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ARTICLE

Synthesis of Fabricated Polyurethane Matrix Based TiO_2–HAp Material

Mamta Sharma[1,✉] and S.S. Tomar[2]

ABSTRACT

In this research work, the composition of polyurethane, titanium di oxide and hydroxyapatite were optimized to obtain a stable polymer nanocomposite microfilm with excellent flexibility and durability, through simple sol-gel synthetic method. The obtained films were further cut by nesting and formed to obtain a flawless stent structure with desirable mechanical, biocompatibility and drug delivery properties. XRD, FTIR, SEM characterizations were performed to study their physical, chemical and biocompatible properties. The tensometer tests, simulated body fluid tests and blood interaction tests showed competitive results that match the properties of conventional materials such as metals and alloys.

KEYWORDS

Nanocomposite, Polyurethane-TiO_2-HAp, Sol-gel, Biocompatible.

INTRODUCTION

There happens to be a saying, “perfect stent does not exist and it will probably never exist”, by a reputed researcher doctor who’s also a pioneer in cardiovascular stent technology [1]. The saying couldn’t be debated for it was the truth which researchers across the world are trying to accept as well as defy, through modern age simulations, mathematical models, material science, manufacturing and production technologies. The fundamental reason for the inability in the product development and research domain to standardize a cardiovascular stent could be attributed to many factors such as optimizing the material composition, enabling flexibility, enabling shape memory effect, lack of methodologies to develop prototypes with intricate shapes *etc*. But, when analyzed in detail, not with respect to the management systems and principles associated with handling sources and resources in developing stents but with respect to the incidents where failure in implanted stents been have been reported, we are left with a unique problem of failure associated with a design what was regarded as a standard. The failures occur not because of the lack of high quality inspection but due to the poor understanding of the fundamental physics, chemistry, mathematics and biology of a stent [2,3]. It’s the concepts of these fundamental sciences that determine the perfection and imperfections within the stent structure. While investigating the perfections and imperfection of the stent design with respect to the hemodynamics of an individual who needs the implant, its effect on the geometry

Author affiliations:

[1]Department of Chemistry, Monad University, N.H. 9, Delhi Hapur Road Village & Post Kastla, Kasmabad, Pilkhuwa-245304, India
[2]Department of Chemistry, R.S.S. (P.G.) College, Pilkhuwa-245304, India

✉To whom correspondence to be addressed:

E-mail: mamtasharma@gmx.com

of the stent and the material composition of stent it can be observed that all the factors discussed are in correlation with respect to the dynamics of the geometry & blood flow (physics), the active sites on the stent structure (chemistry), the interaction of the material with the host's biosystems (biology) and the calculations/models that stiches the concepts of Physics, Chemistry, Biology (Mathematics). These fundamentals, all together are addressed as 'Biomechanics' in the domain of Implant Science and Engineering. It is also this branch of science that's not given the necessary importance while seeking solutions for the menaces faced with respect to the implants (both active structures and passive devices). In Implant Science and Engineering, designing and development of implants are initiated with, i) determining the composition of the material which is proportional to the properties of the material, ii) validating the material properties through conceptualization and prototyping iii) followed by advanced characterizations (*in vivo*, *in vitro*) which results in the production of the product. An overall understanding of biomechanics will eventually result in a successful implant which in turn can help in improving the quality of life of a being (both human and animal alike). This manuscript focuses on explaining the results obtained through a research on synthesis and characterization of polyurethane based TiO_2-HAp nanocomposite and using the same to design and develop a stent inform of whole material and as a coating for a metallic frame work. This paper work also explains the importance of flawless coating and a new method of coating which is addressed as "downward flow solution casting method" and its efficiency in obtaining an efficient coating for implants. A detailed focus on selecting the stent geometry with respect to the hemodynamics too is explained so as to explain the overall biomechanics, from determination of material composition to prototyping; as mentioned above.

EXPERIMENTAL

0.5 g of the synthesized TiO_2 nanoparticles and 2.5 g HAp nanoparticles were introduced into optimized quantities of polytetramethylene ether glycol (PTMEG), toluene diisocyanate (TDI) respectively. The polytetramethylene ether glycol gets a milky white tone while the toluene diisocyanate acquires a dirty white colour. The polytetramethylene ether glycol and toluene diisocyanate are stirred individually using a mechanical stirrer to enable even distribution of the nano-particles within the solution. 1,4-Butanediol (chain extender) and 1,4-diazabicyclo[2.2.2]octane (hardener) were added to the polytetramethylene ether glycol with TiO_2 particles and toluene diisocyanate with HAp nanoparticles respectively. Toluene diisocyanate with HAp and 1,4-diazabicyclo[2.2.2]octane was added to polytetramethylene ether glycol with TiO_2 particles and toluene diisocyanate. The overall temperature generated during the interaction of the two solutions was controlled using an ice bath to slow down the hardening process. When sufficient viscosity was achieved the mixture was quickly transferred to the polystyrene templates to form the ASTM D3039 standard specimen. The specimens were then subjected to characterizations, to study their properties, after drying at room temperature for 80 h with a load of 1 ton, temporarily sealing the open side of the templates.

Downward flow solution casting method (for coating a metallic stent structure): To achieve a uniform and even coating, the method of downward flow solution casting method is adopted. The mechanism behind this method is, when the solvent in which a polymer is dissolved is subjected to rapid evaporation by indirect heating, the polymer content within the solvent resides on to the available structures. The polymer generally resides as a uniform coating onto the walls of the container. If a metallic structure or any material that requires a coating is kept immersed into the polymer solution and if the same is subjected is downward flow solution casting method, a fine layer of polymer coating will reside on the material. The viscosity of solution determines the thickness of coating while the rate at which solvent evaporated determines the uniformity of coating. The same process was used to coat the metallic stent structures prepared by assembly of entwined individual rows of structs. These individual rows of structs were then joined together by polymer adhesives and were given a singular coating through downward flow solution casting mechanism.

Characterizations: XRD, FTIR, SEM, tensile test, simulated body fluid (SBF) test, were performed to explore the nature of the polymeric nanocomposite, its morphology, its ability to withstand temperature, mechanical loads and its ability to be inert under biological environment, respectively.

RESULTS AND DISCUSSION

XRD: Fig. 1 showed the XRD pattern of the nanocomposit and reveal that the nanocomposite is amorphous. The lack of indication of the presence of TiO_2 and HAp could be due to complete shielding of the X-rays by polyurethane.

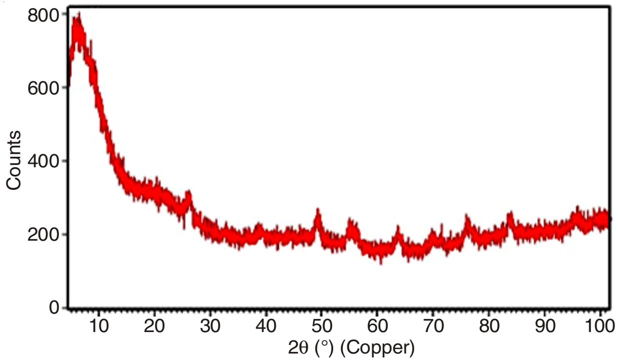

Fig. 1. XRD pattern of the nanocomposite

FTIR: In the FTIR (Fig. 2) of the polymeric nanocomposite the H bonded OH groups, C-H stretching could be observed with the presence of bands between 2400-3500 and 1600-1800 cm^{-1}, respectively which confirms the presence of polyurethane and presence of metal oxide embedded within the structure.

SEM: The SEM analysis of the polymeric composite indicates that the polymer surface is clear (Fig. 3) but not as smooth as a glass surface. It also proves that the nanoparticles are firmly held within the polyurethane structures as none them could be noticed on the surface. This could be due to the denser polyurethane settling at the bottom of the polystyrene templates while casting and the encapsulation of the nanoparticles by the expanding polyurethane.

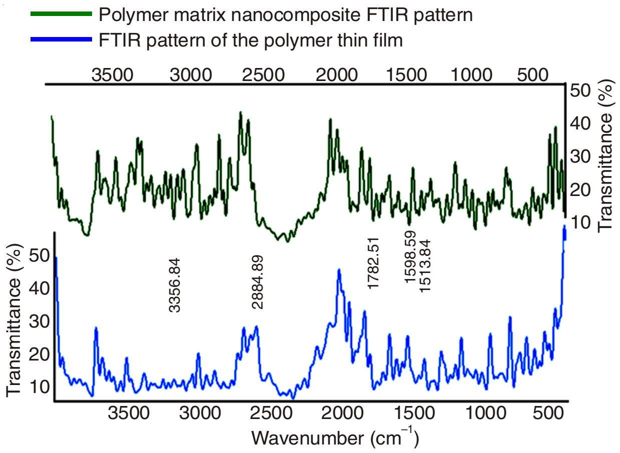

Fig. 2. FTIR of the polymeric nanocomposite

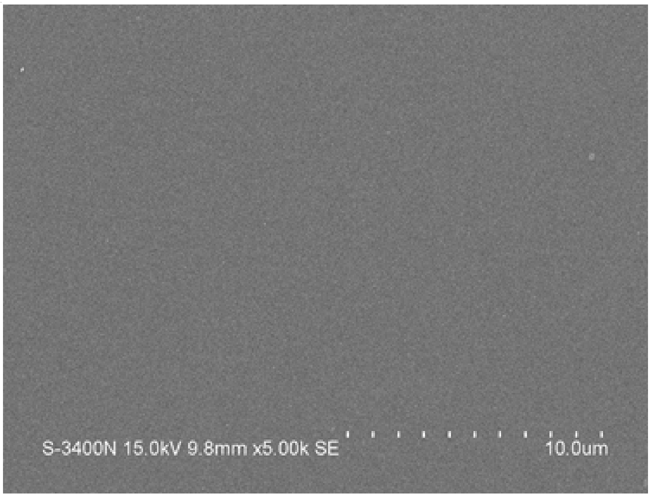

Fig. 3. Polymeric nanocomposite

Tensile tests: The tensile tests of synthesized nanocomposite, indicates the nanocomposite's ability to withstand a load of 17.5 Mpa (Fig. 4). During the measurement process, the composite deformed by elongating thrice the initial dimension before suffering fracture.

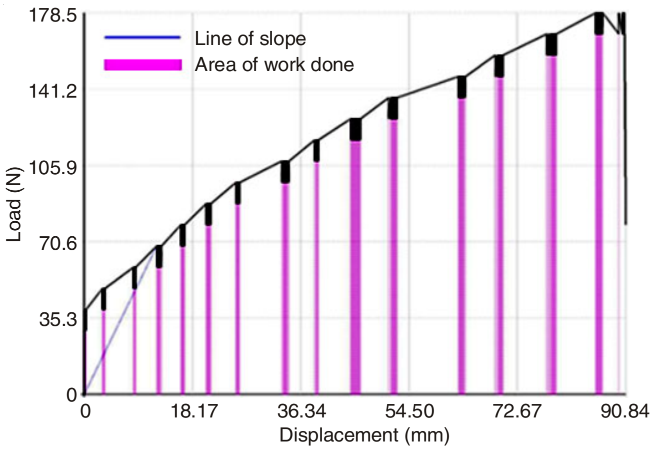

Fig. 4. Tensometer test result (ASTM D3039)

Biomechanics: The biomechanics of material, *i.e.* the physics, chemistry, math, biology, is explored with respect to the material's morphology. The material's structure, its surface properties, the composition, its ability to withstand stress, strain are explored through biomechanics and the same are correlated to a successful cardiovascular stent structure.

Physics: Physics is the visual form of theories, postulates and corollaries. Physics deals with explaining the fundamentals of transformation or origins or even the pre-existence of origins of energy. Anything, when in contact physically with any other matter results in transformation of energy with a condition, that atleast any one out of the interacting matter is in motion or every matter is stationary but in an environment there exists fluidic flow throughout. This, most fundamental scenario, is what could be termed as an absolute equivalent or at least an equivalent to the environment within an artery of a being! The presence of an external intricate or complex structure within an artery faces a challenging fluid flow throughout its life span. When the stent structure is placed within an artery, the blood rushes over the implant again and again. If the stent structure is too rigid or extremely rough, the fragile contents of blood that comes into contact with the material will suffer damage [4,5]. This miniscule damage is sufficient enough to trigger immune response within an individual. Moreover, the material has to be hydrophobic because if it is to attract any water molecule, it will also attract the salts of the body resulting in failure of the implant. Hence, to complement the blood flow and the contents of the blood, the material has to be made out of material that could favour the hemodynamics and the content of the blood. The material that can be durable cum flexible and still be hydrophobic could be an amorphous polymer; in most of the cases as it turns out to be! Not all polymers are hydrophobic but polyurethane is and polyurethane with fillers that can enhance the hemocompatibility and mechanical properties could be added as a coating to any other material to induce the hemodynamic friendly property to other material. The XRD and the tensometer tests prove the material is amorphous and strong enough to face the hemodynamics.

Chemistry: Chemistry of the material determines the interaction of the same with the biomolecules of a being. The material has to be extremely inert towards the biomolecules that always stays in interaction. The surface charges of the material or the active sites within or over the material will attract biomolecules such as blood protein structures to adhere on the surface resulting in failure of the implant [6]. For the material to be inert, the composition has to be either similar to a beings internal structure – say a bone or the composition has to have lesser non terminated groups along the surface that attracts the biomolecules to interact with them. The FTIR spectrum confirms the presence of polyurethane and polyurethane possess almost zero non terminated groups along their structure and with the presence of bone mineral hydroxyapatite within their structure, there would be no problem if an interaction with the biomolecule is to happen.

Biology: A stent structure always suffers a failure, no matter how perfectly it is made or designed to perform! Because, a being's biological elements will never fail to notice the presence of an external material (something that's not biological). But the same could be exploited to improve the material's properties. The material which possesses sufficient mechanical properties and absolute zero toxicity, at one stage will randomly support adherence of soft tissues over it surface. This process will be progressive and not an outbreak. This progressive process will eventually form a safe layer over the polymer structure that results in a complete shielding of the stent material to the external bioenvironment. But for this to happen, the material must be programmed to degrade slowly and steadily and attain the sufficient properties to facilitate the growth of the tissues [7,8]. The simulated body fluid (SBF) test conducted on the sample showed that sample can support growth of soft tissues (Fig. 5).

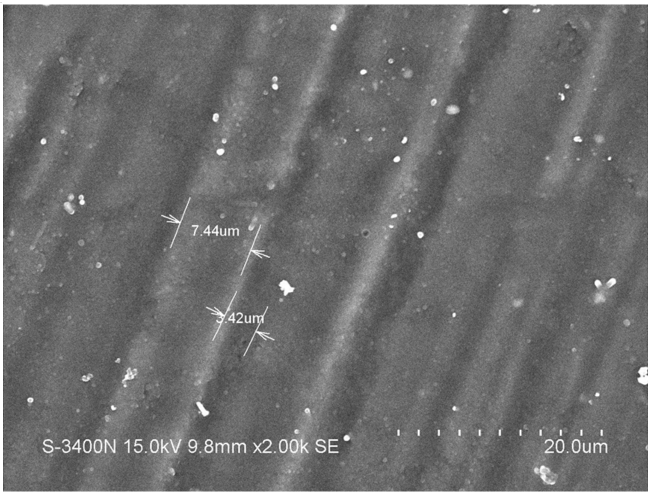

Fig. 5. Sample who's top layer was severed and subjected to SBF tests

Mathematics: Mathematics, the language of all sciences stiches the concepts of physics, chemistry and mathematics to design the material; in form of efficient coating for any metallic stent structure. The mathematical calculation that solves the 3D flow within an unstable circular geometry problem and the solutions that satisfy flow problems, with respect to laminar to turbulent requires a detailed simulation and theoretical study in designing the stent structures. The biodegradability of polyurethane has been reported by many research groups with respect to time within a host. If the principles of the 3D flow, downward flow solution casting, hemodynamics and the biodegradability of the polyurethane could be stitched together by mathemcatical calculations and design modeling, a smart polymer composite with multiple unique layers and programmable biodegradability could be developed to solve the problems related to stents and other implants could be solved.

From Fig. 6, it can be observed that the developed nanocomposite possess the most favourable porous surface for the growth of soft tissues. If the material's outer layers are programmed to degrade with respect to time and bioenvironment, then this nanocomposite could well be the best solution in designing cardiovascular implants and other tissue contact implants.

Conclusion

From the above discussed concepts of biomechanics, it can be understood that necessary change in approach, to solve problems related to biomedical and biomechanical engineering is a must for effective contribution in improving the quality of life of a being (human and animal alike). This fundamental understanding could help in decoding the toughest problems

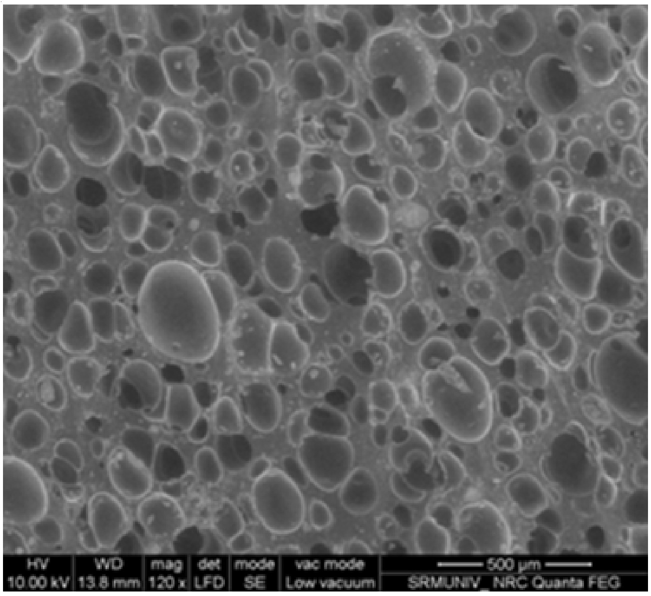

Fig. 6. Inner structure of the developed nanocomposite

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