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Characterization of Tensile Strength Property of Polyurethane –Based Composite Used for Coronary Artery Substitution

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ABSTRACT

Polyurethane elastomers possess a combination of properties that make them particularly well-suited for long-term use in implanted biomedical devices. This work focuses on developing a biomaterial with tensile strength proximally to natural arterial tissue by preparing a polymer blend base elastomer of polyurethane (PU) combined with silicone rubber (SR), taking into consideration the inertness and biocompatibility of both PU and SR. The polymer blending group ratios of (PU/SR) were (98:2), (96:4), (94:6), (92:8), and (90:10) respectively. The prepared blends were used to prepare composite materials by adding additives of (0.2%) titanium dioxide (TiO_2), and (0.5%) of calcium fluoride (CaF_2) to the mother polymer blend (PU/SR) to improve their tensile strength. The tensile test results show that all prepared polymer blends (1B, 2B, 3B, 4B, 5B) have lower tensile strength when PU blended with SR compared to the control reference sample of polyurethane. Adding Titanium dioxide (TiO_2) revealed a higher tensile strength of specimen 3T (94 PU- 6 SR- 0.2 TiO_2) compared to the mother blends and control. Also, adding Calcium fluoride (CaF_2) shows higher tensile strength of specimen 3C (94 PU- 6 SR- 0.5 CaF_2) compared to mother blends and control. The hemolytic index (HI) of the prepared composites was also studied, and the results demonstrated a significant improvement in HI in blends, particularly in mother blends (2B, 3B, 4B, and 5B) and mother blends containing TiO_2(3T, 4T, and 5T) compared to the PU control reference.

Keywords: *Coronary Artery, Tensile strength, Polyurethane, Silicon Rubber*

1. INTRODUCTION

Cardiovascular diseases (CVD) are among the leading causes of morbidity and mortality worldwide. Common types of CVD include coronary artery disease, deep vein thrombosis, and myocardial infarction, often linked to the narrowing (stenosis) and blockage (embolism) of blood vessels [1]. According to the World Health Organization, cardiovascular diseases, encompassing coronary, cerebral, and peripheral artery disease, are the primary cause of death globally. Atherosclerosis, the most prevalent form of CVD, can cause structural alterations in blood vessels, such as narrowing, occlusion, or dilation, leading to insufficient blood flow to organs or the rupture of vessel walls. For patients with advanced stages of these diseases, surgical intervention remains a critical treatment option [2].

Cardiovascular disease progresses over time and can obstruct blood flow through the coronary arteries, resulting in conditions such as angina, heart attacks, and other severe complications. Currently, there is no successful clinical trial for small-diameter vascular grafts (SDVGs) less than 6 mm, which are urgently needed for treating various arterial issues, including coronary artery disease and congenital cardiovascular defects in children. At present, blocked coronary arteries can be treated by partially clearing them using angioplasty and stents, of by performing coronary artery bypass surgery [1, 3].

Both autologous and non-autologous grafts have several limitations that can lead to complications and graft failure [2]:

1. Autologous graft limitations: These include the invasive nature of harvesting, poor quality of the graft material (either too thin or too thick), and insufficient availability, especially in patients withseveresystemic atherosclerosis or those who have already had vessels harvested for previous surgeries.
2. Non-autologous graft limitations: Major issues include acute thrombogenicity, intimal hyperplasia, and infection. Additionally, mismatched elasticity or uneven wall stress can lead to fibrous proliferation and intimal hyperplasia near the anastomosis. The implantation of a permanent foreign body often causes severe infections, contributing to graft failure.

In the field of tissue engineering (TE), significant efforts are being made to overcome these limitations-The goal of tissue-engineered vascular grafts (TEVG) is to create alternatives that integrate with the patient's tissue and function like natural blood vessels, including self-regenerative and growth capabilities. TEVGs consist of three main components: (a) a structural scaffold material. (b) cell-engraftment and tissue remodeling, and (c) biological signals to recruit and organize cells [2]. Figure 1 provides an overview of the key considerations for suitable small diameter vascular grafts (SDVGs), including commonly used materials, surface modification strategies, and various fabrication technologies.

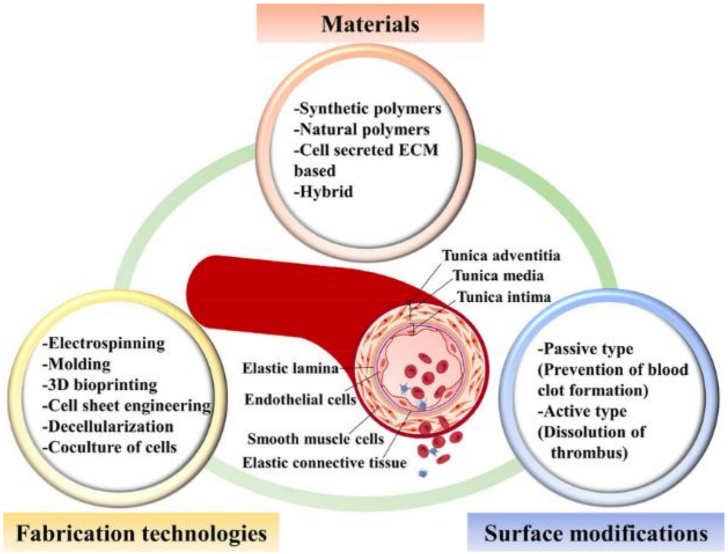


Figure 1. An outline of Materials frequently used, surface modification techniques, and various fabrication technologies for small diameter vascular grafts (SDVGs) [1].

Polyurethanes possess unique mechanical and biological properties, making them suitable for numerous implantable devices. However, their clinical application is hindered by poor biostability and early-stage spontaneous degradation. Certain polyurethanes degrade in vivo; for instance, polyester-urethanes are prone to hydrolytic degradation and are no longer used for long-term implants. While polyether-urethanes are hydrolytically stable, they are vulnerable to oxidative degradation, including environmental stress cracking and metal ion oxidation [1, 3]. Motivation to develop biostable polyurethanes stemmed from the need for elastomeric materials to provide compliant vascular grafts and deformable. Conventional polyurethanes degrade over time, with signs of this process appearing within weeks of implantation. This degradation is primarily due to oxidation, likely caused by superoxide produced by phagocytes (scavenger cells). As degradation progresses, more scavenger cells migrate to the site to engulf and sequester the degrading material. Because phagocytes release that stimulate fibrosis, the degrading material becomes encapsulated, effectively being walled off [4].

By altering the components of the polymer, polyurethanes can be custom-designed for various applications. Their excellent blood and tissue compatibility, along with their strength and flexibility, has led to widespread use in biomedical applications, such as vascular grafts and artificial hearts [3].

Combining polymers with other materials can enhance properties like mechanical strength, surface characteristics, and biocompatibility, allowing the production of materials with superior mechanical and biological properties. Polymer-based composites are increasingly utilized in biomedicine for purposes such as tissue engineering, wound dressings, drug delivery, regenerative medicine, dental resin composites, and surgical procedures. These composites exhibit significantly improved properties compared to their original components [5].

Polymer-based composites are in high demand due to their desirable characteristics, including high strength-to-weight ratio, low density, high modulus, excellent mechanical, thermal, and optical properties, flexibility, elasticity, impact resistance, shock absorption, and environmental inertness. The introduction of reinforcing phases, such as fibers, sheets, fillers, particles, or nanoparticles, can further enhance polymer properties. These reinforcements can be natural (e.g., sugar palm fiber, kenaf, jute) or synthetic (e.g., glass fiber, carbon fiber, graphene particles. graphite oxide, silicon) [6].

Silicone is highly biocompatible and bio-durable when interacting with host tissues its hydrophobicity and low surface tension contribute to excellent hemocompatibility and reduce the risk of encrustation when in contact with various body fluids. Additionally, silicone is generally unaffected by host immune response and repeated sterilization, thanks to its well-known chemical and thermal stability. These properties make silicone an ideal biomaterial for various biomedical applications. Silicone elastomer is used in tubing for catheters or drains, where transparency, flexibility, inertness, lubrication, and biocompatibility are essential. It also serves as insulation for electronic implants, such as pacemaker leads. Furthermore, silicone adhesive or elastomer is commonly used for wound dressings due to its favorable properties. Silicone materials are biocompatible, comfortable, and allow air permeability. Silicone gel is often used to treat hypertrophic bum scars, while silicone rubber is extensively utilized in prosthetics. Silicone elastomers are characterized by a tensile strength ranging from 8 to 15 MPa, an elongation percentage between 300 and 800, a glass transition temperature (Tg) of -130°C, and a water absorption rate of 0.03% [7].

Polyurethane composites can maintain the toughness of polyurethane while enhancing modulus and tensile strength. Filler particles, such as titanium dioxide (TiO_2), can be incorporated into the polyurethane based composite during fabrication. TiO_2 is much stronger and stiffer than polymers, making it an attractive option for polymer reinforcement due to its excellent biocompatibility and antibacterial properties. Additionally, TiO_2can help suppress the immune response commonly triggered after implantation [8]. In this study, we utilized these properties by adding TiO_2 filler particles to enhance the polyurethane-silicone rubber blend composite. Alkaline earth metal fluorides, such as calcium fluoride (CaF_2), have gained attention for various applications, including UV lithography, UM-transparent optical lenses, surface conditioning of glass, promoting biocompatible agents for bone and teeth reconstruction. Due to the high stability and flexibility of the fluorite structure, various ionic substitutions can be incorporated into the CaF_2lattice [9]. In this study, we also considered the stability and biocompatibility of CaF_2, which make it an appealing material for biomedical applications. CaF_2 has been used as an additive to improve the tensile strength of the polyurethane-silicone rubber blend composite.

Our goal is to revolutionize medical vascular grafts for the treatment of end-stage cardiovascular disease, which is the leading cause of death in Western countries. The objective of this study is to prepare a PU-SR Biocomposites with a tensile strength proximally to natural arterial tissue and has an acceptable hemolytic index (an indicator to biocompatibility).

2. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Matrix Materials

a) Polyurethane Elastomer (PU), is the major constituents provides an excellent elasticity and high tearing resistance properties with minimum shrinkage supplied by (MARIS POLYMERS SA) industrial Area of Inofita 32 011 Inofit, Greece, with tensile strength of 8.51MPa.
b) Silicon Rubber is the minor constituents supplied by (POLYSEAL PS), Henkel polybit, United Arab Emirates, with tensile strength of 7.11 MPa.

2.1.2 Additives

a) TiO_2 with median particle size of (0.3μm) and density of (3.18 g/cm^3).
b) $CaF_2$with median particle size of (50μm) and density of (4.23 g/cm^3).

2.2 Equipment

a) Samples of blend composites were prepared by hand lay-up technique with dimensions of (3*16*0.2) cm^{3}and the tensile test was performed according to (ASTM D638–00) at room temperature with 10N applied load and strain rate of 5 mm/min by using tension machine Instron.
b) Laser diffraction particle size analyzer type (SHIMADZU SALD-2101), to identify the median particle size of the additives TiO_2 and CaF_2.
c) A vacuum forming system including a vacuum pump.

2.3 Procedures

2.3.1 Blend Preparation

Molding is a traditional method used to create tissue-engineered vascular grafts. This technique is straightforward to set up and enables the production of customized scaffold shapes, such as tubular vascular grafts or complex branched vasculatures, using polymers. The polymer solution is poured into a specially designed mold with predetermined inner diameter and wall thickness for the vascular grafts [1].

PU/SR blend was prepared by simultaneous polymerization of PU and SR. Homogenous solutions of PU, SR, curing agent and free-radical initiator were prepared at room temperature with different ratios of PU:SR. i.e. (98:2), (96:4), (94:6), (92:8), and (90:10) respectively. The blends were mixed continuously at room temperature for 20 minutes and slowly at speed of 25 rpm to avoid bubbling during mixing, and a 2% wt hardener of Methyl Ethyl Ketone Peroxide (MEKP) were added during the last 5 minutes of mixing. Then solutions were poured into cast molds then closed after being purged with vacuum 30 minutes to ensure the release of bubbles that were formed either during blends mixing or throughout pouring the blends in mold. The solution left for ageing at room temperature for 7days. This step is important to complete the polymerization, best coherency, and to relieve residual stresses [10]. Then composites were prepared by adding the additives titanium dioxide (TiO_2), and calcium fluorite (CaF_2) to the prepared mother blends, individually. Samples details are listed in Table 4.

2.3.2 Tensile Test

Tensile test was performed according to (ASTM D638–78b) at room temperature to measure the force per square area required until the rupture happen, or crack propagation through a polymer sheet from force- extension curve [11]. Equation 1 expresses the Stress-Strain relationship in a simplified form:

$$\sigma = K\varepsilon^n \tag{1}$$

Where σ is true stress, ε represents the true strain, while K and *n* are constants, initially introduced by Ludwike equation [12]. This model is applicable only within the range of uniform plastic strain and does not account for elastic deformation at lower stress levels or for necking. The constant (n) is the slope of a log true stress-log true strain plot, with K the true stress at a strain of unity. The magnitude of (n), the strain -hardening exponent, is an indication of the stretch ability of materials.

2.3.3 Hemolysis Analysis Test

Biocompatibility is one of the major problems that minimize using biomaterials of being used with blood contact like in an environment of cardiovascular system [13]. The hemolysis analysis test was accomplished depending on the ASTM F 756–00. This approach is intended to estimate the in vitro hemolytic properties of the prepared polyurethane based composite when becomes in contact with a blood [14]. For the hemolysis test, 10 m L of saline solution and 0.2 m L of blood anticoagulants were added to each test tube, including those containing samples of control PU, composite blend (PU- SR), and composite blends PU- SR plus additives of - 0.2% TiO_2, and 0.5% CaF_2. After 2 hours of static incubation at 37°C, tubes were centrifuged for 5 minutes at 750 g (g; a relative centrifugal force). Supernatants were filtered and collected in new tubes for hemolytic index measurements. The optical density (OD) of the supernatants was subsequently measured at 545 nm using Drabkin's Reagent and a spectrophotometer. Then HI has been calculated as shown in equation 2[13]:

$$HI\ \% = (\text{Free hemoglobin in tested blood} / \text{Total hemoglobin in blood sample}) * 100\ \% \qquad (2)$$

The hemolysis index guide chart is shown in Table (2).

Table 1 Guide to Hemolytic Index No. [13]

Hemolytic Index No.	Description
0-2	Hemolytic free
2-10	Slightly hemolytic
10-20	Moderately hemolytic
20-40	Markedly hemolytic
Above 40	Severely hemolytic

3. RESULTS AND DISCUSSION

3.1 Tensile Strength

Figure 2 shows a Typical (Stress-Strain) curves for blend groups (PU/SR) and their tensile properties respectively. The plot of log true stress vs. Log true strain is concave upward i.e., *n* increase with increasing strain and the results conducted that the *n* increase for sample 1B and 5B of the mother blends. Then after adding TiO_2 and CaF_2 fillers to Mother blend groups, *n* improved for all samples which affected positively in increasing the elastic properties for all filler groups.

The Stress-Strain curves of the blends 1B, 2B, 4B, and 5B, reveals a decrease in modulus and tensile strength values, except the sample 3B which has lower value of *n*=2.88 and K=1.58, and higher elongation 2 % as explained in tables 2 and 3 respectively which still retaining mechanical properties compared to the control, with SR incorporation.

The decrease in tensile behavior may due to fact that the network topology impacts the material properties, due to disarrangement in PU organization caused by the high flexibility of SR, because polyurethane itself shows a special phase separated structure, its macromolecules contain hard urethane segments and soft segment, in addition the key factors that influence the mechanical properties include the molar mass between cross-linking points, whether through physical or chemical bonds, and the distribution of their weights. Additionally, the presence of dangling chains (chains attached to the network at only one end), chain loops (chains with both ends connected at the same junction), and chain entanglements also play significant roles, as shown in figure 3. Obviously, each parameter impacts the tensile properties; it is well-known that all materials does not have the same structure, and the modulus is actively be dependent on the molar mass between knots (Mc), and cross linking density and that agreed with E. Delebecq, et al.[15].

Uncross-linked rubber behaves as a high-viscosity fluid and will flow under even minimal external stress, resulting in zero tensile yield stress at low elongation speeds and zero cross-link density. In contrast, a cross-linked material redistributes applied stress across the cross-links. As the density of these cross-links increases, the average tensile force on each cross-links decreases. Since a cross-link bond won't break until the tensile force reaches a critical threshold, the tensile yield stress σ_c, rises with an increase in cross-link density. However, at very high cross-link densities, the tensile yield stress begins to decline due to the uneven distribution of tensile forces across the cross-links during tensile loading, given the inhomogeneous nature of rubber-like materials, and that agreed with B. J. Persson et al. [16].

Consequently, some cross-links will fail even when the applied stress is significantly lower than the critical stress required for tensile failure. In cases where the cross-link density is moderate, the rubber near the broken cross-link can behave like a fluid, allowing it to reorganize and alleviate the stress concentration that would otherwise develop around the broken bond. However, at very high cross-link densities, the material becomes brittle, resulting in strong stress concentrations around the broken bond. This can cause additional bonds to break, increasing the stress concentration even more and leading to the rapid propagation of a crack-like defect across the rubber block. Villar et al. demonstrated that the loss modulus is greatly influenced by the concentration and molar mass of dangling chains within a network [15].

On the other hand, the SR network consists of Polysiloxanes have backbones composed of Si-O-Si units, in contrast to many other polymers that have carbon-based backbones. This structural difference makes Polysiloxanes very flexible, as they have larger bond angles and bond lengths compared to simpler polymers like polyethylene, that agreed with A. Colas and J. Curtis [17],this explain why does the blend materials have network consist of long chains, that provide less maximum strength.

Back to elongation at rupture for blend groups results shown in figure 2had revealed an increase in elongation for all blends (1B, 2B, 3B, 4B, and 5B) caused by SR incorporation, this behave may explain that, the elongation to rupture increases with the increase of soft segments molar mass between two physical cross linking ends, that congruent with the findings of E. Delebecq, et al. who indicated that the optimal elongation at break occurs at critical molar mass between entanglements (M_c) of (20 000) g/ mol. A lower cross-linking density at this molar mass can weaken the blend [15].

It is obvious from table 3 and figure 4 that blend 3Bindicates the maximum amount of tensile strength and modulus, also, highest strain at rupture compared with other mother blends and results revealed that adding SR with ratio of 6% to PU is improving their mechanical properties, but further increase in SR addition will tends to decrease the properties gradually.

Natural arteries have an approximate tensile strength and modules of elasticity, 1.4MPa and (1.5–3) MPa, respectively. The current study developed new materials for arterial substitution from blending PU with SR with different ratios that possessed tensile strengths and modules of (4.15–5.19) MPa and (3.1–6.79) MPa, respectively, which could be recommended for coronary artery bypass graft applications. In contrast, expanded polytetrafluororthylene (ePTFE) exhibits a tensile strength of 27 MPa and an elastic modulus of 500 MPa, which differ significantly from the properties of natural vascular tissue, these results are in good agreement with T. Chuang and K. S. Masters [18].

Table 2 (K and n) values for all samples

Sample	K	*n*
Control	4.66	2.98
1B	1.5	3.07
2B	1.15	2.67
3B	1.58	2.88
4B	1.3	2.1
5B	0.44	2.99
1T	1	2.97
2T	0.51	3.3
3T	0.43	3.1
4T	0.44	3.3
5T	0.49	3.3
1C	0.68	3.05
2C	0.64	3.02
3C	0.76	2.79
4C	0.24	3.5
5C	0.19	3.5

Table 3 Tensile strength of prepared polymer blend samples with and without additives

No. of sample	PU	SR	TiO_2 additive	CaF_2 additive	Tensile Strength (MPa)	Modules of elasticity (MPa)	Elongation %
Control	100	0	0	0	8.51	8.17	1.2
1B	98	2	-	-	5.19	6.79	1.5
2B	96	4	-	-	5.08	7.31	1.7
3B	94	6	-	-	7.59	8.22	2
4B	92	8	-	-	5.59	3.84	1.9
5B	90	10	-	-	4.15	3.1	2.4
1T	98	2	0.2	-	7.5	7.8	2.1
2T	96	4	0.2	-	7.85	8.32	2.4
3T	94	6	0.2	-	9.42	9.05	2.7
4T	92	8	0.2	-	6.54	6.8	2.4
5T	90	10	0.2	-	4.69	4.95	2.3
1C	98	2	-	0.5	7.33	7	2.2
2C	96	4	-	0.5	7.67	7.79	2.3
3C	94	6	-	0.5	8.82	8.35	2.6
4C	92	8	-	0.5	3.32	5.64	2.5
5C	90	10	-	0.5	3	4.27	2.4

*B: blends without fillers ** T: blends with TiO2 filler *** C: blends with CaF2 filler

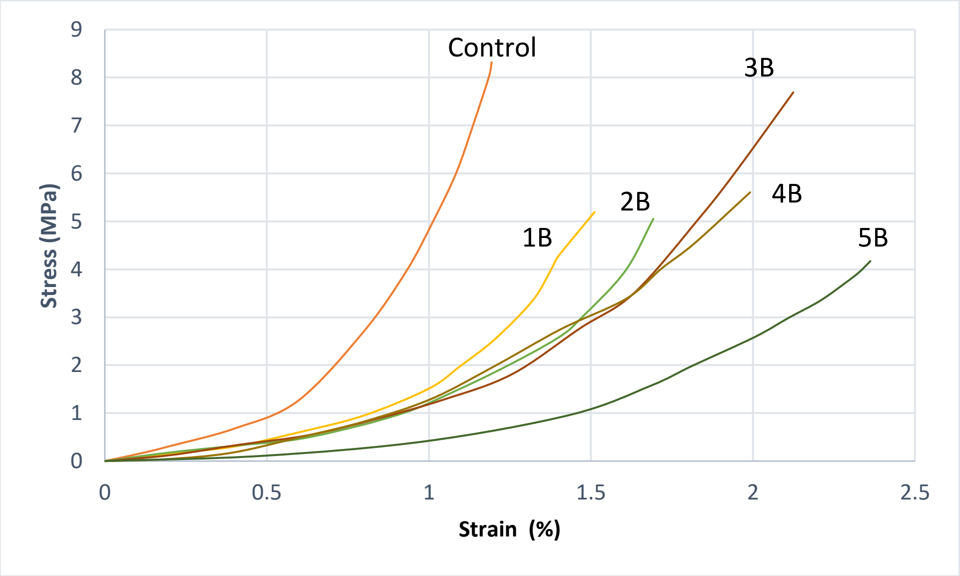


Figure 2. Typical (Stress-Strain) Curve for Mother Bland groups.

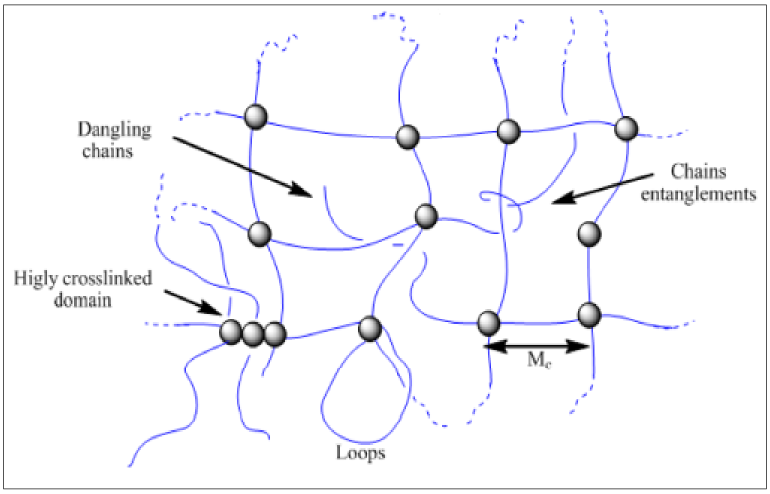
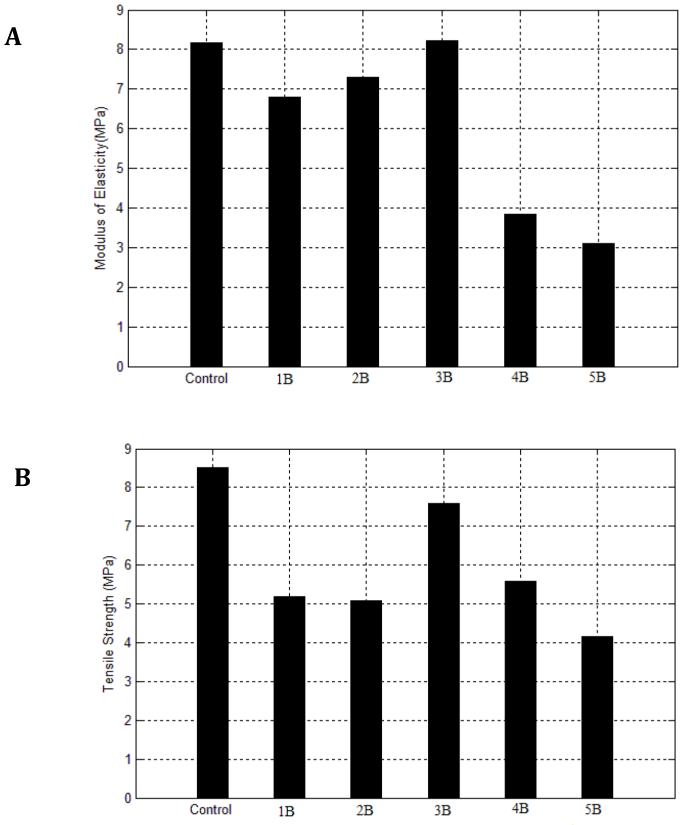


Figure 3. Network topology (structure of elastomer) (15).



C

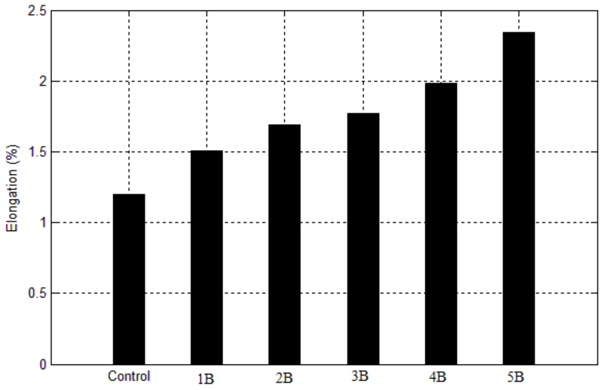


Figure 4. The Mechanical Properties of the Mother Blend groups. Stress–Strain data were utilized to determine (A) The Elastic Modulus, (B) The Tensile Strength, and (C) The Percentage of Elongation at Rupture, Compared to Control (0% SR).

Figures 5 and 6 are showing the revealed results in table 3 which representing the effect of Titanium Dioxide (TiO_2) addition on the mechanical properties of blend groups.

The results disclose arise in values of modulus and tensile strength of blend group composites when TiO_2added, as well as an increase in elongation to rupture, and that may due to existence of TiO_2particulate fillers, which are randomly dispersed in the blend matrix, as a result, the polymer-filler interactions lead to a variation in polymer chain lengths. These interactions, dictated by polymer adsorption, encompass various entanglement interactions and polymer bridging between filler particles.

In agreement with the Payne effect [15], a qualitative model describes a filler network formed either directly between filler particles or via elastomeric domains. In the latter scenario, the elastomer adsorbed on the filler surface behaves rigidly near the filler, causing the modulus to vary with distance from the filler surface. All contributions, including chemical bonds and physical interactions, need to be considered. Although physical interactions are weaker, they significantly enhance tensile properties. The filler increases the orientation and extension of the chains, leading to higher stress and modulus. Chains that sag may adsorb onto the filler surface. When stress is applied, these chains can bear the load and may even accommodate it by slipping along the filler surface. This results in the fillers restricting the movement of the matrix phase near each particulate filler while the matrix transfers a portion of the applied load to the filler, which then bears part of the load, therefore it can be seenthatTiO_2 reinforcing fillers improve tensile properties for blend groups, also, it becomes with an agreement with Yilgor and co-workers[19], results on unfilled and filled model composite, indicated that increasing the molar mass of soft segments, specifically the molar mass between two physical cross-linking points, beyond the critical molar mass where entanglements form, resulted in an increase in tensile strength.

back to Elongation at rupture of blend matrix composite as explained in Table 2,*n* is higher than 3, it is clear that adding a TiO_2filler to the blend groups associated with an initial increase in elastic properties of samples (2T and 3T) then more addition of TiO_2 will result in decrease of elongation as shown in samples (4T,5T), this behave may explain that, the elongation also depend on M_c, in agreement with Etienne et al. results of their studies indicate that optimum elongation at break is found at (20 000) g/mol, at any value exceeding the critical molar mass between cross-links (M_c), where trapped entanglements occur (i.e., the molar mass between two physical cross-linking points or the molar mass of soft segments), leads to the formation of entanglements. Additionally, the molar mass distribution impacts the elastomeric properties of a network, as supported by the findings of E. Delebecq, et al. [15].

Conversely, chains that are elastically inactive, such as loops, dangling chains, and free chains, negatively impact the elastic properties of networks by decreasing the number of elastically active chains. De Gennes proposed the fundamental concept that linear chains are free to reptile [15]. From Figure 6 can be concluded that adding TiO_2 filler improving the mechanical properties of Mother blend group at a certain point and can develop a new composite materials filled with TiO_2 that possess Tensile Strength, modules and Elongation of (9.42 MPa, 9.05 MPa, and 2.7 %) respectively that achieved with specimen 3T which could be recommended for vascular graft applications, it is provide the maximum amounts of tensile strength and modulus accompanied by maximum elongation at break compared to other samples containing TiO_2 and to control reference sample.

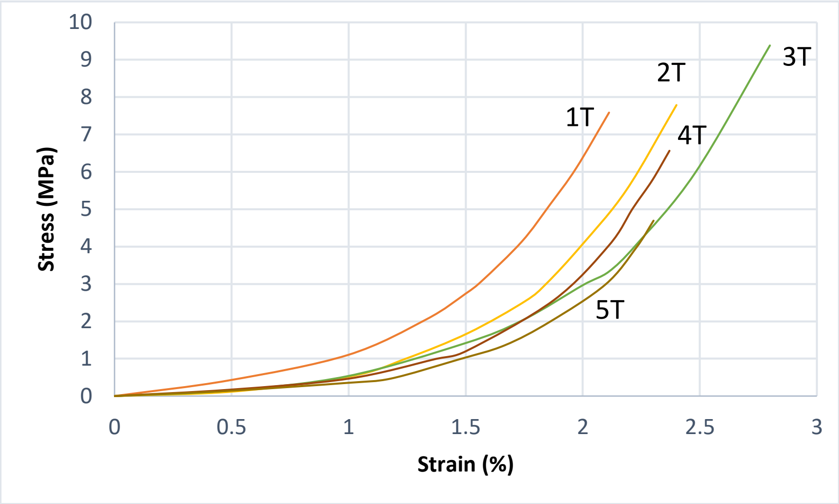
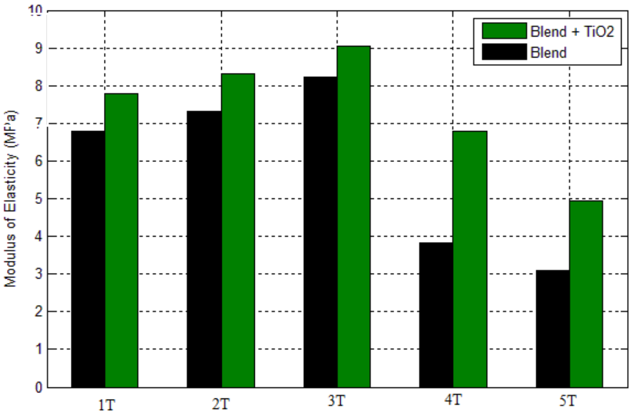


Figure 5. Typical (Stress-Strain) Curve for composite materials with (TiO_2) filler addition.

A



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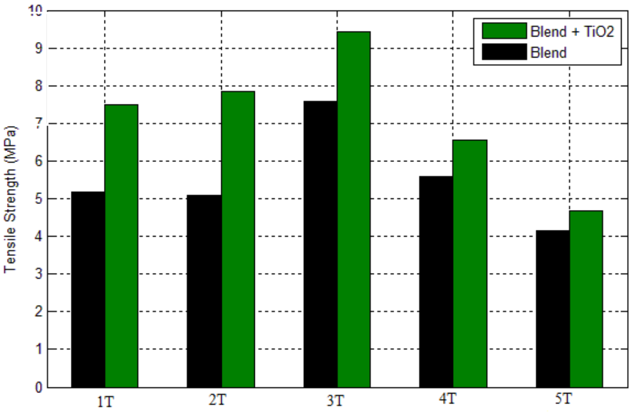

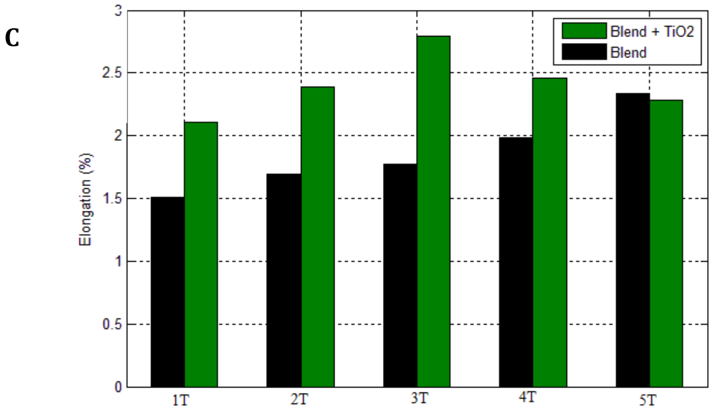

Figure 6. The Mechanical Properties of blends with TiO₂ Fillers. Stress–Strain data were utilized to determine (A) The Elastic Modulus, (B) The Tensile Strength, and (C) The Percentage of Elongation at Rupture, Compared to Mother Blend.

Figures 7 and 8are showing the effect of the Calcium Fluoride (CaF_2) filler, on some of the mechanical properties of blend groups. The results from table 3 of sample 3C had revealed an increase in tensile strength, modulus, and elongation % values (8.82MPa, 8.35 MPa, and 2.6 %) respectively. This behavior is similar to the behavior of mother blend composites filled with TiO_2at which adding CaF_2 filler had improved the mechanical properties of Mother blends group at a certain point. Comparing the results in figures 5 and 7it's obvious that TiO_2 filler increase the tensile properties more than CaF_2filler for mother blends group because ability of dispersionTiO_2 is greater than CaF_2.

The fine particle size of TiO_2 creating higher surface area and provide a greater chance to physical bonds between the polymer and the filler, i.e.an enhancement in modulus and ultimate properties results from a hydrodynamic effect due to the inclusion of rigid particles and an increase in cross-linking density from polymer-filler bonding. Larger CaF_2 filler particles, with a size of ≤ 50 µm, can restrict the movement of the matrix phase near each particle. Meanwhile, the matrix (rubber) transfers a portion of the applied load to the particles, bearing part of the load. While easier dispersion of TiO_2 filler which has a particle size of ≤ 0.3 µm, this tends to hinder or impede the sliding of rubber chains, requiring higher stress to bend them in the narrow spaces between particles, compared to larger CaF_2 particles. Consequently, the matrix bears the majority of the applied load, consistent with the findings of M. Sh. Abed [20].

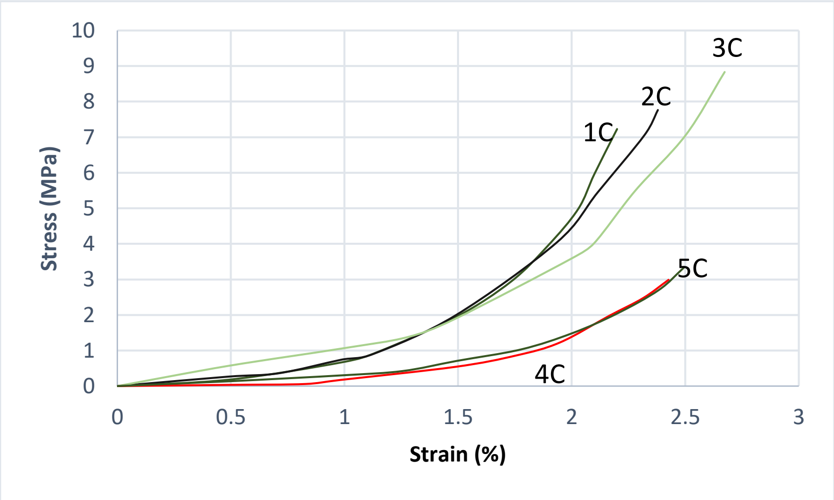

Figure 7. Typical (Stress-Strain) Curve for composite materials with CaF_2 filler addition.

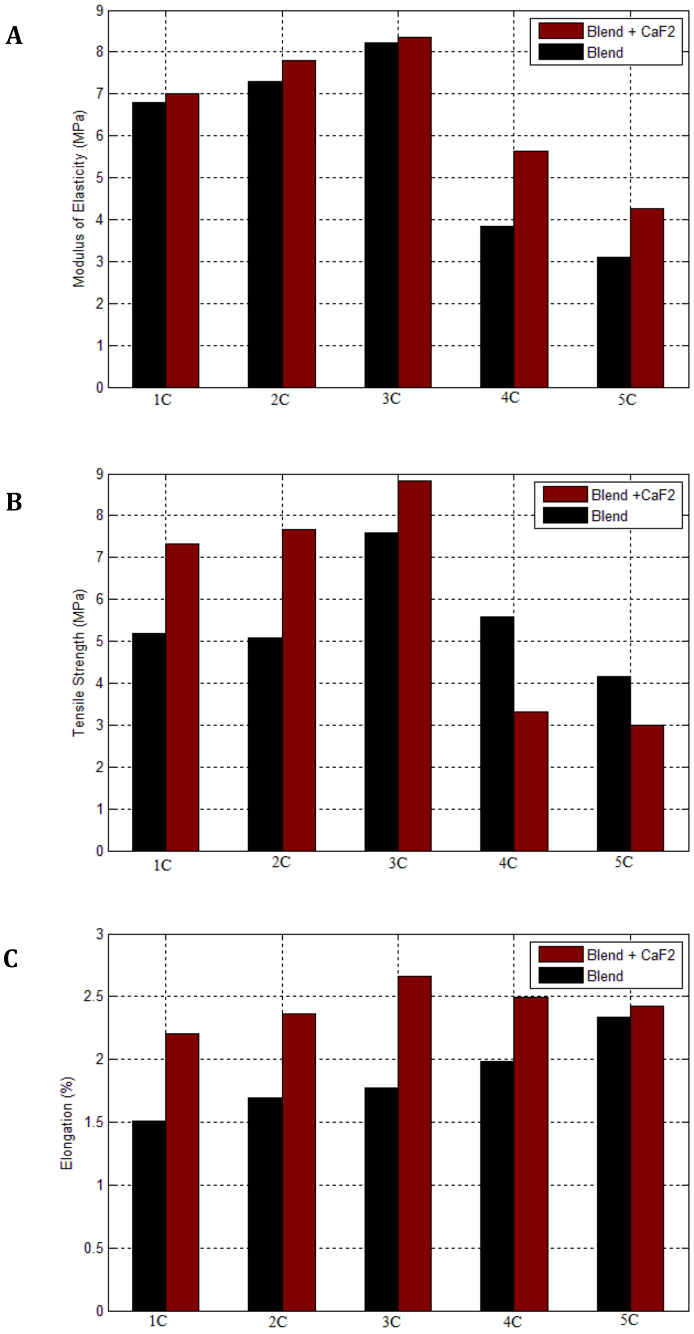

Figure 8. Mechanical properties of composite materials reinforced with CaF_2 fillers. Stress–strain data were utilized to determine (A) The Elastic Modulus, (B) The Tensile Strength, and (C) The Percentage of Elongation at Rupture, Compared to Blend Materials.

3.2 Biocompatibility

Hemolysis of blood is a significant issue related to blood biocompatibility. It is commonly stated that implanted materials may increase hemolysis and that will create a problem of red blood cell rupture and plasma protein absorption on material surface [13].

Table 4 presents the outcomes gained for the hemolysis index (HI) caused by various blend groups. The results are showing that hemolysis index number became less for all PU/SR blend ratios and reached a minimum of 2.3 compared to the HI for control specimen, which is 14. These results indicates that silicones, with their distinct properties of biocompatibility and biodurability, are characterized by terms of hydrophobicity, low surface tension, chemical and thermal stability, that first considered for prevention of blood coagulation since mid-1940s.A. Colas and J. Curtis agreed that for requiring long-term implantation t silicones have an advantageous in many applications because of their chemical stability and modulus of elasticity [21].

Also results in table 5 are showing that the hemolysis index number is lower for all PU/SR ratios when 0.2 % TiO_2 added to the blends, and reached a minimum amount of 2.3 in specimens (3T, 4T, 5T). An addition of 0.5 % CaF_2 to PU/ SR blends had associated with a decrease in HI for all blend ratios and reached its minimum amount of 4.6, which is still lower than the control. The particle size of the fillers affects the Hemolysis Index. Adding TiO_2 to composite blends is exhibiting a higher hemolysis resistance than adding CaF_2. This behavior may explain why there is an absence of good cohesion between polymer and filler that creates gaps in between in some regions of the blend structure. These gaps would likely trap blood and cause hemolysis.

Table 4 Hemolytic indexes number (HI) of tasted prepared polymer blend samples with and without additives

Sample	Ctrl	1B	2B	3B	4B	5B	1T	2T	3T	4T	5T	1C	2C	3C	4C	5C
HI	14	6.9	2.3	2.3	2.3	2.3	6.9	4.6	2.3	2.3	2.3	6.9	6.9	4.6	4.6	4.6

4. CONCLUSION

Tensile results had revealed that all mother blend groups have tensile strength lower than the control, reaching its maximum value with sample 3B when adding SR. The addition of $TiO_2$and CaF_2tends to decrease tensile strength values compared to mother blend groups except for composite blends 3Tand 3C, which show higher tensile strength compared to the reference of PU. Additionally, the hemolytic index (HI) test shows a significant improvement of the biocompatibility of all prepared composite specimens, specifically in mother blends (2B, 3B, 4B, and 5B) and mother blends containing0.2 % TiO_2(3T, 4T, and 5T), where the HI was 2.3 as compared to the PU reference specimen where the HI is 14. Table 5 summarizing the maximum tensile strength that achieved in the study.

Table 5 Maximum tensile strength achieved

No. of sample	**PU**	**SR**	**TiO_2 additive**	**CaF_2 additive**	**Tensile Strength (N/mm)**
Control	100	0	0	0	8.51
3B	96	6	-	-	7.59
3T	94	6	0.2	-	9.42
3C	96	6	-	0.5	8.82

REFERENCES

[1] Mei-Xian Li, Qian-Qi Wei, Hui-Lin Mo, Yu Ren, Wei Zhang, Huan-Jun Lu and Yoon Ki Joung, “Challenges and advances in materials and fabrication technologies of smalldiameter vascular grafts”, Biomaterials Research, vol. 27,no 1, pp.58 ,2023. https://doi.org/10.1186/s40824-023-00399-2.

[2] Bruna B. J. Leal, Naohiro Wakabayashi, Kyohei Oyama, Hiroyuki Kamiya, Daikelly I. Braghirolli and Patricia Pranke,”Vascular Tissue Engineering: Polymers and Methodologies for Small Caliber Vascular Grafts”,Front. Cardiovasc. Med., Sec. Cardiovascular Biologics and Regenerative Medicine, vol.7, pp. 592361, 2021.https://doi.org/10.3389/fcvm.2020.592361

[3] Michael Szycher, “CardioPass TM Coronary Artery Bypass Graft”, CardioTech International, Inc. A progress report. www.mszycher@cardiotech-inc.com,2002.

[4] Leonard Pinchuka, Gregory J. Wilsonb, James J. Barryc, Richard T. Schoephoersterd, Jean-Marie Parele,f, Joseph P. Kennedyg, "Medical applications of poly(styrene-block-isobutylene-block-styrene) (“SIBS”)”. Biomaterials, vol. 29, no.4, pp. 448-460, 2007. doi:10.1016/ j.biomaterials.2007.09.041

[5] Haw-Ming Huang, ”Medical Application of Polymer-Based Composites. Polymers”., 2020, doi: 10.3390/polym12112560.

[6] Deepa Ahirwar, Amit Telang, Rajesh Purohit, Anurag Namdev. “A short review on polyurethane polymer composite”.Materialstodayproceedings, vol. 62, pp. 3804-3810, 2022. https://doi.org/10.1016/j.matpr.

[7] Mina Zare, Erfan Rezvani Ghomi, Prabhuraj D. Venkatraman, Seeram Ramakrishna. “Silicone-based biomaterials for biomedical applications”,Antimicrobial strategies and 3D printing technologies. Journal of Applied Polymer Science, Vol. 138, no. 38, 2021. https://doi.org/10.1002/app.50969.

[8] Qingxia Zhu, Xiaofei Li, Zhaobo Fan, Yanyi Xu, Hong Niu, Chao Li, Yu Dang, Zheng Huang, Yun Wang, and Jianjun Guan. ”Biomimetic Polyurethane/TiO2 Nanocomposite Scaffolds Capable of Promoting Biomineralization and Mesenchymal Stem Cell Proliferation”. Mater SciEng C Mater Biol Appl., vol. 85, pp. 79-87, 2018. doi: 10.1016/j.msec.2017.12.008

[9] Marion Straßer, Joachim H X Schrauth, Sofia Dembski, Daniel Haddad, Bernd Ahrens, Stefan Schweizer, Bastian Christ, Alevtina Cubukova, Marco Metzger, Heike Walles, Peter M Jakob, and Gerhard Sextl. “Calcium fluoride based multifunctional nanoparticles for multimodal imaging”. , vol. 8, no. 1, pp.1484–1493.2017, doi: 10.3762/bjnano.8.148.

[10] Hanna, W. A. ”Characterization of Polyester Base-K2CO3 Composite Used for Biomedical Applications”. Journal of King Abdulaziz University, Engineering Sciences, vol 25, no. 1,2014.http://doi.orq/10.4197/eng.25,1.7.

[11] ASTM International. “Standard test method for tensile properties of plastics”. ASTM international; 2014.

[12] Callister, William D., and David G. Rethwisch, “Materials Science and Engineering: An Introduction”. 11th ed., NJ: John Wiley & Sons, Inc, pp. 123. Hoboken, 2020.

[13] J. Meng, H. Kong, H. Y. Xu, L. Song, C. Y. Wang, S. S. Xie, “Improving the Blood Compatibility of Polyurethane Using Carbon Nanotubes as Fillers and its Implications to Cardiovascular Surgery”, vol. 74 , no. 2, pp. 208-214,2005. https://doi.org/10.1002/jbm.a.30315

[14] ASTM, Designation,”D756–93, Standard Practice for Assessment of Hemolytic Properties of Materials”, American Society for Testing and Materials, 1993.

[15] E. Delebecq, N. Hermeline, A. Flers, and F. Ganachaud,''Looking over Liquid Silicone Rubbers: Mechanical Properties vs Network Topology'', Appled Materials Interfaces, Vol. 4, no. 7, pp. 3353–3363, 2012.

[16] B. J. Persson, O. Albohr, G. Heinrich and H. Ueba:''Crack Propagation in Rubber-Like Materials'', Journal of physics /condensed matter, Vol.17, no. 44, pp.1071-1142, 2005.

[17] A. Colas and J. Curtis. ''Silicone Biomaterials / History and Chemistry & medical Application of silicones'', Elsevier Academic Press, Second Edition 2005.

[18] T. Chuang and K. S. Masters. ''Regulation of Polyurethane Hemocompatibility and Endothelialization by Tethered Hyaluronic Acid Oligosaccharides'', Biomaterials, Vol. 30,no. 29, pp. 5341–5351, 2009.

[19] E. Yilgor, T. Eynur, C. Kosak, S. Bilgin, I. Yilgor, O. Malay, Y. Menceloglu, and G. L. Wilkes: "Fumed silica filled poly (dimethylsiloxane-urea) segmented copolymers: Preparation and properties", Vol.52, no. 19, pp.4189-4198, 2011.

[20] M. Sh. Abed:'' Improving the Properties of the Tire Tread by Adding SiO2and Al2O3 to SBR and NR Rubbers'', M.Sc. Thesis, University of Technology, 2008

[21] A. Colas and J. Curtis. ''Silicone Biomaterials / History and Chemistry & medical Applicationof silicones'', Elsevier Academic Press, vol. 2, pp. 80-85, 2005.