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Overview of High-Temperature Polymers

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1.1 Introduction

In recent years, the wide utilization of new energy sources has made it necessary for power equipment to operate in harsh environments such as high voltage, high power, and high temperature [1, 2]. Therefore, as an essential component of power equipment, dielectric materials have attracted more attention. Solid dielectrics used in power equipment can be divided into polymer dielectrics and inorganic dielectrics. Inorganic dielectric has high temperature stability but also has the disadvantages of low breakdown strength (E_b) and poor flexibility, which cause difficulties in large-scale preparation that cannot be ignored. Different from inorganic dielectrics, polymer dielectrics have the advantages of being lightweight, having good flexibility, and being easy to process [3]. Meanwhile, excellent dielectric properties (high E_b, low dielectric loss [tan δ]) make it widely used in power equipment. With the continued miniaturization and increased power output of electronic and power systems, many fields require polymer dielectrics for reliable operation in harsh environments. For example, control and sensing electronics near the shells of rockets and space shuttles require high-temperature dielectric materials to operate above 250 °C. In underground oil and gas exploration, operating temperatures exceed 200 °C [4]. Unfortunately, the poor thermal stability of traditional polymer dielectrics seriously threatens the reliable operation of power equipment and significantly shortens its life cycle. Therefore, secondary cooling equipment has been used to reduce the working temperature in high-temperature applications. However, secondary cooling is difficult to achieve in view of the extreme temperatures experienced by large facilities such as underground exploration and space stations. Thus, a more attractive strategy is to develop high-temperature-resistant polymer dielectrics that carry out long-term work at high temperatures. This strategy can improve system reliability, reduce costs, and eliminate the need for large cooling systems and the wiring and interconnections required for remote placement of electronics [5, 6].

High Temperature Polymer Dielectrics: Fundamentals and Applications in Power Equipment, First Edition.
Edited by Jun-Wei Zha and Zhi-Min Dang.

Currently, polymers such as polyethylene (PE) and polypropylene (PP) are commonly used, but their operating temperatures are less than 105 °C [7]. This fact can be attributed to the tendency of molecular chains to move or even to break under heating conditions. Polymers with high temperature resistance have been developed such as polyimide (PI), polyetherimide (PEI), and polyetheretherketone (PEEK) [8–14]. The favorable high temperature resistance is primarily caused by the ultra-strong molecular structures derived from the conjugated bonds (multiple bonds or aromatic rings) on the polymer backbone. Furthermore, the hydrogen bonds and cross-linked structures lead to strong interactions within and between the polymer chains, which is directly reflected in the elevated high temperature resistance [15]. In addition, the introduction of an inorganic filler can further optimize the high-temperature polymer [16]. Based on the above strategies, excellent polymer dielectrics are prepared through molecular structure modification and composite structure design to meet the urgent requirement of high temperatures for rapidly developing power equipment.

This chapter briefly introduces the history of high-temperature polymers. Then, the influence of parameters such as glass transition temperature (T_g), melting point (T_m), and thermal conductivity (λ) on the high temperature resistance of polymers is analyzed, and the method of determination of the above parameters is displayed. Subsequently, the research progress of high-temperature polymers and their composite materials is discussed. Finally, the future challenges of high-temperature polymer materials are presented. This chapter will instruct on the development of high-temperature polymers in power equipment.

1.2 Development of High-Temperature Polymers

Since the early twentieth century, the rapid development of commercially available synthetic polymers has led to their widespread usage in military and civilian applications. Research on polymers with high temperature resistance attained its peak in the 1950s. During the development of novel products, functional groups and segments were introduced into polymers for the improvement of high temperature resistance. It leads to poor processability and high costs, which hinder large-scale production. A few high-temperature polymers have been developed and used nowadays, such as PI, PEI, PEEK, and fluorene polyester (FPE). It has been found that they are characterized by aromatic and heterocyclic structures. Table 1.1 summarizes the thermal and electrical properties of high-temperature polymers, suggesting that the common characteristics of high-temperature polymers are high T_g and relatively low dielectric permittivity (ε_r) and tan δ [4, 17]. With the booming development of smart grids, aerospace, electronic packaging, and other technical fields, polymer dielectrics are expected to have excellent thermal stability, mechanical properties, dielectric properties, and long service lives. It is also developing toward being lightweight and low-cost to meet various special applications. For example, Fan et al. [18] introduced alumina (Al_2O_3) nanoparticles into the PEI matrix, and the $T_{d5\%}$ of the prepared composite films was increased from 479 to

Table 1.1 Thermal and electrical properties of high-temperature polymers [4, 17].

Polymer	T_g (°C)	Volume resistivity (Ω cm^{-1})	E_b (MV m^{-1})	ε_r	tan δ (1 kHz)
Kapton (PI)	360–410	2.3×10^{17}	154–303 (7.6–127 μm)	2.7–3.5	0.13–0.26
Upilex (PI)	285–500	10^{16}–10^{17}	147–320 (12.5–125 μm)	3.2–3.5	0.13–0.7
Ultem (PEI)	217–247	10^{17}	200 (25 μm)	3.15	0.12
Ketaspire (PEEK)	150	2.6×10^{16}	150 (50 μm)	3.1	0.3
Kepstan (PEKK)	162	10^{16}	84 (100 μm)	2.6	0.7
PTFE	327 (T_m)	$>10^{18}$	23.6 (2 mm)	2.1	0.03
PET	245–265 (T_m)	10^{15}	~500	3.3	0.3
Isaryl (FPE)	330	10^{15}–10^{17}	220–320 (100–120 μm)	3.2–3.5	0.31–0.7
Cyclotene (BCB)	>350	10^{18}	300 (10 μm)	2.75	0.12

525 °C. Additionally, the E_b also exhibited an increase from 422 to 503 MV m^{-1} at 150 °C. The wide bandgap of Al_2O_3 nanoparticles is the primary factor for the significant increase in E_b. Li et al. [19] incorporated polysulfone (PSF) with a high ε_r into PI matrix. While maintaining high-temperature stability ($T_g = 285$ °C), a dramatic improvement in the ε_r was obtained. When the mass fraction of PSF reached 40%, the composite film exhibited the highest ε_r of 6.4 at 1 kHz, versus 3.25 for pure PI.

1.3 Parameters of Polymers with High Temperature Resistance

The high temperature resistance of polymers determines their practical application. T_g is a vital factor affecting the high temperature resistance of a polymer. T_g is the critical temperature at which the chain segments of the noncrystalline phase of polymers transition from freezing to motion and depends on the difficulty of polymer chain rotation. Chain rotation relies on the types of chemical bonds (such as covalent bonds and hydrogen bonds) and polar groups, as well as the shape of the molecular chains [20]. Firstly, the strength of the covalent bonds plays a major role in the thermal stability of polymers. Table 1.2 lists various chemical bonds in polymers and their fracture energies, which indicates that the fracture energy of double bonds is much higher than that of single bonds [21]. High-temperature polymers are usually composed of aromatic ring structures because they provide

Table 1.2 Cleavage energy of representative chemical bonds.

Chemical bond	$C_{aryl}-C_{aliph}$	$C_{aryl}-C_{aryl}$	C=C	C—N	C=N	C=O
Cleavage energy ($kcal\,mol^{-1}$)	93	100	145	70	147	84
Chemical bond	C—H	C—F	C—S	Si—O	Ti—O	B—O
Cleavage energy ($kcal\,mol^{-1}$)	99	123	62	88	180	185

Source: Cottrell [21]/Elsevier.

more stable covalent bonds. Then, the C—F bond has bond energy of up to 126 $kcal\,mol^{-1}$, significantly higher than the C—H bond. Therefore, fluorinated polymers are more thermally stable than their corresponding hydrogen-substituted polymers. Furthermore, the presence of non-covalent bonds such as hydrogen bonds and van der Waals forces makes the polymer chains more attractive. This has a greater impact on the parameters such as T_g and modulus, so the polymer is more resistant to high temperature. In addition, flexible polymer chains are known to lower the T_g, therefore, polymers containing rigid groups (such as sulfone and cyano groups) have higher T_g than those containing ether bonds. And in the design of polymer molecular structure, the presence of Si, P, B, and F atoms in the main chains of polymers is beneficial to improving the high temperature resistance of polymers.

For crystalline polymers, the melting point (T_m) is more practical than T_g. T_m is the critical temperature at which crystalline polymers change from the crystalline state to the molten state [1, 4]. The molecular chains of crystalline polymers are tightly aligned during the crystallization process. It still has good mechanical properties when the temperature is much higher than T_g. The actual operating temperature is significantly elevated above T_g. Therefore, the crystallinity and regularity of the molecular structure are also one of the reasons for high temperature resistance of the polymer. For example, the oriented PI films show an aligned structure that facilitates their mechanical and thermal properties. Cross-linked polymers typically have superior resistance to high temperatures than linear polymers. The disruption of the molecular chains of cross-linked polymers is only completed when more than two chemical bonds are broken, which effectively suppresses the degradation process.

High T_g and T_m are not enough to protect the polymers from a series of failures caused by heat for a long time. The enhanced λ allows more rapid conduction of heat away from the polymer, reducing the risk of high temperatures. For most polymers, the main mechanism of heat conduction is generated by lattice vibration through phonons. The λ of the polymer can be obtained from the Debye equation, as shown below [22].

$$\lambda = \frac{C_p v l}{3} \tag{1.1}$$

where C_p is the specific heat capacity per unit volume, v is the phonon velocity, and l represents the phonon mean free path. Due to scattering with other phonons, defects, and grain boundaries, the l value of most polymers is quite low, essentially

Table 1.3 Thermal conductivity of high-temperature polymers and their composites [23–28].

Polymers	λ (W m^{-1} K^{-1})	Composite materials	λ (W m^{-1} K^{-1})
Polycarbonate (PC)	0.23	3 wt% Ag + 12 wt% rGO/PI	2.12
PEI	0.21	4.0 wt%MWCNTs @ PPD/PI	0.43
PI	0.27	30 wt%mBN/PI	0.696
PEEK	0.25	rGO-PI/BNNS-PI (total filler loading constant at 3.8 wt%)	1.49

less than 0.5 W m^{-1} K^{-1}. Due to the shortcomings of the complex synthesis process and low preparation efficiency of intrinsic thermally conductive polymers, researchers have gradually focused on the improvement of λ of polymer-based composite materials in recent years [23, 24]. Guo et al. [23] prepared PI composites containing highly aligned hybrid fillers with high thermal conductivity (1.49 W m^{-1} K^{-1}), which is a multifunctional dielectric material with excellent thermal management capabilities. Table 1.3 lists the λ values of polymers and their composites [23–28], where the λ of the polymers is between 0.2 and 0.5 W m^{-1} K^{-1}, as previously described. The λ of polymer-based composite materials has been significantly improved.

1.4 Thermal Analysis Technology

Due to the diversity of polymer characteristics, there are different methods and conditions for measuring thermal properties. A variety of thermal property analysis techniques have been used to evaluate the damage to polymers at high temperatures. Several common analysis techniques for polymers are described below.

1.4.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a commonly used technique for measuring the T_g and T_m of materials. Huang et al. [29] characterized the T_g values of PEEKs containing different side chains by DSC tests, as shown in Figure 1.1a. Figure 1.1b depicts that carboxylated polymer (PEEK-COOH) achieved a maximum T_g of 213 °C. Due to the longer –SO$_2$ side chains and –CN side chains, the T_g of sulfonylated polymer (PEEK-SO$_2$) and cyanylated polymer (PEEK-CN) decreased to 156 and 155 °C, respectively.

1.4.2 Dynamic Thermomechanical Analysis (DMA)

Dynamic thermomechanical analysis (DMA) characterizes the mechanical properties of viscoelastic materials as a function of time, temperature, or frequency. On

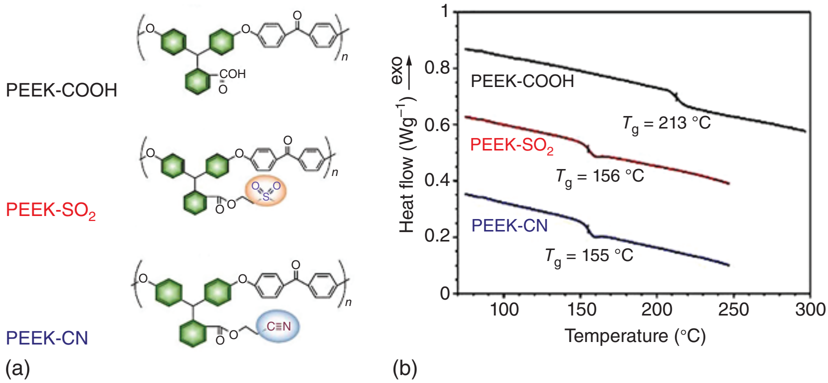


Figure 1.1 (a) Structure formula and (b) DSC of PEEK polymers [29]. Source: Huang et al. [29]. Reproduced with permission of Wiley-VCH.

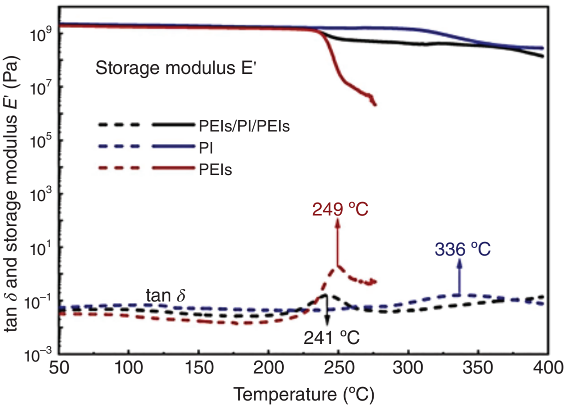


Figure 1.2 E' and tan δ as a function of temperature for PI, PEIs, and three-layer PEIs/PI/PEIs films [30]. Source: Niu et al. [30]. Reproduced with permission of Elsevier.

the one hand, DMA can be used to evaluate the mechanical behavior of materials by giving mechanical properties over a wide range of temperatures and frequencies. On the other hand, the T_g and secondary relaxation processes of polymers can be detected, which are closely related to the chain structure and condensed structure of polymers. Niu et al. [30] characterized the energy storage modulus (E′) and tan δ of PI, PEIs, and sandwich PEIs/PI/PEIs films by DMA tests. As shown in Figure 1.2, the T_g values of PI and PEI and sandwich PEIs/PI/PEIs reached 336, 249, and 241 °C, respectively, indicating excellent high temperature resistance.

1.4.3 Thermogravimetric Analysis (TGA)

TGA is used to characterize the variation of the sample mass in relation to the programming temperature; thus, it is used to analyze the thermal degradation temperature (T_d) and composition of the materials. Liu et al. [31] calculated the imidization degree (ID) of PI from TGA data. As shown in Figure 1.3a,b, the ID was obtained by

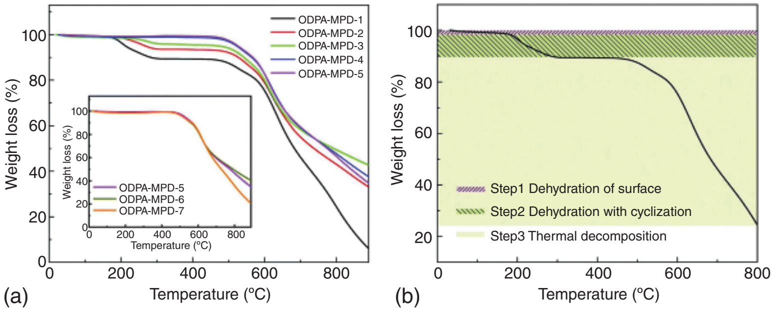


Figure 1.3 (a) TGA curves of the PI films with different IDs. (b) Three steps of the thermal weight loss process for the PI film were obtained from the TGA curve [31]. Source: Liu et al. [31]. Reproduced with permission of the Royal Society of Chemistry.

Table 1.4 Imidization degree and thermal property of the PI films [31].

ODPA-MPD	1	2	3	4	5	6	7
ID (%)	9	52	81	93	≈100	≈100	≈100
$T_{d5\%}$ (°C)	213	268	473	522	520	517	516
$T_{d10\%}$ (°C)	283	527	542	564	565	565	566

Source: Liu et al. [31]. Reproduced with permission of the Royal Society of Chemistry.

Eq. (1.2) based on the weight loss generated in the second step (cyclized dehydration of the PAA chain), and the results of T_d and ID are shown in Table 1.4.

$$\text{Weight loss\%} = \frac{M\left(2\text{H}_2\text{O}\right) \times (100\% - \text{ID})}{M(\text{PAA}) - M\left(2\text{H}_2\text{O}\right) \times \text{ID}} \times 100\% \tag{1.2}$$

1.4.4 Static Thermomechanical Analysis (TMA)

Thermomechanical analysis (TMA) refers to a technique for measuring the functional relationship between the deformation of the materials and the temperature and time under the action of a programmed temperature and non-vibration load, which can be used to measure the coefficient of expansion and phase transition temperature of materials. Figure 1.4c shows the coefficient of thermal expansion (CTE) of the colorless polyimide (CPI) and polyamideimide (PAI) films measured by TMA [32]. The CTE value of the CPI film is relatively high due to the bulky trifluoromethyl side groups. PAI films are obtained by the polymerization of diacids with diamines Figure 1.4a. Figure 1.4b demonstrates that intermolecular interactions between the amide units restrict the motion of the PAI chain segments. As the temperature approaches T_g, the films start to swell due to the increased mobility of the molecular chains. The PAI-1 (CTE = 15 ppm °C^{-1}) and PAI-2 (CTE = 21 ppm °C^{-1}) films have higher dimensional stability compared with CPI

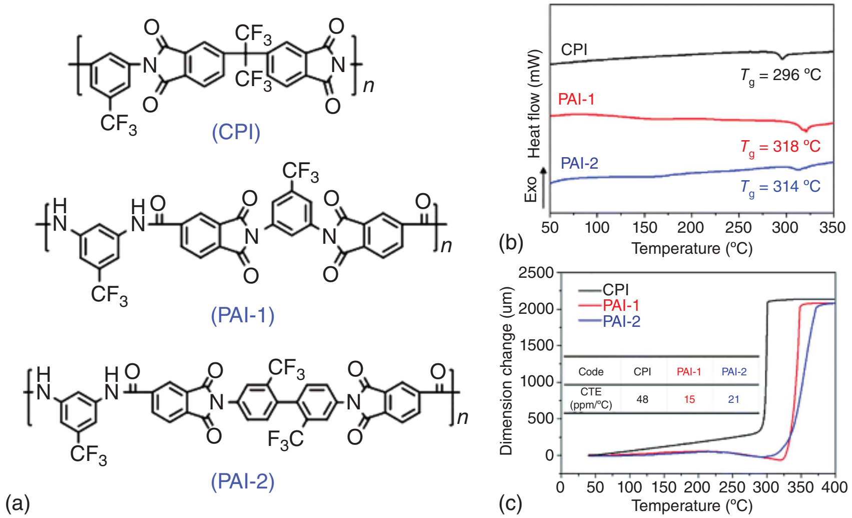


Figure 1.4 (a) Structure formula, (b) DSC, and (c) TMA of CPI and PAI films [32]. Source: Zuo et al. [32]. Reproduced with permission of the Royal Society of Chemistry.

films due to the rigid-rod amide units that increase the linearity and rigidity of the polymer chains.

1.4.5 Thermal Conductivity

Thermal conductivity reflects the ability of materials to conduct heat. Polymer materials with high thermal conductivity are conducive to emitting waste heat generated during operation, so they are beneficial to the optimization of electrical properties, life cycle, and reliability of power equipment. Zhou et al. [33] introduced a sandwich-structured PAI composite film as shown in Figure 1.5. The design of the layered structure and highly oriented functionalized BN bring about high

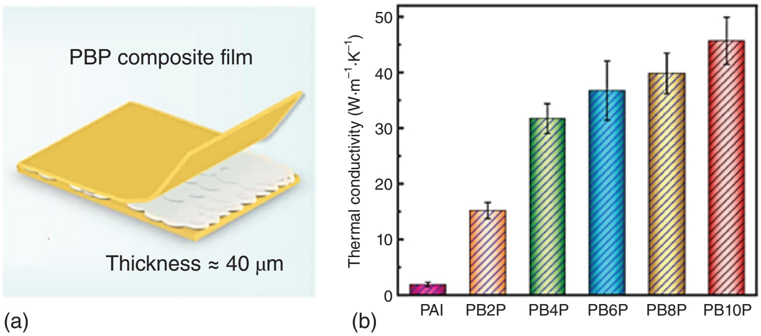


Figure 1.5 (a) Schematic diagram of the structure of PBP composite film. (b) $\lambda//$ of pure PAI and PBP composite films with different numbers of filler layers [33]. Source: Zhou et al. [33]. Reproduced with permission of Elsevier.

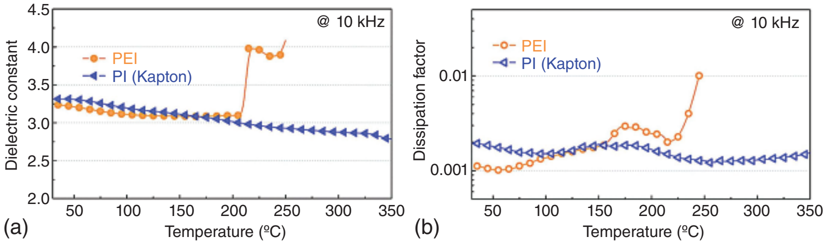


Figure 1.6 Temperature-dependent (a) ε_r and (b) tan δ of PI and PEI measured at 10 kHz [34]. Source: Li et al. [34]. Reproduced with permission of Nature Publishing Group.

in-plane thermal conductivity (λ//). The composite film achieved a high λ// of 45.7 W m^{-1} K^{-1} with 23 wt% BN loading.

1.4.6 Dynamic Dielectric Analysis (DEA)

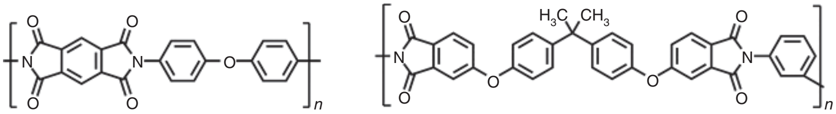
Dynamic dielectric analysis (DEA) is a technique for analyzing the ε_r and tan δ of dielectric materials as a function of temperature and frequency under electric fields. As shown in Figure 1.6, the ε_r of PI steadily decreases from 3.3 to 2.8 and remains low tan δ (<0.3%) as the temperature increases from 25 to 350 °C [34]. Although the ε_r of PEI remains stable between 25 and 200 °C, its relatively low T_g causes the ε_r and tan δ of PEI to change dramatically with increasing temperatures above 200 °C. Furthermore, a significant relaxation peak in tan δ is observed at about 175 °C.

1.5 High-Temperature Polymer Materials

Compared with metal and ceramic materials, high-temperature polymers have the advantages of being lightweight, easy to process, and having tunable properties. This section describes high-temperature polymers and their composite materials that are widely used in electronic power systems.

1.5.1 Commercial High-Temperature Polymer

Figure 1.7 shows the structural formulas for several high-temperature polymers. PI is a thermosetting polymer containing imide rings, which is one of the most high-temperature-resistant polymer materials available in practice. PI is usually prepared through a traditional two-step process. Firstly, the dianhydride and diamine monomers form PAA through polycondensation. Then the PAA is converted to PI by the imide reaction. PI with different properties can be synthesized by selecting different types of diamine and dianhydride monomers. One of the most commercially valuable PI films is the Kapton film, made by DuPont. Kapton is synthesized from pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) monomers. Marketed since the mid-1960s, it has been widely used for high-temperature wire and cable insulation on aircraft with continuous operating



Polymide (Kapton)

Poly(ether imide) (PEI)

Poly(ether ether ketones) (PEEK)

Poly(ether ketone ketones) (PEKK)

Polytetrafluoroethylene (PTFE)

Poly(phenylene sulfide) (PPS)

Figure 1.7 The structural formula for several common high-temperature polymers.

temperatures of 300–350 °C [35, 36]. Aromatic polyimides have strong rigidity, which brings difficulties for processing and manufacturing. In order to improve the processing properties of PI, researchers have introduced flexible groups (such as ether bonds and alkyl groups) into the PI molecular chains. For example, PEI is obtained by introducing flexible groups (such as ether bonds) onto the PI skeleton. The classic PEI is ULTEM, produced by SABIC using the disodium salt of bisphenol A and 1,3-bis(4-nitrophthalimido) benzene [37]. The existence of the flexible bond makes PEI transform into a thermoplastic polymer and obtain a lower $T_g = 217\,°\mathrm{C}$. Thermoplastic PEI has excellent machining properties, including extrudable, injectable, and compressible molding, and is soluble in a variety of organic solvents, which provides conditions for application in different equipment [38].

PEEK is a semi-crystalline polymer material with ether bonds and ketone carbonyl groups in molecular chains, which is formed by the polymerization of 4,4′-difluorophenone and dibenzoate. PEEK not only has good high temperature resistance ($T_g \approx 150\,°\mathrm{C}$), but also excellent mechanical strength, flame retardant, radiation resistance, insulation, and other advantages [5]. The semi-crystalline characteristics of PEEK make it have hot melting characteristics, which can be directly wounded with copper wire at high temperatures, and then the corresponding insulation products are prepared. The thermal properties of polyketone materials can be adjusted by changing the ratio of ether bonds and ketone carbonyl groups. For example, when the ratio of ether bond and ketone carbonyl group is changed from 2 : 1 in PEEK to 1 : 2, poly(ether ketone ketone) (PEKK) with a similar structure to PEEK is obtained. PEKK is generally polymerized from diphenyl ethers and benzene dicarboxylic acid halides [39]. The commercial PEKK named Kepstan, manufactured by Arkema, has a high T_g of 162 °C [40].

PTFE (polytetrafluoroethylene) can be prepared from tetrafluoroethylene monomers by polymerization. PTFE was accidentally discovered by Plunkett in 1938 [41]. As a semi-crystalline polymer, PTFE also has a high T_m of 327 °C, which gives it excellent thermal stability at 260 °C [42]. In addition, PTFE is widely used in the aerospace field due to its corrosion resistance, electrical insulation, and good anti-aging durability. Polyphenylene sulfide (PPS) is a thermoplastic crystalline resin composed of aromatic rings connected with sulfur. Although the T_g of PPS is only 120 °C, it can work in the range of 200–240 °C for a long time, and the maximum temperature can reach 260 °C for a short time. Moreover, the T_d of PPS in the air is higher than 500 °C. In addition to excellent thermal stability, PPS also has good corrosion resistance (second only to PTFE), electrical performance, and flame retardancy [43]. However, its high crystallinity (75%) and rigid molecular structure lead to its high brittleness and low toughness.

Although some widely used high-temperature polymers have been discussed above, they still have different shortcomings in practical application. Thus, it is necessary to develop novel high-temperature polymers. The recent research progress in high-temperature polymers and composite materials from the perspectives of molecular structure design and composite structure optimization is presented as shown below.

1.5.2 Molecular Structure Modification of High-Temperature Polymer

Homogeneous high-temperature polymer films can be obtained based on molecular structure modification strategies. There are extremely few defects in the film-forming process, which is conducive to large-scale preparation. Suppressing the motion of molecular chains is an effective strategy to make polymers with excellent high temperature resistance. This can be achieved by enhancing intermolecular forces, such as by building rigid and cross-linked structures. Researchers have made a lot of valuable progress in this field.

Most high-temperature-resistant polymers have rigid structures, and their molecular chains should contain aromatic rings or heterocyclic rings. In addition, the conjugate structure can be further designed on the main chains to improve the rigidity of polymers. Based on the above design concept, Pan et al. [44] incorporated rigid and asymmetric phenyl phthalazinone ether ketone molecules into the polymer skeleton to obtain poly(phthalazinone ether ketone) (PPEK). The T_g of PPEK was 250 °C, and $T_{d5\%}$ reached 490 °C. Although the presence of conjugated structures improves the high temperature resistance of polymers, the stacking of π–π structures leads to a reduction in bandgap, which deteriorates electrical properties. Figure 1.8a depicts that Wu et al. [45] synthesized polyoxafluoronorbornene (POFNB) through ring-opening metathesis polymerization reaction using Grubbs generation 2 catalyst. The aromatic structure was replaced by a saturated, fused bicyclic structure in the polymer. This nonplanar and non-conjugate rigid structure allows the polymer to achieve high temperature resistance while avoiding bandgap reduction due to π–π stacking between benzene rings. As shown in Figure 1.8b, POFNB achieved a high T_g of 186 °C and a wide bandgap of 4.9 eV. The wide

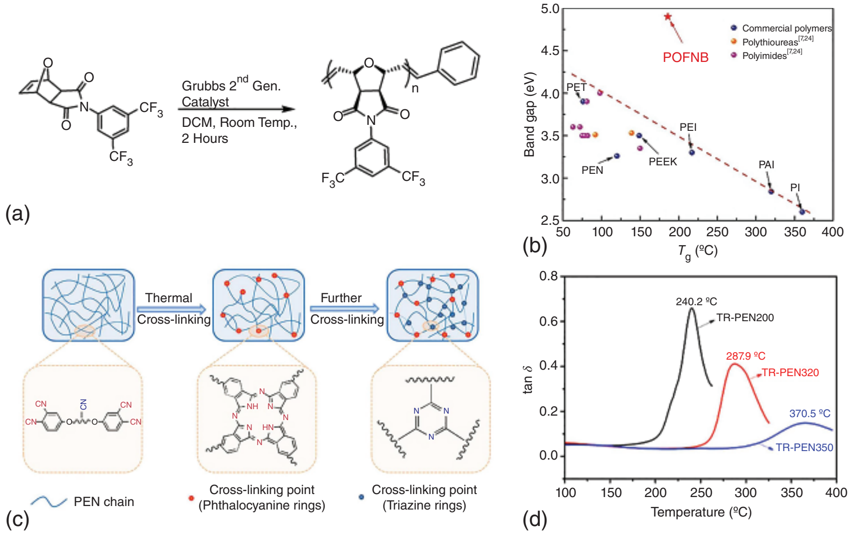


Figure 1.8 (a) Schematic of the synthesis process for POFNB. (b) The bandgap versus T_g for POFNB and high-temperature polymers [45]. Source: Wu et al. [45]. Reproduced with permission of Wiley-VCH. (c) Fabrication of the cross-linked PEN. (d) DMA of the PEN treated at different temperatures [46]. Source: You et al. [46]. Reproduced with permission of the American Chemical Society.

bandgap enables the conduction current of POFNB to be effectively restrained at high temperatures and in high fields, thus obtaining excellent insulation performance at 150 °C.

Cross-linking is a process in which polymers are linked by covalent bonds to form networks. There are substantial intermolecular forces in cross-linked polymers that significantly restrict the movement of molecular chains. For example, You et al. [46] synthesized self-cross-linking poly(arylene ether nitriles) (PEN) at different temperatures, and the high temperature resistance of PEN was significantly improved. As shown in Figure 1.8c, the phthalocyanine rings were formed by the cross-linking of phthalonitriles at the end of PEN at 320 °C, while the –CN groups on the side chains of PEN participate in the reaction to form triazine rings at 350 °C. Figure 1.8d illustrates that the 350 °C cross-linked PEN had a high T_g of 370 °C, and its operating temperature reached 300 °C.

Strong intermolecular interactions resulting from the introduction of polar groups in polymer chains have also been used to suppress the motion of molecular chains and improve high temperature resistance. Zhu et al. [47] synthesized a new type of diamine monomer with two ortho-position nitrile groups in the benzene ring through chemical reactions and obtained a series of PI after reacting with different dianhydrides. It was found that T_g was improved by the introduction of nitrile groups. Moreover, the strong interaction between nitrile groups enhances the mechanical properties of PI. Tang et al. [48] achieved the improvement of T_g and Young's modulus of polystyrene (PS) by introducing nitro groups. It is worth noting that the thermal decomposition of nitro groups results in a slight decrease in T_d of the polymer.

1.5.3 High-Temperature Polymer-Based Composite Materials

Polymers have great designability due to their diverse chemical structures. Moreover, it is also an effective way to enhance the high-temperature properties of traditional polymers by introducing fillers to prepare polymer-based composites.

Inorganic fillers have the advantages of excellent thermal stability and electrical properties, which can be combined with the advantages of machinability and high E_b of the polymers through the two-phase composite method. The thermal stability of inorganic/polymer composite materials is generally higher than that of pure polymers, which is more obvious at high temperatures. For example, Zahra et al. [49] added 5 wt% sepiolite nanowires into PEI matrix to prepare sepiolite/PEI composite materials. Compared with pure PEI, the T_g of composite material increased from 215 to 223 °C, and the $T_{d5\%}$ increased from 478 to 487 °C. At high temperatures, the polymers will be softened. It was found that the addition of carbon nanotubes (CNTs) enhanced the mechanical properties of polymers at high temperatures. Mamedov et al. [50] fabricated CNTs/PEI composites using a layer-by-layer deposition method. Compared with pure PEI, the modulus of the CNT/PEI composites increases from 0.3 to ~11 GPa, and strength increases from ~9 to 325 MPa. As shown in Figure 1.9a,b, Li et al. [34] thermally cross-linked divinyltetramethyldisiloxane-bis (benzocyclobutene) (BCB) in the presence of boron nitride nanosheets (BNNSs) to obtain c-BCB/BNNS nanocomposites ($T_g > 350$ °C). Due to the high thermal conductivity and wide bandgap of BNNS, the excellent thermal conductivity of 1.8 $\mathrm{W\,m^{-1}\,K^{-1}}$ and high-temperature insulation performance (403 $\mathrm{MV\,m^{-1}}$ at 250 °C) of c-BCB/BNNS were achieved.

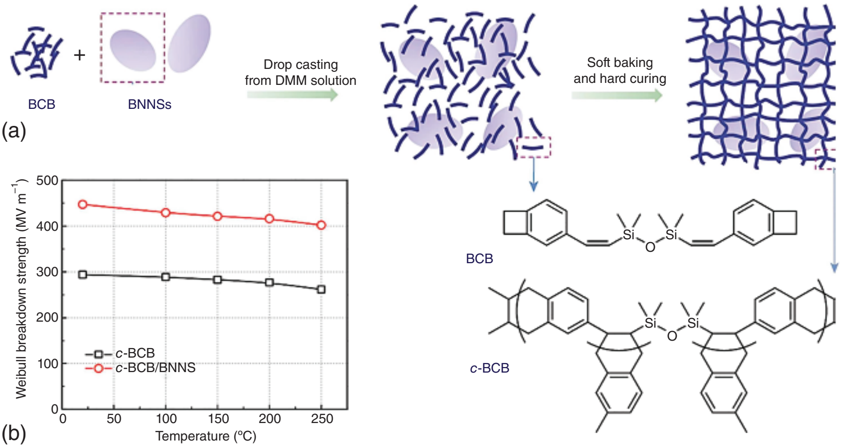


Figure 1.9 (a) Schematic of the synthesis process for c-BCB/BNNS. (b) Weibull breakdown strength of c-BCB and c-BCB/BNNS as a function of temperature [34]. Source: Li et al. [34]. Reproduced with permission of Nature Publishing Group.

The incorporation of inorganic fillers has improved the high temperature and electrical properties of the polymers. However, the introduction of a large number of inorganic fillers leads to poor interfacial compatibility between the two phases, which destroys the flexibility of nanocomposite materials. Compared to polymer-based nanocomposite materials, all-organic composite materials ensure great high-temperature properties while maintaining the inherent flexibility of polymers, which enhances the possibilities of high-temperature polymer applications. Polyacrylonitrile is further dehydrogenated to form a trapezoidal conjugated structure (PcLS) at 400–600 °C. Liao et al. [51] prepared PcLS/PI all-organic composite films by in-situ polymerization, which had an excellent $T_{5\%}$ of 600 °C. Zhang et al. [52] chose PEI and PI to obtain composite materials with excellent high-temperature insulation performance by co-blending method. The strong electrostatic interaction between positive and negative delocalized electrons was used to improve the packing density of molecular chains, thereby reducing voids and lowering the free volume. The composite material of 50 wt% PEI and 50 wt% PI not only had the T_g of 246 °C but also obtained excellent insulation performance (E_b of $550\,\mathrm{MV\,m^{-1}}$) at 200 °C. Zhang et al. [53] designed a novel 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)/PEI composite film. As a molecular semiconductor, NTCDA has high electron affinity, which significantly inhibits carrier migration, thus improving the high-temperature insulation performance of PEI. Compared with PEI film ($E_b = 440\,\mathrm{MV\,m^{-1}}$), the E_b of NTCDA/PEI composite film was $510\,\mathrm{MV\,m^{-1}}$ at 200 °C.

1.6 Summary and Outlook

In summary, researchers have conducted a lot of exploratory experiments on the structure design, preparation process, performance optimization, and application scenarios of high-temperature polymer materials. It is remarkable that many high-temperature polymers have been commercialized and applied to power equipment. The development of high-temperature polymers makes it possible to break through the bottleneck of their poor temperature resistance. However, as the power equipment in various fields needs to cope with a more severe working environment, higher requirements are put forward for high-temperature polymers. The growth of high-temperature polymer materials needs to pay attention to the following issues:

1. Based on the design of molecular structure, it is crucial to optimize the morphology of molecular chains through the preparation process for intrinsic high-temperature polymers. In order to ensure the uniform dispersion and reasonable distribution of the fillers in the polymer matrix, the surface modification of the fillers and the design of the multiple structures should be paid attention to in polymer-based composite materials.
2. It is crucial to explore and understand the inherent mechanisms of high-temperature polymers with the participation of various simulation models. On

the one hand, the molecular structure of the initial screen can be obtained by molecular simulation of the intrinsic polymers, which reduces the cost of the traditional “trial and error” method. On the other hand, simulation models are often used to understand the influence of two-phase interfacial compatibility on the properties of high-temperature polymer-based composite materials. In addition, the screening conditions for high-temperature polymers should not be limited to their high thermal stability and electrical properties. Film forming and mechanical properties should be considered together to greatly improve the possibility of future applications.

3. In the early development stage of high-temperature polymers, excessive attention is paid to their thermal stability while their processability is ignored. For example, the introduction of a large number of aromatic rings increases the thermal stability but makes the polymer insoluble and difficult to reprocess. The cooperative regulation mechanisms of processability and high temperature resistance should be established. In the long term, successful production of high-temperature polymers requires innovative structural design and preparation processes to balance the relationship between the above two parameters.
4. On the basis of the third issue, excellent electrical properties such as high insulation, corona resistance, and low loss should be maintained at high temperatures to meet the different requirements of each electrical field. It is necessary to strengthen the coordination between high-temperature polymers and application scenarios to provide targeted performance optimization.

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