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Modification of Selected Bioactive and Mechanical Properties of Polydimethylsiloxane for External Medical Applications

Extended Abstract

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Advances in materials engineering, particularly in the field of polymeric materials, alongside the increasingly stringent demands of the medical industry, have necessitated the search for alternative solutions, frequently centered on biomaterials and biofillers. The selection of polymers and the methods used for their modification, including the incorporation of fillers, is dictated by the intended application and its specific requirements. These materials must exhibit biocompatibility, often in combination with other properties depending on their use, such as antibacterial, antifungal, or anti-allergic characteristics. Numerous approaches incorporating both inorganic and organic fillers are well-documented, often leveraging synergistic interaction mechanisms to simultaneously influence the biological and physicochemical properties necessary for the intended application. A comprehensive literature review indicates that polymeric materials can be effectively modified with organic fillers for medical applications. Polymers are utilized in a wide range of applications, including medical equipment components, implants, hygiene products, and wound dressings, which determines their functional requirements. Despite the availability of numerous existing solutions, there is a compelling need to develop new materials that can serve as alternatives to current dressings, particularly for long-term use on wounds, while maintaining the necessary antibacterial properties that significantly influence the healing process. A promising response to these needs may lie in the development of biocomposites based on elastomeric materials, specifically modified to confer antibacterial properties.

One of the most commonly employed elastomeric materials is silicone, specifically polydimethylsiloxane (PDMS). Its biocompatibility, high gas permeability, chemical inertness, and thermal stability make PDMS highly desirable for applications requiring both flexibility and durability. In the medical sector, PDMS is utilized in various products, including bandages and wound dressings, which play a crucial role in protecting wounds from infection and facilitating the healing process. Although a range of dressings modified with inorganic additives exists, their production is often associated with time-consuming processes, increased costs, and the need for various chemical agents. Organic additives, which are widely available, may offer a more efficient solution to these challenges. The preparation of materials modified with organic fillers typically requires less time and financial investment, while also reducing the use of chemicals.

Materials derived from plants, including herbs, have a longstanding history in traditional medicine for the treatment of various diseases, largely due to their content of polyphenols and terpenoids, which possess antibacterial, anti-inflammatory, antioxidant, and anti-allergic properties. Many herbal additives are currently being incorporated into polymeric matrices, and studies have demonstrated their beneficial effects on biological properties, particularly in the context of wound dressings.

Based on an extensive literature review, several key points have emerged:

- Polydimethylsiloxane (PDMS) is widely utilized in medical applications due to its biocompatibility, high gas permeability, flexibility, and low reactivity. However, PDMS lacks antibacterial properties.
- Given the growing concern over bacterial resistance, alternative solutions are being explored. Inorganic fillers have been introduced to enhance the antimicrobial properties of dressings, but the production of such materials is costly and time-intensive.
- Natural plant compounds exhibit bioactive properties, but their incorporation into polymer matrices is challenging due to their sensitivity to heat and potential interference with the polymerization process.

Consequently, there is a justified need to explore the development of new PDMS-based materials with enhanced antibacterial properties.

Based on preliminary studies and an extensive literature review, the thesis of this work was developed. **The introduction of specially prepared organic fillers, derived from selected parts of bioactive herbs, into polydimethylsiloxane significantly enhances its antibacterial activity while maintaining the necessary functional properties for external medical applications, such as dressings, i.e., mechanical and physicochemical properties, while at the same time ensuring long-term functionality and reliability in medical contexts.**

To enhance the bioactive properties of PDMS, herbal fillers were selected based on specific criteria, including polyphenolic content, availability, antimicrobial activity, and associated health benefits. The selected herbs were thyme, sage, and rosemary, which were introduced in their raw, modified, and extract forms. Initial experiments revealed that the high content of fats and terpenoids in these herbs inhibited the cross-linking process in the biocomposites, or diminished the functional properties of the materials. Consequently, it was necessary to prepare the fillers by grinding (all herbs), pre-extracting soluble fractions with ethyl alcohol (sage and rosemary), and, in the case of rosemary, additionally exposing the material to water vapor. These modifications successfully reduced the fatty compounds that interfered with PDMS cross-linking, thereby improving the stiffness of the resulting biocomposites. The final group of fillers consisted of polyphenolic extracts from the selected herbs. All fillers were characterized in terms of their morphology, density, total polyphenol content, and phytochemical composition to assess their impact on the desired material properties.

Biocomposites were produced using PDMS with varying concentrations of each herb: 2.5%, 5%, 7.5%, and 10 wt.%, through gravity casting. For unmodified thyme and sage, only two biocomposites were produced, at 5% and 10% concentrations. Due to the significant impact of fatty acids and terpenoids in rosemary, the production of biocomposites from unmodified rosemary was not feasible. To evaluate the effects of fillers with differing structures and phytochemical compositions on the physicochemical, mechanical, and biological properties of the biocomposites, the materials were subjected to a series of tests, including density, wettability, absorbance, crystallinity, rebound resilience, hardness, abrasion resistance, static tensile testing, antibacterial activity, and cell viability assay. In the final phase, accelerated degradation tests were conducted in an artificial plasma environment, mimicking the conditions of potential applications. The impact of modifications and degradation on the structural changes in the material was assessed through FTIR spectral analysis.

The results of the study demonstrate that the incorporation of selected herbal additives into polydimethylsiloxane significantly affected the mechanical properties of the resulting materials. Biocomposites containing unmodified herbal additives exhibited a notable reduction in both tensile stress and tensile strain at break. This reduction can be attributed to the presence of large particles within the unmodified herbs, which tended to detach under tensile stress, leading to the formation of voids that acted as notches, thereby decreasing the overall tensile strength of the material.

The modification of the herbs, primarily through the reduction of terpenes, fatty acids, and larger particles, resulted in a substantial improvement in the mechanical properties of the biocomposites. However, the materials containing modified sage and rosemary fillers still demonstrated inferior mechanical properties compared to those based on thyme. Microscopic analysis of the fracture surfaces revealed that these differences were largely due to the presence of agglomerates in the sage and rosemary composites. By contrast, biocomposites incorporating herbal extracts displayed lower mechanical properties than those with either unmodified or modified herbs, suggesting that both fatty and polyphenolic compounds play a critical role in defining the material properties.

Although the biocomposites exhibited lower stress at break, certain materials, particularly those incorporating modified thyme, displayed higher strain at break values than pure PDMS. This increase in strain is a desirable attribute for applications where flexibility is critical, such as wound dressings, as it enhances patient comfort. The largest variations in value were observed in biocomposites containing unmodified herbs, while materials with modified fillers showed smaller deviations from the reference material, with strength reductions of up to 23%. Similar patterns were observed in hardness tests, where changes did not exceed 10%. However, the variability in hardness results was influenced by both the measurement methodology and the inherent hardness of the fillers. Moreover, higher filler concentrations generally resulted in more consistent property measurements, likely due to the increased herb content leading to sedimentation, which contributed to a more uniform distribution within the matrix.

Several factors likely contributed to the variability in the results, including the methods used to prepare and incorporate the fillers, sedimentation, particle agglomeration, and detachment during testing. These findings were further corroborated by FTIR spectroscopy, which revealed a reduction in the intensity of peaks associated with the mechanical strength of the material.

Additionally, the hydrophobic nature of PDMS remained largely unaffected by the addition of herbal fillers, regardless of their type or concentration. Contact angle measurements for the biocomposites were consistent with those of the reference material, indicating that the incorporation of polyphenolic compounds, known for their hydrophilic properties, had minimal impact on the overall hydrophobicity of the material.

Antibacterial activity assays confirmed that the biocomposites inhibited the growth of *Staphylococcus aureus*, a common pathogen responsible for wound infections. All tested materials, except the unmodified PDMS, exhibited either bacteriostatic or near-bactericidal activity against *S. aureus*. However, the antibacterial efficacy decreased when modified herbs were used as fillers. While the unmodified additives resulted in a 4.4 log reduction, the modified herbs only achieved approximately 2.5 at the same filler concentrations, highlighting the role of terpenes and fatty acids in inhibiting biofilm formation.

Based on these findings, PDMS composites containing modified herbal fillers were selected for further investigation due to their potential use in wound dressings. The reference material, unmodified PDMS, was also subjected to additional testing.

In vitro absorption studies in an artificial plasma environment indicated that the hygroscopic nature of the herbal fillers and the morphology of the leaves from which they were derived played a significant role in water retention. Among the tested biocomposites, those containing rosemary exhibited lower water retention due to the waxy nature of its leaves, whereas those containing sage and thyme, characterized by a dense network of trichomes on the leaves, demonstrated higher moisture retention. The sample preparation method, which involved cutting and the interaction of fillers with the plasma environment, contributed to the variability of the results, particularly as the incubation period extended. Despite this variability, biocomposites with the lowest filler content (2.5 wt.%) showed stabilization of absorption after 72 hours. The presence of water was further confirmed by FTIR analysis, which identified a broad peak corresponding to hydroxyl groups. In the context of wound dressing applications, absorption is a critical property, as it facilitates the effective management of exudate, thus promoting an optimal healing environment.

Another important group of properties related to the potential application of the developed biocomposites, particularly for ensuring patient comfort in wound dressings, includes rebound resilience and abrasion resistance. In terms of resilience, all thyme-based biocomposites, except those with the highest filler concentration, exhibited higher resilience compared to the reference PDMS samples. In contrast, the other biocomposites showed reduced resilience relative to unmodified PDMS. These variations can be attributed to the specific properties of the fillers. For instance, the increased stiffness of rosemary particles contributed to a stiffer material overall, which in turn diminished its ability to recover its original shape after deformation. The smaller particle size of thyme and sage, on the other hand, contributed to enhanced resilience. However, at higher filler concentrations in sage- and rosemary-based composites, the formation of agglomerates disrupted the even distribution of impact energy, leading to reduced flexibility. Notably, the resilience tests were conducted on a thin layer of pure PDMS. This choice was made because the side with higher filler concentrations is intended to contact the wound, while the pure PDMS side would be exposed to external factors, such as clothing.

Regarding abrasion resistance, all biocomposites exhibited a reduction in resistance as filler concentration increased. Similar to the rebound resilience outcomes, the formation of agglomerates negatively impacted abrasion resistance. Additionally, higher concentrations of fatty compounds resulted in greater material loss. The degree of crystallinity also influenced these results, as lower crystallinity values indicated a more amorphous and less stiff material, which made the biocomposites more prone to wear. These trends were correlated with the hardness measurements, where reduced resistance to deformation was associated with increased susceptibility to wear upon contact with rigid surfaces. It is important to emphasize that the testing conditions for abrasion were more demanding than those encountered during typical use, suggesting that the materials' real-world performance could be more favorable. Spectral analyses from FTIR confirmed the impact of fillers on the mechanical properties.

Furthermore, accelerated degradation studies were conducted in an artificial plasma environment to simulate conditions of use. Tensile tests and FTIR analyses were employed to assess the changes in mechanical properties during degradation. For the reference PDMS material, a decrease in stress at break was initially observed, followed by an increase after seven days of incubation, suggesting increased cross-linking. This was confirmed by stronger peaks in the FTIR spectra. Thyme-based composites demonstrated similar behavior, except for those with the highest filler concentration, which consistently showed a decline in stress due to the excessive filler content. Sage-filled composites exhibited more variable behavior, with higher filler concentrations often reducing both stress and strain at break. Rosemary-based composites showed the lowest values for stress and strain, with increased filler content further decreasing tensile strength. These changes were attributed to filler content and distribution, rather than chemical structure, as confirmed by infrared spectral analysis. It is important to maintain adequate flexibility in wound dressings, even after exposure to accelerated degradation conditions, which are more demanding than typical use scenarios.

Although the primary focus of this research was to develop bioactive materials with antibacterial properties for wound dressings, a complementary cell viability test was conducted to assess their safety for use in direct contact with the human body. Thyme-based composites consistently met or exceeded the 70% cell viability threshold, with lower filler concentrations yielding optimal results due to beneficial compounds such as thymol and tannins. A 10-day extract of the 2.5 wt.% sage-filled composite showed improved cell viability, although it still fell short of the minimum required level. This may be due to the antimicrobial and antiproliferative properties of sage, which are associated with its phytochemical compounds, such as salvianolic acid and luteolin. High filler concentrations in thyme-based biocomposites reduced cell viability, likely due to an excess of bioactive compounds that limited cell proliferation; however, the values remained above the required minimum threshold.

In summary, the thesis of this work was confirmed. The results clearly demonstrate that the developed bioactive materials exhibited enhanced antibacterial activity while maintaining essential functional properties for medical applications, particularly wound dressings. Key findings include:

- The composition of herbal fillers influenced the cross-linking of PDMS, impacting its antibacterial and physicochemical properties.
- Filler density and polyphenol content were linked to modification methods, with extracts exhibiting higher values than unmodified herbs, suggesting the effectiveness of the applied modifications.
- Alcohol and water vapor reduced terpene and fatty acid levels in sage and rosemary, improving mechanical properties but reducing antibacterial activity. Modified fillers exhibited lower antibacterial efficacy compared to unmodified ones.
- Filler geometry and wettability affected mechanical performance, with extract particles better wetting the matrix and particle size playing a significant role.

- Biocomposites with modified herbs exhibited slightly higher density but reduced mechanical properties compared to PDMS. Nonetheless, they outperformed biocomposites containing unmodified herbs, with hardness remaining comparable across all materials.
- Herbal fillers did not alter the hydrophobicity of PDMS, a crucial feature for preventing bacterial infections, but they reduced abrasion resistance and rebound resilience, which correlated with lower crystallinity.
- Accelerated degradation in an artificial plasma environment revealed varied responses, with thyme-based composites showing the highest stress and strain at break values, and rosemary-based composites the lowest. High filler content accelerated degradation, while rosemary-based biocomposites exhibited evidence of further cross-linking. Despite these changes, all biocomposites retained acceptable mechanical properties.
- Thyme-based composites were non-toxic and exceeded 70% cell viability, whereas sage-based composites did not meet the cell viability threshold, and higher filler content increased cytotoxicity.
- The methods used for filler preparation, including sedimentation, agglomeration, hardness, particle size, and phytochemical composition, significantly influenced the material properties and contributed to variability in the results.