

ORIGINAL RESEARCH ARTICLE

Research Progress of Low Dielectric Benzoxazine Resin

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ABSTRACT

Benzoxazine resin, a new type of phenolic resin, has many advantages such as strong molecular design, no small molecular release in the curing process, excellent thermal stability and mechanical properties, and high residual carbon ratio. Thus, it is important for electronic communication industry matrix material. To meet the needs of high-frequency and high-speed communication technology for low-dielectric polymer resin, the low dielectric modification of benzoxazine resin is of great significance to the high frequency and high speed propagation of the signal, which causes a wide range of materials researcher's attention. In this paper, we reviewed a series of studies on the low dielectric modification of benzoxazine resin in recent years, including the synthesis of new monomers, inorganic - organic hybridization, copolymerization with other resins, and low molecular weight benzoxazine Resin research trends were outlined.

KEYWORDS: Benzoxazine; Dielectric properties; Copolymerization; Modification

In the twenty-first century, human being is surrounded by cloud computing, internet, and big data, satellite communications, mobile phones and Bluetooth technology. These are the representative of evolution of the information into high-frequency, high-speed, high-capacity signal transmission era. The high frequency, high speed, and small light weight of electronic information products result in higher requirements for polymer resin as an information transmission carrier and its important components. According to the International Semiconductor Association road map, the dielectric constant (k) of the low dielectric material should be less than 2 to increase the frequency signal transmission speed. Benzoxazine resin has the advantages of low dielectric constant, low hygroscopicity, high heat resistance, dimensional stability of processing, and good flame retardancy, so that it has attracted much attention in the field of electronic information products [1,2]. Benzoxazine is an intermediate from the oxygen-containing heterocyclic structures synthesized from phenols, amines and paraformaldehyde as raw materials. Its formation requires the ring-opening polymerization under the action of heating and / or catalyst, with no small molecules are being released during the polymerization process. This process forms the nitrogen-like and phenolic resin-like network structure of the polymer, namely polybenzoxazine or benzoxazine resin.

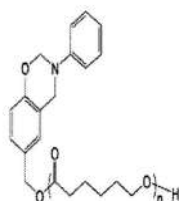
In the integrated circuit, the signal transmission rate is proportional to the square root of the dielectric constant, while the signal loss is proportional to the square root of the dielectric loss [3]. To meet the development requirements of the electronic information industry, it is necessary to use low dielectric constant and low dielectric loss materials as the substrate to reduce the loss of signal and transmission rate. However, the dielectric constant (k) of polybenzoxazine resin is approximately 3.5 [4]. In addition, it fails to meet the requirement of high frequency and high speed ($k < 2$). Therefore, it is important to discuss the impact of low dielectric modification to benzoxazine resin. The main principle of reducing the dielectric constant of benzoxazine resin is to increase the free volume inside the molecule and reduce the polarity of the molecule. The most common used methods are: (1) through the molecular design, the introduction of fat (ring) chain, fluorine atoms, oxazole ring, dicyclopentadiene, and other low polarity or large volume chemical structure; (2) the introduction of inorganic micro-nanoparticles such as polyhedral oligomeric silsesquioxanes (POSS), mesoporous silica, graphene oxide, etc. into the system to form a pore structure, the use of air low dielectric constant to improve the dielectric properties of the entire system; (3) and cyanic acid Ester, epoxy resin, polyurethane and other polymer copolymerization, the introduction of low polar groups or consumption of benzoxazole ring-opening polymerization of hydroxyl.

1. New structure of benzoxazine resin

In recent years, the researchers used the molecular design to insert fat (ring) chain, fluorine atoms, dicyclopentadiene, oxazole ring and other low polarity or large volume chemical structure to benzoxazine, forming benzoxazine resin. This low dielectric modification provides the possibility and many new results.

Su et al. [5] used 4-hydroxybenzyl alcohol, formaldehyde, and aniline as raw materials to synthesize benzoxazine monomer (pa-OH), and also cyclohexyl lactone (PCL) reaction to produce cyclohexyl lactone modified benzo (Pa-PCL). The chemical formula is showed in Fig. 1. Further, the copolymer resin of pa-PCL and bisphenol A type benzoxazine was heated and refluxed, and then dried to obtain a composite resin having a porous structure. The results showed that the dielectric constant of the composite resin can reach 1.95 (1MHz) when the mass fraction of pa-PCL is 25%, which is mainly due to the introduction of the aliphatic ring and porous structures. In addition, Kumar et al. [6] reacted polydimethylsiloxane (PDMS) with benzoxazine monomers to form a novel benzoxazine containing polydimethylsiloxane (with chemical formula as shown in Fig. 2), Studies have shown that the introduction of siloxanes favors the decrease in dielectric constant of the composite resin. It is worth noting that the long-fat hexanediamine has a lower dielectric constant of 2.42 and a dielectric loss of 0.0022 (1 MHz) for the copolymer of benzoxazine and PDMS synthesized by amine source. This is mainly due to the addition of PDMS increased the free volume in the system, and the long-fat chain amine source reduced the polarity of the composite system. Zhang et al. [7] synthesized a novel benzoxazine containing a benzoxazole group using a non-solvent method. The new resin has a dielectric constant of 2.1 at a frequency of 10 MHz and a dielectric loss of 0.01. This property is much smaller than the average polybenzoxazine due to the introduction of a rigid bulk oxazole ring structure in the molecule, resulting in larger volume. Moreover, Zhang et al. [8] also synthesized a bridged benzoxazolyl benzoxazine, and the dielectric constant of the copolymer resin with bisphenol A benzoxazine was gradually decreased with the increase of the addition amount. The results showed that the incorporation of oxazole ring into benzoxazine reduced the dielectric constant of polybenzoxazine while increasing the thermal stability. However, the difficulty in the synthesis of benzoxazolyl benzoxazine and brittle may limit its application to some extent.

The fluorine atoms are used to replace hydrogen atoms because they have strong electron-attracting effect, which effectively reduces the electron polarization. Therefore, the introduction of fluorine atoms can reduce the polarity of the benzoxazine resin system, thereby reducing the dielectric constant. Herrera et al. [9,10] synthesized high fluorinated backbone benzoxazine resins by using high fluorinated diamines, high fluorinated bisphenol A, and formaldehyde as raw materials. The results showed that the dielectric constant of benzoxazine resin with high fluorination degree was low, and the dielectric constant and dielectric loss of fluorinated polybenzoxazine reached 2.2 and 0.008, respectively at 1GHz frequency. Moreover, the dielectric constant of the fatty amine type benzoxazine resin is lower than that of the aromatic amine type benzoxazine resin under the same fluorination, which is mainly due to the low polarity of the aliphatic chain. Next, Parveen et al. [11] synthesized three different benzoxazines with three different fluorinated aniline (4-fluoroaniline, 2,4-difluoroaniline and 2,3,4-trifluoroaniline.) The phosphorous oxide resin with the highest fluorine content had the lowest dielectric constant, the dielectric constant was 2.0, and the dielectric loss was 0.002 (1MHz). While Su et al. [12] used 4- (trifluoromethyl) aniline, hexafluorobisphenol A, and paraformaldehyde to synthesize a fluorine-containing benzoxazine monomer (F-1). The dielectric constant and the dielectric loss of the copolymer resin were 2.36 when the mass fraction of F-1 was 50%, and the dielectric constant of the copolymer resin was decreased by 2.36 and 0.00444 (100 kHz).



pa-PCL

Fig. 1

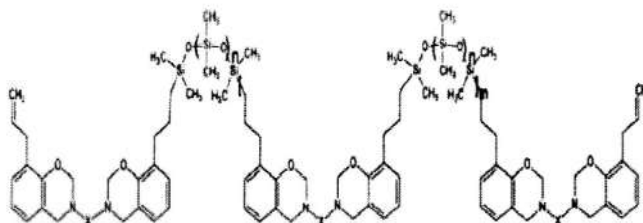


Fig. 2

Dicyclopentadiene (DCPD) is mainly from C5 fractions of ethylene by-product of petroleum cracking and coal coking by-products. As the molecular structure of DCPD contains two unsaturated double bonds, thus its chemical properties are highly reactive. DCPD benzoxazine gives benzoxazine more excellent properties, such as lower dielectric constant and dielectric loss, more excellent thermal properties, and mechanical properties. Shieh et al. [13]

synthesized a novel benzoxazine resin with dicyclopentadiene phenol as the starting material (as shown in Fig. 3) with good dielectric properties and a dielectric constant of 2.95 (1 MHz). This is mainly due to the introduction of non-planar structure of dicyclopentadiene, making the intermolecular spacing increases, thus increasing the free volume in the system. In addition, the introduction of a low polarity aliphatic dicyclopentadiene can also reduce the dielectric constant. Hwang et al. [14] studied the dielectric properties of dicyclopentadiene-type benzoxazine and its copolymer with melamine phenolic resin and phosphorus-containing phenolic resin. Under the same conditions, dicyclopentadiene-type benzoxazine resin had the lowest dielectric constant, dielectric loss, and water absorption.

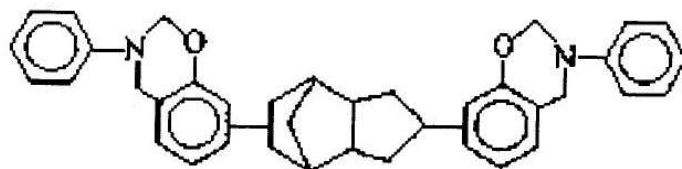


Fig. 3

2. Inorganic - organic hybrid composites

In recent years, benzoxazine and fiber, polyhedral oligomeric silsesquioxane (POSS), mesoporous silica, graphene oxide (GO) formed inorganic - organic nanocomposites, has been able to make dielectric constant to approximately 2, making benzoxazine composite resin has better potential value in the field of electronic information industry.

The organic and inorganic fiber reinforced benzoxazine resin with some advantages such as excellent thermal stability, low thermal expansion coefficient, and excellent mechanical properties. It is mainly due to the good interaction between the fiber and the benzoxazine resin matrix, which reduces the interfacial polarization, and effectively inhibits the movement of molecular segments. This leads to lower dielectric constant and dielectric loss. Furthermore, Liu et al [15] synthesized laminate products by blending phenol/aniline type benzoxazine, propargyl functional benzoxazine, and silicon-containing aromatic acetylene resin in a certain proportion, and glass fiber cloth together with hot forming. The dielectric constant of the composites decreases with the increase of the frequency. When the mass fraction of the silane-containing acetylene resin is 14.3%, the composite material has a low dielectric constant of 2.72 and dielectric loss of 0.021 (10MHz). Xiao et al. [16] discovered that a better dispersion effect was achieved when combined benzoxazine/aromatic sulfonamide fiber and benzoxazine/glass fiber. This is due to the gradually increased frequency in dielectric constant and downward trend in dielectric loss of a downward. Wang et al. [17] compared three kinds of composite resin base plate products, such as quartz fiber/cyanate ester, quartz fiber/diallyl-type benzoxazine/cyanate ester and quartz fiber/bisphenol A benzoxazine/cyanate. In the three composite systems, the quartz fiber/bisphenol A benzoxazine/cyanate ester has the minimum dielectric constant of 3.07 and a dielectric loss of 0.0067 (60 MHz).

POSS is an organic and inorganic composite structure with excellent thermal stability and mechanical properties, and the molecular design is strong, and the polymer matrix compatibility is good [18]. The introduction of POSS into the benzoxazine resin matrix, the three-dimensional cage structure can greatly improve the free volume inside the composite system, thus effectively reducing the dielectric constant of benzoxazine resin. To increase the compatibility of POSS and benzoxazine resin matrix, many studies have been carried out on the functional modification of POSS. Further, the chemical reaction between POSS and benzoxazine functional groups has been improved to improve the compatibility between POSS and resin matrix c, and dispersion of POSS in the resin matrix. Tseng et al. [19] carried out the Diels-Alder reaction by the furan group in the benzoxazine monomer and the methyl methacrylate group (chemical structure shown in Fig. 4) of the modified POSS, enabling the POSS to be uniformly dispersed in the resin matrix. When the mass fraction of modified POSS is 70%, the composite has a lower dielectric constant of 1.9 (1MHz). Vengatesan et al. [20] used bisphenol Z allyl-terminated benzoxazine monomer and maleimide phenyl polysilsesquioxane (OMPS) as raw materials, in the process of mixing heat curing OMPS then branched onto benzoxazine, followed by the formation of nanocomposites with benzoxazine. With the increase of OMPS content, the dielectric constant and dielectric loss of the system decreased gradually. It is worth noting that the water absorption of the composite material also showed a corresponding downward trend, and the decrease of the water absorption rate also caused the system to reduce the dielectric constant and dielectric loss. Vengatesan et al. [21] also studied the copolymer system of epoxy siloxane oligomeric silsesquioxane (OG-POSS) with bisphenol Z-type benzoxazine with hydroxyl groups at the end. The dielectric constant of nanocomposites decreased when OG-POSS was added. When the mass fraction of OG-POSS was 7.5%, the dielectric constant was 2.12 (1MHz). Kumar et al. [22] copolymerized with benzoxazine monomers, hydroxyl terminated POSS, and diisocyanate to form a layered network structure of POSS-polyurethane-benzoxazine nanocomposites. When the mass fraction of POSS is 30%, the dielectric constant reached a minimum of 1.94 and a

dielectric loss of 0.0124 (1 MHz). Sethuraman et al. [23] used allyl-terminated benzoxazine and mercapto-functional polyhedral oligomeric silsesquioxane to synthesize benzoxazine monomer POSS under the ultraviolet light will be grafted onto benzoxazine monomer POSS. Nanocomposite material has a dielectric constant of at least 2 (1MHz). Thalukumaran et al. [24] synthesized eugenol-based benzoxazine monomers with by compounding bis-aminophenol sulfone, formaldehyde and eugenol with aniline-containing polyhedral oligomeric silsesquioxane (OAPS). When the mass fraction was 1%, 3% and 5%, the dielectric constants were 1.53, 1.42 and 1.32, respectively, and the dielectric losses were 0.22, 0.18 and 0.12 (1MHz). These findings were the minimum dielectric constant test results obtained from the studies on the benzoxazine dielectric properties in recent years. However, not all studies are able to achieve the desired results. For example, Chandramohan et al. [25] discovered that the combination of phosphorus bismaleimide-type benzoxazine and aniline and epoxy siloxane POSS complex, followed by the POSS grafted to Benzoxazine and composite modification of the nano-composite material did not significantly improve the dielectric properties.

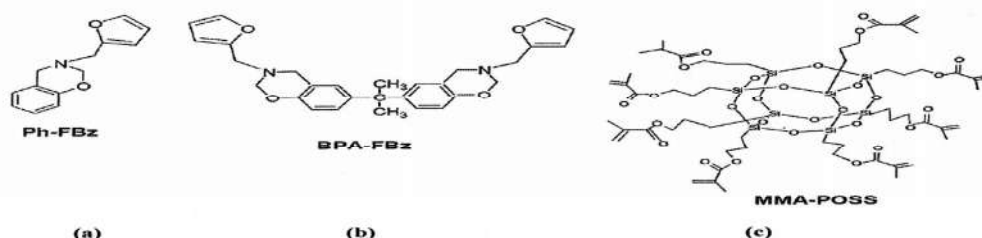


Fig. 4

To further improve the compatibility and interaction between POSS and benzoxazine resin matrix, the research on the functional modification of benzoxazine monomer to POSS has been carried out recently. The functionalized POSS of benzoxazine monomer can form a copolymer with the macromolecular matrix and open the nanopore pores, which effectively reduces the dielectric constant of the composite resin. Liu et al. [26] synthesized a new structure of benzoxazine Bz-BES with bisphenol A, paraformaldehyde and 3-aminopropyltriethoxysilane as raw materials, and then subjected to sol-gel method and thermal polymerization to form poly Benzoxazine bridged polysilsesquioxane (PBz-BPSSQ). The structural formula is showed in Fig. 5. PBz-BPSSQ is a layered structure consists of a polybenzoxazine-enriched layer and a polysilsesquioxane-enriched layer with the thickness between 80 and 100 nm and a dielectric constant of 1.57 (1MHz). Kumar et al. [27] copolymerized with benzoxazine functionalized POSS and bisphenol Z benzoxazine to obtain nanocomposites with layered network structure. When the mass fraction of modified POSS was 30%, the electrical constant can reach 1.7, the dielectric loss was 0.0019 (1MHz). Zhang et al. [28] first modified the POSS to obtain a phenol-containing benzoxazolyl-based POSS (OPS) and used it as a phenolic to synthesize benzoxazine functionalized POSS (OPS-Bz) (the structural formula as shown in Fig. 6), and then bisphenol A type benzoxazine in different proportions copolymerization, a series of nanocomposites. When the mass content of OPS-Bz was 30%, the dielectric constant of the composite system reached 2.20 and the dielectric loss was 0.009 (1MHz), with the thermal stability and mechanical properties are also excellent.

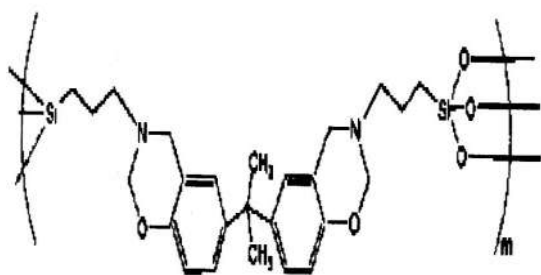


Fig. 5

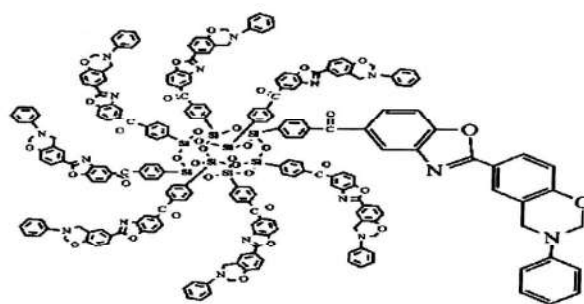


Fig. 6

Mesoporous silica is a kind of new inorganic material with high specific surface area, large pore volume, morphology and size control. It has the advantages of high chemical stability, convenient synthesis and low cost, and it is widely used in polymer composites, resulting in a wide attention in the field of applied research. In view of the porous structure of mesoporous silica itself, the combination with benzoxazine resin will improve the dielectric properties of the matrix resin. Kumar et al. [29] copolymerized siloxane-modified benzoxazine and mesoporous silica-modified benzoxazine (BTMS) to obtain mesoporous silica / benzoxazine nanocomposites. When the BTMS mass fraction was 7%, the dielectric constant (2.06) and the dielectric loss (0.0173) of the composite are the smallest at 1 MHz. While Vengatesan et al. [30] synthesized the siloxane-containing benzoxazine monomer (BZ) by using phenol, paraformaldehyde, and 3-aminopropyltriethoxysilane as raw materials, followed by grafting mesoporous silica (SBA-15) grafted onto benzoxazine monomer, BZ/SBA-15, and copolymerizing with bisphenol A benzoxazine in different

proportions to obtain a series of nanocomposites. When the mass fraction of BZ/SBA-15 was 7.5%, the dielectric constant of nanocomposites was 1.75 (1MHz). Selvaraj et al. [31] synthesized mesoporous silica/benzoxazine nanocomposites with copolymerization of casoxyl-type benzoxazine and mercapto-functional mesoporous silica (TSBA-15). When the mass fraction of TSBA-15 was 5%, the dielectric constant of the composite system was 1.947 and the dielectric loss was 0.06 (1MHz). It was also found that there was a long chain in the polymer network, and the low polarity of the aliphatic chains had a certain effect on the decrease of the dielectric constant. The main reason is that the introduction of mesoporous silica increased the internal free volume, thereby reducing the dielectric constant. However, the heat resistance of composite materials is not excellent enough, glass transition temperature is low, which are needed to be resolved in the future research.

Graphene oxide (GO) has quasi-two-dimensional layered nanostructures. It contains hydroxyl, carboxyl, epoxy, carbonyl and other groups, with high specific surface area, excellent thermal conductivity, mechanical strength, and insulation [32-34]. Zeng et al. [35,36] used in situ intercalation polymerization to prepare the graphene/benzoxazine nanocomposite resin. It was found that GO promoted the ring-opening polymerization of benzoxazine and, to a certain extent, transition temperature and thermal stability. Kumar et al. [37] also studied the dielectric properties of the graphene/benzoxazine complex system by carrying out the condensation reaction of the benzoxazine monomer functionalized triethoxysilane with the hydroxyl group of GO to form an ether bond. They found that when its mass fraction of 10%, the dielectric constant of bisphenol Z type benzoxazine resin was significantly reduced to 1.95, while dielectric loss from 0.029 to 0.007 (1 MHz). The thermal stability is also improved.

3. Benzoxazine complex

It is an important method to study the compound modification of benzoxazine resin by constructing binary, ternary or quaternary copolymer resin system. Through the benzoxazine and cyanate esters, epoxy resin, polyurethane, bismaleimide and other polymers copolymerization, the introduction of low polar groups or consumption of benzoxazole ring polymerization polymerization of hydroxyl, can effectively reduce the polarity and dielectric constant of the resin.

Lin et al. [38] used bisphenol A-type cyanate ester and diamine-type benzoxazine to copolymerize. They discovered that benzoxazine resin was slightly decreases when the mass fraction of benzoxazine was 30%, the dielectric constant was 2.78 (1GHz). In addition, Yan et al. [39] used bisphenol A-type cyanate ester and bisphenol A benzoxazine as raw materials to prepare the copolymer. When the mass fraction of benzoxazine was 15% and the test frequency was 60MHz, the electrical constant is 3.06, the dielectric loss is 0.0045. Comparatively, the dielectric constant of the cyanate ester was 3.21, and the dielectric loss was slightly lower than 0.0062. Furthermore, Li et al. [40] studied the copolymer of bisphenol A type benzoxazine and bisphenol A cyanate ester ester. The results showed that the dielectric constant and dielectric constant of the composite system with the increase of cyanate ester content. While the thermal stability and mechanical properties of the copolymer were also improved.

Lin et al. [41] copolymerized the phosphorylated benzoxazines containing phenolic hydroxyl groups and propargyl ether with bisphenol A type and phenolic type epoxy resin. The four kinds of binary copolymers obtained have excellent flame retardancy and can reach the V-0 level. As the resin curing, the propargyl ether polymerization occurs at the same time, will increase the system of cross-linking density, with propargyl ether phosphate esterification of benzoxazine copolymer binary resin has a lower dielectric constant. In addition, the propargyl ether containing phosphorylated benzoxazine polymerization produces less hydroxyl, but also can reduce the polarity of the entire system. Krishnadevi et al. [42-44] synthesized benzoxazine-epoxy resin composite system (Bz-Ep), with amine-terminated cyclic phosphazene (ATCP) and silane-functional rice husk ash (FRHA) ATCP/FRHA/Bz-Ep composites. The composite resin has more excellent flame retardancy and dielectric properties after adding the reinforcing agent when compared to benzoxazine-epoxy resin binary resin. The dielectric constant of ATCP/FRHA/Bz-Ep with 1.62 and the dielectric loss with 0.091 were achieved when the mass fraction of ATCP and FRHA was 15% and 5%, respectively at 1MHz. Various types of hydrogen bonds present in the composite system help to reduce the polarization of the interface, thereby reducing the dielectric constant of the system [5]. Li et al. [46] also synthesized bisphenols by using bisphenol A benzoxazine, bisphenol A cyanate ester, and bisphenol A type epoxy resin as raw materials. Under the 1 GHz test conditions, the terpolymer resin has lower dielectric constant (3.62) and dielectric loss (0.0067) compared to pure resin and binary copolymer resin.

Jamshidi et al. [47,48] synthesized p-nitrophenol-terminated polyurethanes by copolymerizing poly (tetramethylene ether) diol, 2,4-tolylene diisocyanate and p-nitrophenol at different molecular weights and reacted with different masses fraction of bisphenol A type benzoxazine. The dielectric constant of the copolymer resin reduced to 2.6 and the dielectric loss was as low as 0.013 (1MHz) when the benzoxazine mass fraction was 40%.

Many studies have been carried out on bismaleimide resin (BMI) modified benzoxazine. Compared with pure BMI, BMI-modified allyl-type benzoxazine (Bz-allyl) has a lower dielectric constant and dielectric loss [49]. Moreover, the dielectric constant and the dielectric loss of the copolymer decrease gradually as the content of Bz-allyl increases. Wang et al. [50,51] also studied allylbenzoxazine, bismaleimide and bisphenol A cyanate ester (BADCy) ternary resin systems.

They discovered that the dielectric constant of the ternary resin system was lower than that of the BMI/BADCy binary resin system under the same conditions

Zhang et al. [52] partially replaced nitrile rubbers with casoxyl benzoxazine (as shown in Fig. 7) and copolymerized with bisphenol A type epoxy resin and diaminophenylsulfone to form quaternary complexes. Casoxyl benzoxazine is able to copolymerize with other components as it has excellent thermal stability, thus effectively increasing the crosslinking density of the system. In regard to increase of benzoxazine content, the thermal stability of the quaternary system becomes more excellent. In addition, the dielectric constant and dielectric loss of the composites decrease with the increase of benzoxazine content, which is mainly due to the introduction of a large number of low polarity saturated aliphatic chains in the composite system, and the high polarity groups Saturated double bond or the relative reduction in the proportion of cyano.

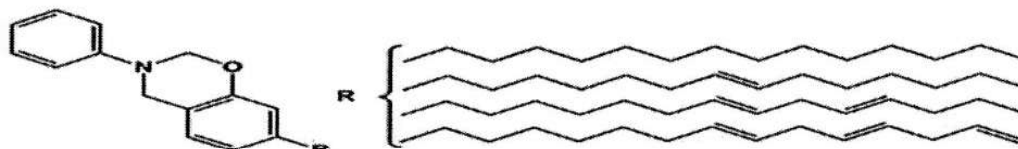


Fig. 7

4. Prospects for the study of low dielectric properties of benzoxazine resin

At present, the research on benzoxazine resin focusing on molecular design and synthesis, curing mechanism and curing reaction kinetics, micro-nano composite resin construction, and characterization and molecular simulation, has made a great breakthrough. Although, there are few studies on the theory and application of low dielectric properties of benzoxazine resin, however, there are still many problems to be solved in the development of benzoxazine resin in the field of electronic information. For examples, (1) structural design and optimization of preparation conditions, (2) dielectric properties and network structure of the structure-activity relationship is not clear, (3) in the polymerization process of structural control and quantitative characterization needs to be further explored, (4) high frequency thermal, dielectric, mechanical and other comprehensive performance of the resin is still not easy to prepare, and (5) application of the depth and breadth of the need to further strengthen. The modification of benzoxazine resin to enhance the dielectric properties is a very cost-effective way to prepare high-frequency, high-speed and high-density electronic information products. In view of our country is still new in the field, relevant theoretical and applied research should be carried out to enhance China's international competitiveness.

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