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Advancements in Polymeric Capillary Materials for Chromatographic Applications

Amar Mohite[1],*, Jayant Rajaram Pawar[2], Rohan S. Phatak[3]

Abstract

Traditionally, glass capillaries have been the material of choice due to their inertness, transparency, and precision in delivering small sample volumes. However, glass capillaries have significant drawbacks, including fragility, limited flexibility, and difficulties in modification for specialized applications. Recent advancements in polymer chemistry have introduced novel polymeric capillary materials that offer several advantages over conventional glass capillaries. Additionally, they exhibit enhanced durability and resistance to a broad range of chemicals, expanding their applicability in complex analytical procedures. These materials can be engineered to possess specific surface properties through polymer modifications and specialized coatings, improving sample adhesion and migration behavior. Such enhancements contribute to more accurate and reproducible chromatographic results, addressing the increasing demand for high-performance analytical tools in modern laboratories. The development of polymeric capillaries also facilitates miniaturization and integration into advanced analytical systems, such as microfluidic devices, where traditional glass materials may be impractical. Moreover, polymeric capillaries can be produced more cost-effectively and in diverse geometries, allowing for tailored solutions to specific analytical challenges. This paper explores the evolution of polymeric capillary materials, their functional advantages over traditional glass capillaries, and their expanding role in analytical chemistry. It also discusses the potential future directions for polymer innovation to meet the growing needs of precise and efficient chromatographic analysis.

Keywords: Polymeric capillaries, chromatography, polydimethylsiloxane, polytetrafluoroethylene, surface modification, analytical chemistry

INTRODUCTION

Chromatography [1] is a vital analytical technique used in various scientific disciplines, including pharmaceuticals, environmental science, and biotechnology. It is important to note here about the Capillaries which play a crucial role in sample application and migration, particularly in capillary electrophoresis and microfluidic chromatography [2]. Traditionally, glass capillaries have been the standard choice due to their transparency, chemical inertness, and well-established manufacturing processes.

Polymeric capillaries, derived from materials such as polydimethylsiloxane (PDMS), polytetrafluoroethylene (PTFE), and polyether ether ketone (PEEK), have emerged as promising alternatives due to their enhanced mechanical properties, chemical compatibility, and ease of fabrication. These materials offer several

***Author for Correspondence**
Amar Mohite

[1]Researcher, Department of Research, Krishna Vishwa Vidyapeeth (Deemed to be University), Karad, Maharashtra, India
[2]Associate Professor, Department of Biotechnology, Krishna Institute of Science and Technology, Krishna Vishwa Vidyapeeth (Deemed to be University), Karad, Maharashtra, India
[3]Assistant Professor, Department of Pharmacognosy, Krishna Institute of Pharmacy, Krishna Vishwa Vidyapeeth (Deemed to be University), Karad, Maharashtra, India

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advantages over glass, making them suitable for a broader range in chromatography and related analytical techniques [3].

PDMS-based capillaries facilitate easy integration with lab-on-a-chip systems, allowing for efficient sample handling and manipulation in biological and chemical assays. Additionally, PDMS can be molded into complex geometries, making it an ideal candidate for custom-designed chromatography systems.

PTFE, commonly known as Teflon, is another important polymer used in capillary applications. It is chemically resistant to a wide range of solvents, acids, and bases, making it particularly suitable for liquid chromatography systems where harsh chemical environments are encountered [4]. PTFE capillaries also exhibit low surface energy, which reduces sample adsorption and improves analyte recovery, leading to more accurate analytical results.

Unlike glass capillaries, PEEK capillaries are less prone to breakage, making them more durable and reliable in demanding analytical conditions. Moreover, PEEK's compatibility with a wide range of solvents and buffers further enhances its utility. [5]

Beyond material properties, the fabrication and surface modification of polymeric capillaries are crucial for optimizing their performance in chromatography. Surface coatings and treatments, such as plasma treatment or chemical grafting, can be employed to modify the hydrophilicity, charge, or functional groups of the capillary walls. These modifications can improve separation efficiency, reduce analyte adsorption, and enhance signal detection in analytical instruments.

The transition from glass to polymeric capillaries represents a significant advancement in chromatography, driven by the need for more robust, flexible, and chemically resistant components [6]. With ongoing research and development, polymeric capillaries continue to evolve, offering new possibilities for improving separation techniques, increasing analytical throughput, and expanding the range of detectable compounds in complex samples. As chromatography techniques advance, polymeric capillaries will play an increasingly vital role in enhancing analytical precision and efficiency across diverse scientific fields.

COMPOSITION AND PROPERTIES OF POLYMERIC CAPILLARIES

Polymeric materials used in capillary fabrication must possess specific properties, including high thermal stability, resistance to solvents, and low adsorption of analytes [7]. These properties are essential for ensuring accurate and reproducible analytical results, such as chromatography, microfluidics, and electrophoresis. Several polymers are commonly employed in capillary fabrication due to their advantageous characteristics.

Polydimethylsiloxane (PDMS)

PDMS is flexible, biocompatible, and optically transparent, making it ideal for applications requiring visualization of fluid flow [8]. Additionally, PDMS can be easily molded using soft lithography techniques, allowing for the fabrication of intricate microchannel designs. Despite its advantages, PDMS has some limitations, including its inherent hydrophobic nature, which can lead to analyte adsorption.

Polytetrafluoroethylene (PTFE)

PTFE, commonly known by its trade name Teflon, is another polymer frequently used in capillary fabrication. It is characterized by its exceptional chemical inertness, non-reactivity, and high-temperature resistance, making it suitable for handling aggressive solvents and harsh chemical environments [9-10]. PTFE's low surface energy provides excellent non-stick properties, reducing sample adsorption and improving analytical precision. However, its low surface energy also makes bonding and fabrication more challenging, often requiring specialized techniques such as thermal bonding or surface activation.

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Table 1. Comparative Properties of Common Polymeric Capillary Materials.

Property	PDMS	PTFE	PEEK
Flexibility	High	Moderate	Moderate
Chemical Resistance	Moderate	Excellent	Good
Thermal Stability	Low	High	High
Surface Energy	High (hydrophobic)	Low (non-stick)	Moderate
Ease of Fabrication	Easy (soft lithography)	Difficult (specialized bonding)	Easy (extrusion)
Transparency	Transparent	Opaque	Opaque
Biocompatibility	High	High	High

Polyether Ether Ketone (PEEK)

PEEK can be easily extruded into precise capillary dimensions, ensuring consistency and reliability in analytical instruments. However, PEEK may have some limitations involving extreme pH conditions or highly oxidative environments.

Polyacrylamide and Polyethylene Glycol (PEG) Coatings

Surface modification plays a crucial role in capillary fabrication, especially when it comes to minimizing analyte adsorption and improving performance. Polyacrylamide and PEG coatings are commonly used to modify the surface properties of polymeric capillaries [11]. Polyacrylamide coatings help reduce electroosmotic flow (EOF) in electrophoresis applications, leading to improved separation efficiency. PEG coatings, on the other hand, are widely employed to create hydrophilic surfaces that resist protein and biomolecule adhesion. These coatings are particularly useful in bioanalytical applications, where sample integrity and reproducibility are critical. Table 1 has shown the comparative properties of common polymeric capillary materials.

ADVANTAGES OF POLYMERIC CAPILLARIES OVER GLASS CAPILLARIES

Enhanced Durability

One of the most significant advantages of polymeric capillaries is their durability. Unlike glass, which is inherently fragile and prone to breakage, polymeric materials are much more resilient. This increased durability reduces the risk of accidental breakage, which is particularly beneficial in laboratory settings where handling delicate components is routine [12]. The reduced likelihood of breakage also minimizes the risk of injuries to researchers and technicians, ensuring a safer working environment. Additionally, avoiding breakage helps prevent sample loss, which is crucial when working with rare, expensive, or sensitive materials.

Flexibility

This flexibility allows for easier handling and integration into complex systems where precise bends or curves are necessary [13]. For example, in microfluidic devices, where precise control over fluid movement is essential, polymeric capillaries can be customized to fit specific geometries. Additionally, their adaptability makes them ideal for portable or field-based system, where rigid materials may pose challenges in terms of handling and transportation.

Superior Chemical Resistance

Chemical resistance is a critical factor when selecting capillaries, especially for system involving harsh substances. Certain polymeric materials exhibit superior resistance to acidic and basic conditions, ensuring that they maintain their structural integrity and functionality over extended periods [14]. Unlike glass, which can be etched or degraded by strong acids and bases, chemically resistant polymers remain stable, preventing contamination and degradation. This characteristic is particularly beneficial in analytical chemistry, biopharmaceutical processes, and environmental testing, where exposure to reactive chemicals is common. The enhanced longevity of polymeric capillaries reduces the frequency of replacements, ultimately leading to greater efficiency and cost savings.

Cost-Effectiveness

Another compelling reason to choose polymeric capillaries over glass alternatives is their cost-effectiveness. The production of polymeric capillaries is often more economical than that of precision-cut glass capillaries [15]. Glass requires intricate manufacturing processes, including precise cutting and polishing, which can drive up production costs. In contrast, polymeric materials can be mass-produced using cost-efficient techniques such as extrusion or injection molding. The affordability of polymeric capillaries makes them accessible for a wide range of industries, including academic research labs, industrial testing facilities, and commercial diagnostic applications. Furthermore, their durability and chemical resistance contribute to long-term cost savings by reducing the need for frequent replacements.

SURFACE MODIFICATIONS AND COATINGS FOR IMPROVED PERFORMANCE

Polymeric capillaries have gained significant attention due to their durability, flexibility, and cost-effectiveness. However, their performance can be further enhanced through surface modifications and specialized coatings. These treatments allow for improved control over fluid dynamics, analyte interactions, and chemical compatibility, making polymeric capillaries even more suitable for advanced applications in chromatography, microfluidics, and biomedical analysis [16]. Below are some key strategies used to enhance the performance of polymeric capillaries.

Hydrophobic and Hydrophilic Coatings

One of the most common ways to optimize polymeric capillary performance is by tailoring the surface to be either hydrophobic or hydrophilic, depending on the intended application.

- *Hydrophobic coatings:* reduce surface wettability, preventing water and polar solvents from adhering to the capillary walls. This is particularly beneficial in gas chromatography (GC) and other applications where nonpolar interactions dominate [17]. Hydrophobic coatings can also help minimize unwanted adsorption of biological molecules, improving accuracy in biomedical assays.
- *Hydrophilic coatings*: on the other hand, enhance water compatibility, which is essential in liquid chromatography (LC) and electrophoretic separations. These coatings improve the migration of aqueous solutions, reducing capillary fouling and enhancing separation efficiency.

Functionalized Nanoparticles for Enhanced Selectivity and Sensitivity

The integration of functionalized nanoparticles onto the surface of polymeric capillaries represents a cutting-edge approach to improving analyte detection and separation. Benefits are as follows;

- *Increased surface area*: Nanoparticles significantly enhance the available reactive surface, allowing for better interaction with analytes.
- *Improved selectivity*: Functional groups attached to nanoparticles can be tailored to bind specific molecules, improving target analyte detection. For example, attaching antibodies or aptamers to nanoparticles enables precise biosensing applications.
- *Enhanced sensitivity:* The presence of nanoparticles can amplify signals in detection techniques such as fluorescence, electrochemical, or surface-enhanced Raman spectroscopy (SERS), leading to higher sensitivity in analytical measurements.

Plasma Treatment and Grafting Techniques for Flow Optimization

- *Plasma treatment*: exposes the capillary surface to ionized gas, altering its chemical composition and increasing adhesion sites for subsequent coatings or modifications. This technique is commonly used to enhance hydrophilicity for improved flow dynamics in thin-layer chromatography (TLC) and microfluidic systems [18].
- *Grafting techniques*: involve covalently attaching functional molecules onto the polymer surface. This allows for precise control over surface charge, wettability, and chemical compatibility, leading to improved separation performance in analytical applications.

APPLICATIONS IN THIN LAYER CHROMATOGRAPHY (TLC) AND OTHER ANALYTICAL TECHNIQUES

TLC Spotting and Analysis

Thin-layer chromatography (TLC) is a widely used technique for separating and analyzing chemical compounds. Polymeric capillary devices enhance TLC performance by enabling more precise sample application and controlled solvent evaporation.

- *Precision in sample spotting*: Traditional sample application methods can result in irregular or oversized spots, leading to poor resolution. Polymeric capillaries allow for controlled deposition of small, uniform sample spots, improving separation quality.
- *Controlled solvent evaporation*: The material properties of polymeric capillaries help regulate solvent delivery, reducing evaporation inconsistencies and ensuring reproducible results.

Improved Handling and Safety: TLC Spotting and Analysis

- Thin-layer chromatography (TLC) is a widely used technique for separating and analyzing chemical compounds. Polymeric capillary devices enhance TLC performance by enabling more precise sample application and controlled solvent evaporation.
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- *Controlled solvent evaporation*: The material properties of polymeric capillaries help regulate solvent delivery, reducing evaporation inconsistencies and ensuring reproducible results.
- *Improved handling and safety*: Unlike fragile glass capillaries, polymeric alternatives are easier to handle, reducing breakage-related sample loss and contamination.
- With these advantages, polymeric capillaries are becoming essential tools for pharmaceutical quality control, food safety testing, and forensic analysis.
- Microfluidic Systems and Lab-on-a-Chip Devices
- Polymeric capillaries are widely used in lab-on-a-chip devices, which integrate multiple laboratory functions into a small, portable platform for rapid diagnostics and analysis.

- *Efficient fluid transport*: Polymeric capillaries facilitate controlled fluid flow in microfluidic channels, ensuring precise reagent mixing and reaction control.
- *Point-of-care diagnostics*: Lab-on-a-chip devices utilizing polymeric capillaries are used for quick medical diagnostics, such as blood tests, infectious disease detection, and cancer biomarker screening.

By incorporating polymer-coated capillaries, researchers and industries benefit from:

- *Enhanced Separation Efficiency*: Polymer-coated capillaries provide improved analyte interactions, leading to sharper chromatographic peaks and better resolution.
- *Minimized Sample Contamination*: Glass capillaries may introduce silanol interactions or metal ion contamination, while polymer-coated capillaries offer inert surfaces that reduce unwanted interactions.
- *Greater Chemical Compatibility*: Certain polymeric coatings exhibit superior resistance to harsh solvents, enabling more robust and long-lasting performance in chromatography.

Biomedical Applications: Drug Screening and Biomolecule Analysis

- The biomedical field greatly benefits from polymeric capillary-based methods in drug screening and biomolecule analysis.
- *Drug discovery and testing*: Capillary electrophoresis with polymeric capillaries is used for high-throughput drug screening, allowing for rapid analysis of pharmaceutical compounds.
- *Protein and DNA analysis*: Polymeric capillaries provide a stable and inert environment for separating and analyzing proteins, nucleic acids, and other biomolecules, which is essential in genetic research and personalized medicine.
- *Minimal sample requirements*: Polymeric capillary-based techniques require very small sample volumes, making them ideal for applications involving scarce or expensive biological specimens.

Microfluidic Systems and Lab-on-a-Chip Devices

Microfluidics is a rapidly growing field that relies on the precise control of fluids at the microscale. Polymeric capillaries are widely used in lab-on-a-chip devices, which integrate multiple laboratory functions into a small, portable platform for rapid diagnostics and analysis.

- Efficient Fluid Transport: Polymeric capillaries facilitate controlled fluid flow in microfluidic channels, ensuring precise reagent mixing and reaction control.
- Point-of-Care Diagnostics: Lab-on-a-chip devices utilizing polymeric capillaries are used for quick medical diagnostics, such as blood tests, infectious disease detection, and cancer biomarker screening.
- Cost-effective Manufacturing: Unlike glass microfluidic systems, polymeric capillary-based devices can be mass-produced using economical fabrication techniques like injection molding.

High-Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC)

Polymeric capillaries play an important role in HPLC and GC, two of the most widely used analytical separation techniques. By incorporating polymer-coated capillaries, researchers and industries benefit from:

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FUTURE PERSPECTIVES AND INNOVATIONS

Self-healing Polymers

Self-healing polymers are one of the most promising innovations in the field of polymeric capillaries [19]. This breakthrough is particularly beneficial in applications where capillaries are exposed to harsh conditions, frequent handling, or prolonged use.

- *Repairing microcracks and damage*: Over time, polymeric materials can develop microcracks or other forms of mechanical damage. Self-healing polymers can autonomously seal these cracks through chemical or physical reactions, restoring the material's original integrity.
- *Reduced waste and maintenance*: Since self-healing polymers can recover from damage, the frequency of replacements is reduced, leading to less material waste and lower operational costs. This is especially important in industries like pharmaceuticals, environmental monitoring, and medical diagnostics, where capillary systems must operate reliably over long periods [20].
- *Increased lifespan in extreme environments*: These polymers can withstand high-stress environments or chemical exposure, maintaining functionality even in challenging conditions. Self-healing polymers are particularly advantageous in applications like high-performance liquid chromatography (HPLC), where capillaries are subject to constant fluid flow and potential wear.

Smart Polymeric Capillaries

Smart polymers are designed to respond dynamically to changes in external stimuli such as pH, temperature, or electric fields. pH-Responsive Capillaries: Some polymeric materials change their structure or properties in response to pH shifts [21]. For example, the inner diameter of a polymeric capillary may expand or contract based on the acidity or alkalinity of the fluid passing through it. This can be useful in applications like ion-exchange chromatography or biological assays, where precise control over fluid behavior is critical.

- *Temperature-responsive capillaries*: In applications like microfluidics or drug delivery systems, temperature-responsive capillaries can change their permeability or flow characteristics, enabling adaptive fluid handling.[22]
- *Electric field-responsive capillaries*: Polymers that react to electrical stimuli can enable the development of capillary systems that control fluid flow or separation processes in response to applied voltages, benefiting applications like capillary electrophoresis or electrokinetic separations.[23]

3D Printing and Nanotechnology Integration

3D printing is particularly valuable in the field of microfluidics, where precise channel design is critical to controlling fluid movement and ensuring efficient separation [24]. 3D-printed capillaries can also be produced on demand, reducing lead times and manufacturing costs. The integration of nanotechnology with polymeric capillaries allows for the development of capillaries with functionalized surfaces at the nanoscale. Nanoparticles or nanomaterials can be incorporated into the polymer structure to enhance properties such as surface area, chemical resistance, or sensitivity [25]. For instance, incorporating gold or carbon nanotubes can improve the capillary's ability to detect trace levels of target analytes. Additionally, nanostructured surfaces can increase the efficiency of separations in chromatography and electrophoresis.

CONCLUSION

The transition from traditional glass to polymeric capillaries represents a pivotal advancement in chromatographic applications, marking a shift toward more efficient, durable, and versatile systems. Polymeric materials offer significant improvements over glass, particularly in their superior mechanical properties. Unlike glass, which is fragile and prone to breakage, polymeric capillaries are much more robust, reducing the risk of damage during handling and preventing sample loss or contamination. Their chemical resistance is another key advantage, as certain polymers are better equipped to withstand exposure to aggressive solvents and acidic or basic conditions, ensuring longevity and reliability in a range of analytical processes. Polymeric capillaries are also more cost-effective to produce, offering a more economical alternative to glass, which often requires precision cutting and additional processing. This affordability makes them an attractive option for large-scale manufacturing and routine use, particularly in industries like pharmaceuticals, environmental testing, and food safety. As innovation in polymer chemistry and surface engineering continues, further enhancements are expected. Advances in functional coatings, self-healing materials, and smart polymers responsive to environmental changes will broaden the application scope of polymeric capillaries, improving efficiency and performance. With these ongoing developments, polymeric capillaries are poised to play an even more significant role in shaping future chromatographic techniques, ensuring their widespread adoption in both research and industrial settings.

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