Recent Progress in the Research and Industrialization of Polyarylene Sulfide Resins

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Abstract: Polyarylene sulfide resins are regarded as one of the most important high performance polymers and have expanded their application fields rapidly due to their excellent mechanical, thermal and electrical properties. The advances in the synthesis, modification and industrialization of several important polyarylene sulfide resins including PPS, PASS, PASK, PASA and PACS are reviewed. Directions in the research and development of PAS resins are also suggested.
Keywords: High performance polymer; Polyarylene sulfide; Polyphenylene sulfide; Industrialization

Introduction

Polyarylene sulfide (PAS) resins, with the repeating structural unit $[\text{-Ar-S-}]_n$, which the athioether and aromatic group bonded alternately in the main backbone, have attracted intensive attention as one of most important high performance engineering plastics during the past decades. Benefiting from their special chemical constituent and rigid molecular structure, PAS resins usually possess outstanding heat resistance, chemical resistance, fire retardance and dimensional stability over conventional engineering plastics such as nylon, polycarbonate, polybutylene terephthalate and polyacetal et al. Due to their excellent comprehensive properties, the PAS family and their copolymers are a highly versatile group used in various industrial applications including composites, fibers, films and coating materials [1].

Commercially available PAS resins include polyphenylene sulfide (PPS), polyarylene sulfide sulfone (PASS), polyarylene sulfide ketone (PASK), polyarylene sulfide sulfone imide (PASSI) and polyarylene sulfide amide (PASA). These PAS resins are all of industrial interest for their excellent mechanical and thermal properties. The incorporation of different polar groups into the molecular structure of PPS usually changes its physical properties. For example, PPS and PASK are crystallizable while PASS is amorphous. PASA is able to form liquid crystalline phase, and PASSI possesses the advantages of polyimide (PI). Moreover, the preparation of polyarylene sulfides with pendant nitriles or methyl groups, such as PASN and amorphous PPS, has also been reported. Representative examples of PAS resins are listed in Table 1.

1. Polyphenylene sulfide (PPS) [1-3]

Polyphenylene sulfide (PPS) is undoubtedly the most attractive PAS resin which has applied widely in the fields of electronic, electric, automobile and other general machine parts. Various synthesis routes of PPS reported in academic researches and industrial manufacture are concluded in Fig 1.

Despite its superior performances, pure PPS resin has several intrinsical defects which hinder its further expansion in practical applications:

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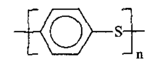
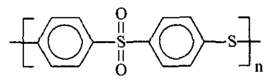
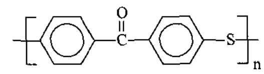
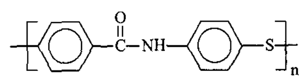
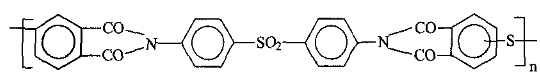
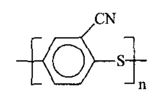
Tabel 1 Several possible PAS resins with different chemical structures

Polymer	Repeat unit
Polyphenylene sulfide (PPS)	
Polyarylene sulfide sulfone (PASS)	
Polyarylene sulfide ketone (PASK)	
Polyarylene sulfide amide (PASA)	
Polyarylene sulfide sulfone imide (PASSI)	
Poly(arylene sulfide nitriles) (PASN)	

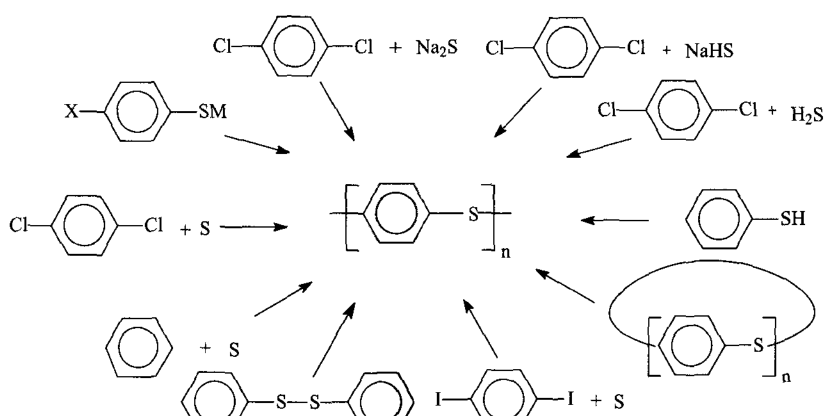


Fig 1. The synthesis routes of PPS resin

(1) Pure PPS with rigid backbone possesses a crystallization degree of nearly 75%, which results in its notable brittleness. Different reinforcing and toughening technologies for different PPS composites are necessary in order to improve the toughness of PPS resin;

(2) The cost of PPS is 1~2 times higher than that of conventional engineering plastics;

(3) PPS exhibits good chemical resistance but also poor colorability;

(4) The high melting temperature of PPS (about 285°C) leads to high processing temperature, which increases the feasibility of thermo-oxidative cross-linking and decreases the fluidity of PPS during processing.

Furthermore, the moderate strength of pure PPS makes the mechanical modification of PPS becomes the critical issue in the research. The main research contents related includes:

(1) Strengthening [4]: Through melt blending, PPS resin compounded with other material (inorganic material, organic material or other polymers), presents improved mechanical properties: enhance the tensile strength greatly while retain other properties. By this way, the high-performance antistatic

materials can be achieved.

(2) Toughening [5-8]: PPS are usually brittle and easily cracked, rubber modification has been found to be efficient in improving the toughness of brittle PPS resins. Moreover, PPS nano-composites, prepared via melt-graft and melt mixing method, is also an effective modifying way to decrease the brittleness of PPS.

(3) Tribological behaviour [9-13]: As a kind of polymeric friction materials, PPS and its composition show excellent heat-resistance in specific rigorous conditions such as high temperature bearing. It is necessary and significant to exploit new PPS friction composites and to analyze their mechanism of wear influencing the wear characteristics. Commercial available PPS friction materials including the composites of PPS filled with other self-lubricated materials such as PTFE and TLCP, which the friction coefficient and the wear loss of the PPS can be greatly reduced.

(4) To enhance the electrical performance and develop novel functional hybrid materials [14-16]: PPS is reported to have good compatibility with many kinds of inorganic functional fillers and versatile processing methods can be utilized to process their hybrids. Therefore, functionalized structural materials with brilliant mechanical, chemical, electrical, optical and thermal properties can be manufactured by blending various functional filler with pure PPS resin, which will absolutely broaden the application fields of PPS and represents the main trend in the development of function-structure materials.

Now, with the global yield exceeding 70000 t/a, PPS resins have becoming the primary class of high-performance plastics and the sixth engineering materials. However at present, only USA, Japan and China hold related synthesis techniques of PPS and can offer commercial PPS resin. The Chevron-Phillips Chem.(USA), Kureha Corporation(Japan), Fortron Industries, DIC (Japan) and Deyang Science & Technology (PRC) are the main manufacturers of PPS resins in the world.

Hotspots in the researching and exploitation of PPS include fibers and films [17-22]. In 1983 the high-performance PPS fibers were firstly industrialized by Phillips Fibers Corporation (USA). Later, in the year of 1987 the Toray, Toyobo, Teijin and Kureha Corporation, etc. had also announced their own PPS fiber products. At the same time, Daiwabo Rayon (Japan) was the first corporation which commercialized PPS fibers as industrial filtration cloth. Thanks to the excellent heat resistance, chemical resistance, fire retardance and outstanding filtration efficiency, the PPS fibers now has been used in applications requiring high resistance to chemical media and heat, such as flue gas filtration media for coal fired power generation stations and refuse incineration plants.

The studies on the PPS films began in 1980s. Toray Company applied for patent of the technique of PPS biaxial stretching film in 1987. Then the synthesis of film-grade PPS resin and the processing of PPS films were industrialized in the same year by Toray Corporation and Phillips Petroleum Company simultaneously. PPS films are the F-grade insulation film with outstanding performance-price ratio. PPS films are the primary candidate for heat resistance electronic component manufacture and can be used in preparing high-performance composites in the fields of aeronautics and aerospace.

Unlike the injection-grade, PPS resins for fiber and film use have to meet the requirement in the molecular weight, the molecular weight distribution and purity. At present, Japan has achieved great progress in these fields. In 2007, Deyang Science and Technology Co., Ltd and China Textile Academy have taken a join-research program of "the industrialization of PPS spinning" which is financially supported by Science research committee of China. Moreover, the PPS film research performed by Sichuan University (SCU) has been listed in the 863 program of China.

In China, the primary and the most successful forces for PPS related research are come from the cooperation between SCU and Sichuan Deyang Science and Technology Corporation. The Materials Science and Technology Institute of SCU joined in the research and development of PPS as early as 1970s, and have undertake the related national projects for more than 20 years, and has become the most comprehensive and authoritative organization of PPS industry in China. The investigation of PPS in the SCU, such as synthesis route, properties, characterization and industrialization, as well as manufacture and exploitation, has impact on the world. Although Deyang Science and Technology Cooperator engages in the development of PPS resin in recent years this do not prevent this company becoming the most successful leading enterprises in the field of PPS in China. Deyang Science and Technology Cooperator built up the kiloton PPS synthesis equipments at the end of 2002 and for the first time to produce and sell the PPS resin in 2003. Thereafter, the company became the chief domestic PPS manufacturer and exporter of China. In 2007, one suit of 6 kt/a integrated PPS synthesis equipments was put into production, and in 2008 another new suit of 5 kt/a will be built up in Deyang. At present, the production scale of the company is still expanded steadily.

2. Polyarylene sulfide sulfone (PASS) [23-33]

Polyarylene sulfide sulfone (PASS) or polyphenylene sulfide sulfone (PPSS), firstly reported by Phillips Petroleum Company in 1988, is another important member with good thermal properties in the PAS family. PASS has been described as an amorphous polymer with a T_g around 215~216°C, having excellent electrical and mechanic properties, outstanding heat, chemical resistance and fire retardance.

Compared with PPS, PASS reinforced composites have increasing strength retention at high temperature and better flame retardancy, which suggest the resin is more suitable for heat-resistant composite materials. The solubility of PASS suggests new possibilities in the processing of film- and fiber- forming polymer from solution. PASS can also serve as compatilizer of crystalline and noncrystalline resin.

Currently, the improvement in the synthesis methods of PASS as well as expanded application of the resin has attracted widely attention. PASS was first commercialized by American Phillips Petroleum with the trade name of Ryton S. SCU has carried out the study of PASS synthesis since 1970s. Recently, the research of PASS in SCU has made great progress under the support of the high technology (863) program of China. At present, high molecular weight PASS product can be achieved stably at atmospheric pressure. Corresponding pilot test program for the synthesis of PASS resin is in process. Various PASS products with high heat and corrosion resistance, such as dense film, flat membrane, hollow fiber and nanofibers, have been prepared and characterized successfully.

3. Polyarylene sulfide ketone (PASK) [33-36]

Polyarylene sulfide ketone (PASK) or polyphenylene sulfide ketone (PPSK) is a new kind of crystalline PAS with good heat resistance and chemical resistance. PASK has a melt temperature (310-380°C) which is close to the T_m of polyether ether ketone (PEEK) but a cost which is much cheaper than that of PEEK. PASK have excellent heat resistance and moldability and have utilities in coating materials, molded objects, fibers and films.

PASK resin was first developed by Japan Toson Corporation in 1968 and realized industrialization production by Japan Kureha Chemical Industry Co., Ltd in 1987. Currently, other organizations which still carrying on the research of PASK are Phillips Petroleum Company in U.S.A, SCU and Shandong

University of Technology in China。

4. Polyarylene sulfide amide (PASA) [37-42]

Another important member of the PAS family is polyarylene sulfide amide (PASA), which possesses the improved heat resistance and dissolubility, and exhibits the liquid crystalline behavior at certain temperature due to the strong polar amide group in the main chain. PASA has similar processbility with PPS and can serve as molded objects, fibers and films. Moreover, PASA can dissolve in concentrated sulfuric acid, NMP/LiCl, and other polar organic solvents.

In 1988, Ishikawa Tomohiro firstly prepared PASA from an amide group-containing dihalide and an aromatic dihalide with sulfidation agentsby. Zuowang Zhou and Qixian Wu synthesized PASA by polycondensation of thiourea and sulfur, in stead of sodium sulfide with 4-chloro-N-(4'-chlorophenyl)-benzamide. The research on PASA still focuses on the synthesis, nanofibers and the application; however, there are absent industrial report all over the world right now.

5. Polyarylene sulfide sulfone imide (PASSI) [42-47]

To enhance the thermal properties of the PPS, various modifications of the polymer structure have been proposed, including the introduction of appropriate conjugate substituent into the polymer backbone, during which a monomer containing the ring of imides was firstly synthesized and then imide ring was introduced into PAS backbone to give a novel thermoplastic material—Polyarylene sulfide sulfone imide (PASSI) with improved heat-resistance.

The novel heat-resistant material PASSI has a glass transition temperature T_g about 252.4°C and the initial thermal decomposition temperature around 484.9°C. An important tendency which combines functional groups of PPS and PI in the new thermoplastic material is now under research, and bear an important enlightening significance in the development of advanced materials.

6. Polyarylene sulfide nitrile (PASN) [48-49]

Polyarylene sulfide nitrile (PASN) was first synthesized by Tetsuya, a Japanese researcher, in 1983. The introduction of polarized side group onto the PPS's backbone significantly increased the heat resistance of the polymer. Compared with PPS, PASS, PASK, the thermal stability of PACS has greatly improved. The melting point of PACS is up to 440~460°C, however solubility of the polymer is the very poor. It can not be dissolved in common organic solvents except the concentrated sulphuric acid. The excellent solubility can be ascribed to the existence of oil resistant nitrile group. In the automotive, electronic, precision instruments, optoelectronic communications and aerospace and other fields PACS have broad prospects. Synthesis and preparation research of PACS are mainly performed in Japan, and no related research has so far been reported in China.

7. Research and development on PAS resins

The main development directions of the PAS resins could be concluded as follows:

(1) To develop novel PAS resin with higher heat resistance and more excellent performance to meet the specific demand of high technology. **[50-51]**

(2) To explore new synthetic route of PPS-- the latent revolution, that is prepare the highly purified and high performance PPS resin at room temperature and atmosphere pressure.

(3) To realize the industrialization of special PAS resins, such as fiber-grade, film-grade, extrusion-grade and resin used in preparing high performance composites.

(4) To prepare and develop novel PAS fibers, films, nanofibers and other functional materials.

In the next five years, it is expected that the demand of PPS of the world will increase by at least 10% per year. The demand of PPS will enlarge more rapidly with the development of automobile, electronic technology and other new high-tech industry, which implying a good chance as well as a great challenge for the PPS industry.

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