermic peaks within the temperature range of 50 °C to 300 °C. This indicates that the modified silicone resins have completely cured during the curing process, and the cured fluorosilicone resins remain chemically stable within this temperature range without undergoing secondary crystallization.

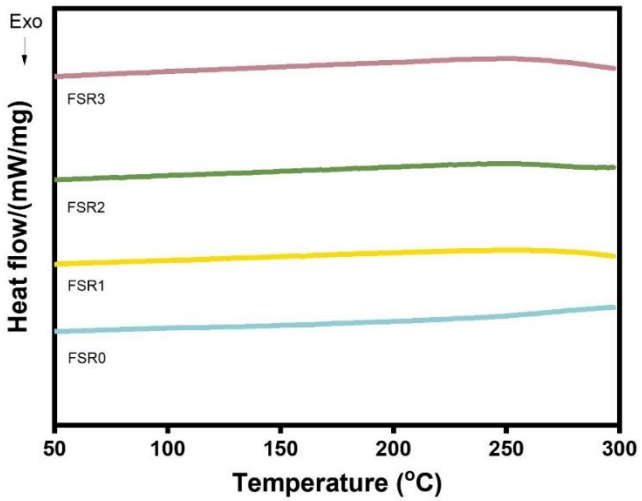


Figure 5 The DSC curve of condensation type PFCB fluorosilicone resin

3.4 Mechanical property analysis

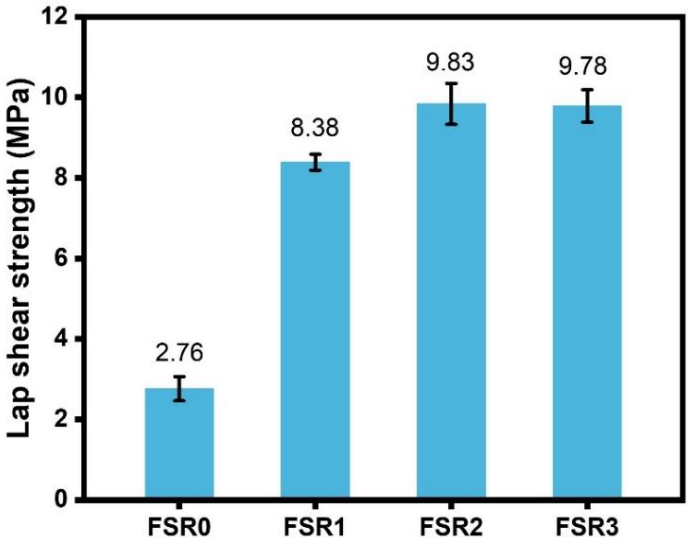


Figure 6 The bonding strength of condensation type PFCB fluorosilicone resin

The mechanical properties of fluorosilicone resins with different PFCB structures are shown in Figure 6. Compared with the silicone resin without PFCB structure, when PFCB structure is introduced, the lap shear strength of the modified silicone resin increases significantly. This is because the perfluorocyclobutyl framework and aromatic rings contained in the PFCB structure belong to rigid structures, which can significantly enhance the rigidity of the fluorosilicone resin molecular chains[20]. Moreover, due to the high electronegativity of the perfluorine structure, it can enhance the intermolecular interaction force and improve the material's cohesion, facilitating the

stress transfer at the bonding interface. Also, as PTMS is introduced as a tri-functional crosslinking monomer into the fluorosilicone resin to form a dense three-dimensional crosslinked network, it forms a synergistic effect with the rigidity enhancement of PFCB.

3.5 Contact angle analysis

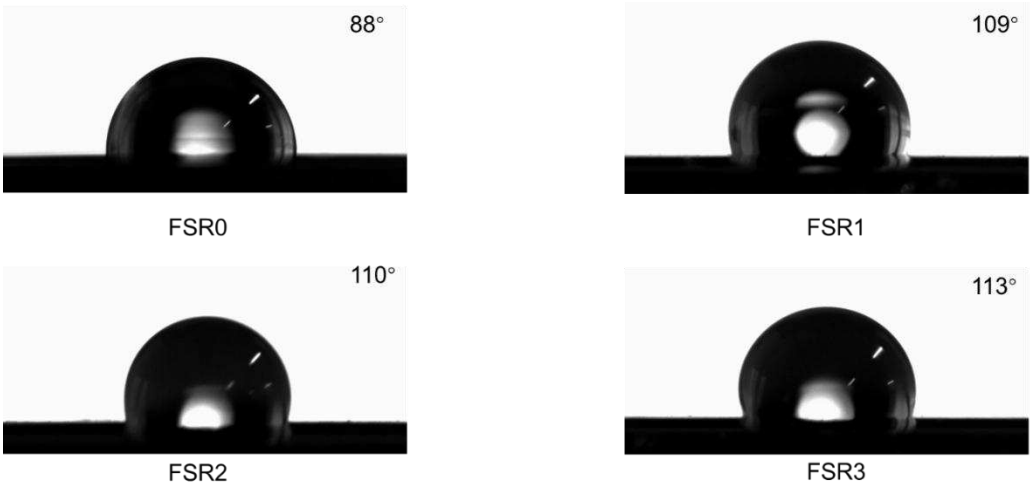


Figure 7 The contact angle of the condensation type PFCB fluorosilicone resin

Due to the highly polar nature and low electron cloud density of the C-F bond, introducing fluorine elements into silicon resins can improve their hydrophobicity. To verify the effect of introducing the PFCB structure on the hydrophobic properties of the silicon resin, contact angle tests were conducted on the cured fluorosilicone resins (Figure 7). When the PFCB structure was introduced into the silicon resin, its contact angle was greater than that of the silicon resin without the PFCB structure. This was because the C-F bonds in the PFCB structure have extremely low surface energy and chemical stability. After introducing the PFCB structure into the silicon resin system, the perfluorocyclobutyl groups have the characteristic of spontaneously migrating to and concentrating on the material surface, forming a low surface energy dense layer on the material surface. This can significantly weaken the wetting adhesion of water molecules to the material surface, thereby increasing the contact angle of the fluorosilicone resin. Moreover, as the content of the PFCB structure increases, the contact angle of the fluorosilicone resin shows an increasing trend. The results indicate that by regulating the content of PFCB, the hydrophobic properties of the cured

fluorosilicone resin can be effectively regulated.

3.6 Transparency analysis

The light transmittance test of the sample is shown in Figure 8. The perfluorocyclobutylaryloxy group structure in the PFCB structure is a non-planar structure. When this structure is introduced into the organic silicone resin, the original regular molecular chain structure is disrupted. The benzene ring structure and the perfluorocyclobutyl structure in the PFCB structure act as rigid groups, which will increase the spatial volume steric hindrance. The molecular chain is difficult to form a crystalline region, and the F atom in the perfluorocyclobutyl structure replaces the H in the C-H structure, avoiding the attenuation of light in the near-infrared region caused by the C-H bond. Therefore, modifying the silicone resin with the PFCB structure has good optical transmittance.

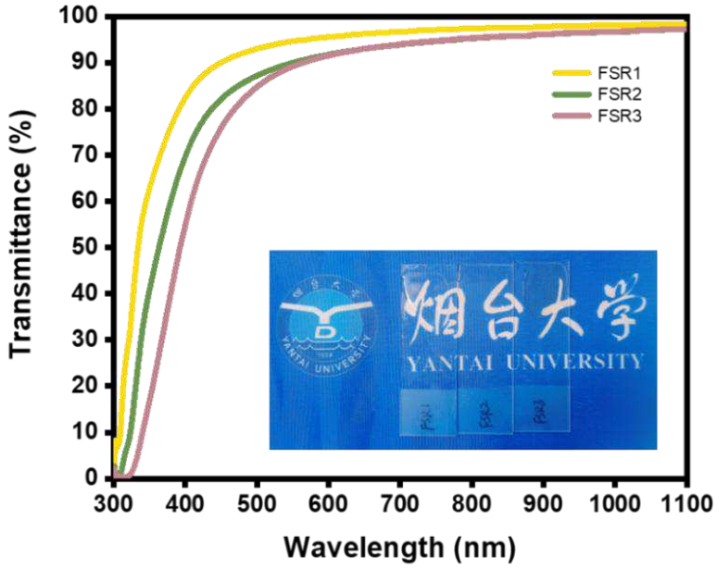


Figure 8 Transparency of condensation-type PFCB fluorosilicone resin

3.7 Dielectric property analysis

Dielectric constant is a key parameter for evaluating a material's ability to store electric charge in an electric field. Fluorosilicone resins with low dielectric constants have considerable potential for application in high-frequency electronic packaging. The experimental results are shown in Figure 9. As the content of PFCB structure increases, the dielectric constant of the fluorosilicone resin decreases. This is because the electronegativity of fluorine atoms is relatively low, and the presence of aromatic rings

and perfluorocyclobutyl rigid structures in the PFCB structure introduces spatial steric hindrance. After introducing the molecular chain, the rigidity of the molecular chain increases as the content of PFCB increases, and the polarization lag phenomenon intensifies, resulting in a decrease in the polarization rate, and thus the dielectric constant decreases.

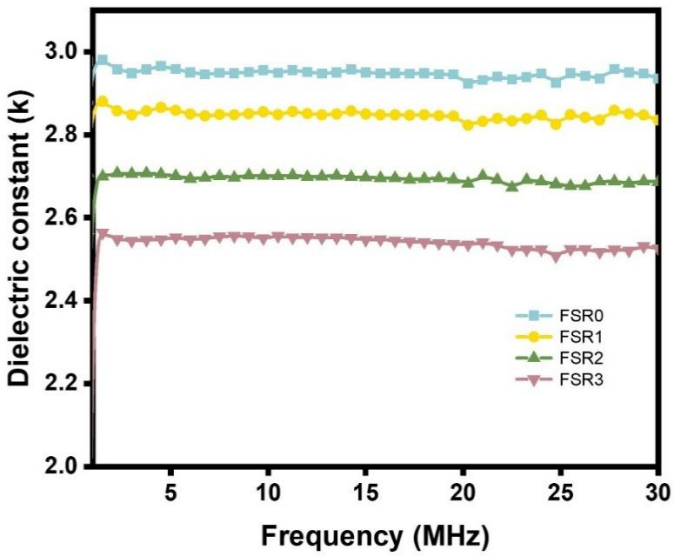


Figure 9 The dielectric constant of condensation-type PFCB fluorosilicone resin

4 Conclusions

In conclusion, this paper synthesizes perfluorocyclobutyl aryl ether siloxane monomers and conducts hydrolytic condensation reactions with phenyl trimethoxysilane and methyl phenyl dimethoxysilane to prepare fluorosilicone resins with PFCB structures in their main chains. By adjusting the molar ratio of the three siloxane monomers, the content of PFCB in the fluorosilicone resins can be controlled. The study found that the PFCB structure can enhance the thermal stability, hydrophobicity and dielectric properties of the fluorosilicone resins, but it has a certain impact on the mechanical properties of the resins. The synthesized fluorosilicone resins with PFCB structures have the synergistic advantages of low surface energy of organic fluorine and excellent thermal resistance of organic silicon, and exhibit a low dielectric constant. This indicates that they have certain potential application in the fields such as electronic packaging insulation materials, encapsulation materials and high-

temperature protective coatings.

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