Natural Rubber Nanocomposite with Human-Tissue-Like Mechanical Characteristic

Riri Murniati, Nanda Novita, Sutisna, Edy Wibowo, Ferry Iskandar and Mikrajuddin Abdullah*

Material Electronics Research Group, Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung Jalan Ganesa 10 Bandung 40132 Indonesia

*din@fi.itb.ac.id

Abstract. The blends of synthetic rubber and natural rubber with nanosilica were prepared using a blending technique in presence of different filler volume fraction. The effect of filler on morphological and mechanical characteristics was studied. Utilization of human cadaver in means of medical study has been commonly used primarily as tools of medical teaching and training such as surgery. Nonetheless, human cadaver brought inevitable problems. So it is necessary to find a substitute material that can be used to replace cadavers. In orthopaedics, the materials that resemble in mechanical properties to biological tissues are elastomers such as natural rubber (latex) and synthetic rubber (polyurethanes, silicones). This substitution material needs to consider the potential of Indonesia to help the development of the nation. Indonesia is the second largest country producer of natural rubber in the world. This paper aims to contribute to adjusting the mechanical properties of tissue-mimicking materials (TMMs) to the recommended range of biological tissue value and thus allow the development of phantoms with greater stability and similarity to human tissues. Repeatability for the phantom fabrication process was also explored. Characteristics were then compared to the control and mechanical characteristics of different human body part tissue. Nanosilica is the best filler to produce the best nanocomposite similarities with human tissue. We produced composites that approaching the properties of human internal tissues.

1. Introduction

In medical, cadavers had been used as an object of study and research, especially for medical surgical training. However arise some problems behind the use of this cadaver such as durability, costly, availability, and issues of morality. The cadavers that will be studied by medical students come from a range of ages and conditions were completely random [1]. As medical science has progressed, it has become increasingly important to provide non-human interactive formats for teaching patient care. While it is desirable to train medical personnel in patient care protocols before allowing contact with real patients. On the other hand, allowing inexperienced students to perform medical procedures on actual patients that would allow for the hands-on practice cannot be considered a viable alternative because of the inherent risk to the patient. Non-human interactive devices and systems can be used to teach the skills needed to successfully identify and treat various patient conditions without putting actual patients at risk [2].

Such training devices and systems can be used by medical personnel and medical students to teach and assess competencies such as patient care, medical knowledge, practice-based learning and systems
based practice. The training devices and systems can also be used by patients to learn the proper way to perform self-examinations. In particular, structures for simulating body tissue for use in practicing surgical and/or clinical techniques. In the medical field, it is necessary for students, doctors, and surgeons to be able to practice surgical and clinical techniques. Especially, they need to practice incisions, the removal of various kinds of complaint (such as cysts, and melanomas), access to venous structures below the epidermis and the insertion of sutures. As an alternative to providing an actual body or part of an actual body for practicing such techniques, there is a need for artificial means whereby they can be practiced. Known structures providing simulations of body tissue suffer from the disadvantage that they are not sufficiently analogous, either visually or physically, to actual body tissue [3].

We use a substitute material to create a mimicking human cadaver through this study. This is due to the urgency of material selection in accordance with the potential of Indonesia. Indonesia is a country with a long history in agriculture and plantations. So in the manufacture of replacement cadaveric material need to choose a material that has become a mainstay product Indonesia for a long time. Rubber production in Indonesia also have to be a concern, still not fully used by the industry in Indonesia and the price drops dramatically. Indonesia is the second largest rubber producer in the world. Excess production of rubber will then be exported without being processed or in a raw state. It is very worrying that should be considered a solution to steer this product to a more promising alternative industries.

Natural rubber (NR) is known to exhibit numerous outstanding properties such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength; having properties resembling those of synthetic rubbers. Natural rubber coming from latex is mostly polymerized isoprene with a small percentage of impurities in it. This will limit the range of properties available to it, although addition of sulfur and vulcanization are used to improve the properties. Synthetic rubber is any type of artificially made polymer material which acts as an elastomer. Synthetic rubber serves as a substitute for natural rubber in many cases, especially when improved material properties are needed. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvements in processing [4]. Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus [5,6]. The idea of blending synthetic rubbers with natural rubber is certainly not a new one, but it is only now that this can be shown to be possible with consistently positive results, by the use of new techniques developed over the last five years. These compounds are capable of forming a chemical link between these dissimilar rubbers to produce a technologically compatible blend. The blend vulcanizes thus produced exhibit enhanced physical properties by judicious selection of the NR: HSR ratio [7]. The use of carbon black is synonymous with the history of tyres. Although it has lost some ground to other reinforcing fillers such as silica, by virtue of its unrivalled performance, it is still the most popular and widely used reinforcing filler. However, the primary properties of carbon blacks are normally controlled by particle size, surface area, structure, surface activity and they are in most cases interrelated [8].

Silicone-based tissue-mimicking phantom is widely used as a surrogate of tissue for clinical simulators, allowing clinicians to practice medical procedures and researchers to study the performance of medical devices [9]. Polydimethylsiloxane (PDMS) tissue simulating phantoms with tuneable optical properties to be used for optical system calibration and performance testing in visible and near infrared domain also had been studied. Compared to liquid phantoms, cured PDMS phantoms are easier to transport and use, and have a longer usable life than gelatine based phantoms [10].

Matrix materials typically are water, gelatine, agar, polyester or epoxy and polyurethane resin, room-temperature vulcanizing (RTV) silicone, or polyvinyl alcohol gels. The water and hydrogel materials provide a soft medium that is biologically and biochemically compatible with the addition of organic molecules and are optimal for scientific laboratory studies. Polyester, polyurethane, and silicone phantoms are essentially permanent matrix compositions that are suitable for routine calibration and testing of established systems. The most common three choices for scatters have been: lipid-based emulsions, titanium or aluminium oxide powders, and polymer microspheres [11].
2. Methods

The novelty of this study uses natural rubber-based tissue mimicking human tissue. This is due to the urgency of material selection in accordance with the potential of Indonesia. So in the manufacture of replacement cadaveric material need to choose a material that has become a mainstay product Indonesia for a long time. The product is natural rubber. This study investigates using some formula of materials to create the desired mechanical properties and surgery characteristics of a tissue-mimicking tissue. The substitute materials have been determined as well as the composite material to be mixed into the rubber material. To be able to have the cadaver characteristics, we choose three types of filler material: caolin, calcium carbonate, and nanosilica. This is to see which is most effective filler in modifying natural rubber character resembles a human cadaver, and nanosilica is the one. Then the use of filler will be further optimized by using a variation of the volume fraction. It also conducted a matrix constituent mix between natural rubber and silicone rubber. Then it will do a comparison between the two materials. Silicone itself has a price that is much more expensive than natural rubber. So the comparison also serves to optimization apart from evoking the characteristics of a human cadaver in natural rubber by using a mixture of silicone rubber.

Basically, this experiment is divided into several phases: Phase design and manufacture of hot press mold and incision test equipment, the synthesis of samples, material characterization and retrieval of data, and analysis phase. Molds needed with special specifications, good material, size, and performance. A molding used is made of stainless steel, with a length of 10 cm, width 7 cm, and height 3 cm. That is not only as container scored but also serves as a heater that will enhance curing maturation. The precursors will be made by the optimization of the type of base material used rubber (liquid latex and silicone rubber). Samples were synthesized by mixing several chemicals (Table 1), the formula that is used depends on the type of materials used, the order of input materials, stirring time and the amount of material used. All formulas were found to be tested and repeated continuously until it was the most appropriate formula to produce nanocomposite most similar in structure mechanics with human flesh.

Table 1. Formula of the Materials

| Materials             | phr (part per hundred rubber) |
|-----------------------|-------------------------------|
| Latex-silicone rubber | 100                           |
| Filler                | 1.5                           |
| TiO₂                  | 1                             |
| Minarex oil           | 7.5                           |
| ZnO                   | 0.5                           |
| Stearat acid          | 0.5                           |
| Parafin wax           | 0.5                           |
| Food coloring         | 1                             |
| Texapan               | 1                             |
| CMC                   | 0.5                           |
| Sulphur               | 0.5                           |
| Gelling agent         | 0.5                           |

Do mixing precursor liquid latex with a foaming agent and a curing agent for a certain time (according to the formula), then added with a stabilizer and gelling agent. Meanwhile, another sample was mixed using filler then mixed with a stabilizer and gelling agent. Then the precursors and the material is dried and burned [12]. For a variety of rubber, natural rubber is mixed in advance with silicone rubber before being added foaming agent, gelling agent, curing agent and stabilizer. Also use softener and activator to facilitate the mixing process of the composite, and then put into the oven for 2 hours at a temperature of 150 °C, and then inserted into the mold molding and curing hot press for 1 hour at 100 °C. The sample was tested with the incision test equipment that had been designed specifically to testing of meat slicing (surgery-like) using tools that created by our team. Testing of the
control samples was also performed on samples made from synthetic rubber (silicone) and beef. The material crosslink densities measured by swelling using the Flory–Rehner theory and the filler volume fractions are calculated with the component densities. The control samples also tested and compared. Data obtained from this characterization then compared with reference to mechanical strength and morphology meat/human cadaver to see the similarity of the material and what could be improved for future research.

Mechanical tests were performed using an Universal Testing Machine, the sample needs to be formed into the shape of a small dumbbell. The length of each sample was homogeneity to facilitate the processing of data. In addition, the material needs to be in a solid phase to perform this mechanical test. Actually for mechanical tests, not only the stress-strain testing needs to be done, but also the viscoelastic characteristics [13]. The data obtained from this test in the form of stress-strain curve then we can calculate the Young's modulus of composites. In an undeformed thermoplastic polymer tensile sample [14-15], the polymer chains are randomly oriented. When a stress is applied, a neck develops as chains become aligned locally. The neck continues to grow until the chains in the entire gage length have aligned. Elastic modulus is the mathematical description of an object or substance's tendency to be deformed elastically (i.e., nonpermanently) when a force is applied to it. The elastic modulus of an object is defined as the slope of its stress-strain curve in the elastic deformation region.

3. Results and Discussion

We conducted a study of variation filler, the filler used in this experiment is kaolin, CaCO3, and nanosilica. The sample with nanosilica filler shows experimental results that more constant and material strength is better than other fillers. The nanosilica filler mass then optimized then we get the sample with 12 grams nanosilica filler is the best one to be added to the composite before the gelling agent added, with filler volume fraction variation can be obtained a variety of composite strength obtained by difference filler [16]. The properties of rubber will determine which kind of rubber is best-suited for any sort of application, or perhaps whether or not a combination of the two kinds of rubbers is necessary. Such an occurrence happens with automobile tires, which are constructed out of a mixture of natural gum rubber and synthetic rubber. On the other hand, the design of aircraft tires necessitates that they be made completely out of natural rubber. Clearly then, there are things which distinguish the two products, as no matter how great science and technology is today, it cannot perfectly replicate natural rubber.

![Figure 1](image_url)

**Figure 1.** Curve of Young’s Modulus of Natural-Silicone Rubber Composition.

In the Figure 1 shown the area elastic force curve of the change in length along the slope dF / dl are then used to calculate the Young's modulus. Elastic behavior is a reversible behavior that often shows a linear relation between stress and strain. In an undeformed thermoplastic polymer tensile sample, the
polymer chains are randomly oriented. When a stress is applied, a neck develops as chains become aligned locally. The neck continues to grow until the chains in the entire gage length have aligned. Then the strength of the polymer is increased. The data will then be compared to the literature of cadavers or human flesh characteristics.

![Figure 2. Hardness and Crosslink Density of Natural Rubber Volume Fraction.](image)

Each material that added give hardness contribution in compound, specially for fillers and the elastomers. Kaolin and Calium Carbonate give hardness contribution + 0.25 shore A / 1 phr, nanosilica give hardness contribution + 0.5 shore A / 1 phr, natural rubber (latex) + 40 shore A / 1 phr, and silicone rubber + 44 shore A / 1 phr. We can see the hardness calculation results as seen in Figure 2 and Figure 3, hardness of the composite is linear with nanosilica filler and silicone rubber volume fraction, reverse with natural rubber volume fraction, and relative with natural-silicone rubber combination.

![Figure 3. Hardness and Crosslink Density of Silicone Rubber Volume Fraction.](image)

The cross-link density was determined by immersing a small amount (known mass) of sample in 100 ml toluene to attain equilibrium swelling. After this the sample was taken out from the toluene and the solvent was blotted from the surface of the sample and weighed immediately. This sample was
then dried out at 80 °C to constant weight. Then the chemical cross-link density was calculated by the Flory–Rehner equation[17]. Higher crosslink density is observed in Figure 3 for the compounds containing 100 phr elastomers with combination of 75% natural rubber and 25 % silicone rubber, or containing 58.8 % natural rubber volume fraction and 19.6 % silicone rubber volume fraction of all materials in the composite. Natural rubber has a quality known as “tack,” meaning that it adheres well to itself and to other materials. Silicone rubber has chemical resistance, it cannot be readily changed when it comes into contact with other materials. Silicone and natural rubber combination properties is non-reactive: both are chemically resistant to many fluids including water and weak acids. Excellent as an adhesive or a protective coating. Both can undergo vulcanization, meaning that chemical bonds are strengthened by sulfur. The backbone of silicone contains silicon and oxygen, while the backbones of most of the other rubbers contain carbon-carbon bonds. Silicone can be distinguished from rubbers by the atomic structure.

Calculation results of Young's modulus of this experiment then compared to references that can be seen in Table 2. Referring to this table, it can be seen that composite with natural-silicone rubber composition with nanosilica filler shows experimental results that relatively constant close to the mechanical characteristic of some human body part. So that using nanosilica filler, it will be easier to manipulate characteristics, then the experiment will be conducted the filler mass variation of nanosilica [18].

### Table 2. Mechanical Characteristic of Human Body

| Body                             | Gender  | Age (year) | Modulus Young (Mpa) | Ref. |
|----------------------------------|---------|------------|---------------------|------|
| Bicep Muscle                     | Man     | 65         | 49.02               | [19] |
| Bicep Muscle                     | Man     | 85         | 59.15               | [19] |
| Bicep Muscle *                   | Man     | 75         | 48.74               | [19] |
| Leather Back                     |         | 30         | 200                 | [20] |
| Leather Back                     |         | 9          | 0.42                | [20] |
| Cartilage in the knee            | Man     | 16         | 0.13                | [20] |
| Cartilage in the knee            | Woman   | 65         | 1.91                | [20] |
| Shoulder Muscle (Anterior)       |         |            | 16.5                | [22] |
| Shoulder Muscle (Middle)         |         |            | 6                   | [22] |
| Shoulder Muscle (Posterior)      |         |            | 4.1                 | [22] |
| Esophagus                        |         |            | 0.077               | [22] |
| Gut                              |         |            | 0.0356              | [22] |
| Gut*                             |         |            | 0.0359              | [22] |
| Pericardium                      |         |            | 2.51                | [22] |
| Achilles tendon                  |         |            | 819                 | [23] |
| Patellar tendon                  |         |            | 643                 | [24] |
| Ligament (cruciate ligament)     |         |            | 345                 | [24] |
| Semitendinosus tendon            |         | 26         | 362.2               | [25] |
| Ligament (ligamentum flavum)     | young   |            | 98                  | [26] |
| Ligament (ligamentum flavum)     | old     |            | 20                  | [26] |
| Ankle ligament (anterior talofibular ligament) | Woman | 27 | 86 | [27] |
| Cartilage (HWA of femoral condyle, superficial zone) | | | 5 | [28] |
| Cartilage (HWA of femoral condyle, middle zone) | | | 3.1 | [28] |
| Cartilage (LWA of femoral condyle, superficial zone) | | | 10.1 | [28] |
| Cartilage (LWA of femoral condyle, middle zone) | | | 5.4 | [28] |

The increase in young’s modulus in Figure 6 may be due to the fact that an increasing volume fraction of nanosilica caused the vulcanization reaction to increase and create more active cross-link sites in the rubber compound. From both crosslink density and young’s modulus results, the
compounds with 7.84 % volume fraction of nanosilica filler have given higher result. From these studies, a balancing correlation has obtained for the same compounds under standard abraders.

4. Conclusion
Nanosilica is used in filler has nano-sized particles while the caolin and CaCO3 that used in powder size. Visually, hardness and density of material obtained that a composite rubber calcium carbonate and kaolin is not too much different from the rubber control. While the nanosilica composite rubber is much denser and Young's modulus values obtained from the composite rubber nanosilica also greater than calcium carbonate and kaolin composite rubber. Young's modulus data compared between the experimental results and the human body characteristics, it can be concluded that the rubber composite of 25 % natural rubber and 75 % silicone rubber (0.07 MPa), and 100 % silicone rubber (0.08 MPa) has mechanical characteristics that resemble human esophagus (0.077 MPa). Rubber composite of 50% natural rubber and 50 % silicone rubber has characteristics resembling cartilage in the knee man teens (0.13MPa). While the composite rubber of 75% natural rubber and 25 % silicone rubber (0.22 MPa) has characteristics resembling children leather back (0.42 MPa). Nanosilica volume fraction shows the best result at 58.8 % natural rubber volume fraction and 19.6 % silicone rubber volume fraction with 12 gram nanosilica filler (10 per hundred rubber), the highest young’s modulus and crosslink density are performed.

5. References
[1] Kaku M 2011 Physics of the Future: How Science Will Shape Human Destiny and Our Daily Lives by the Year 2100 (New York: Doubleday).
[2] Lowe S 2015 Surgical simulation models, materials, and methods Patent US9123261 B.
[3] Cooper CM, Sunderland J 1998 Method of Making A Surgical And/ Or Clinical Apparatus. Patent US005775916A.
[4] Tinker AJ, Jones KP 1998 Blends of natural rubber novel techniques for blending with specialty polymers (London: Chapman and Hall).
[5] Choi SS, Nah C, Lee SG, Joo CW Effect of filler-filler interaction on rheological behaviour of natural rubber compounds filled with both carbon black and silica 2003 Polym. Int 52 (1) 23.
[6] Heinrich G, Kluppel M, Vilgis TA. Reinforcement of elastomers 2002 Curr Opin Sol. State Mater Sci 6 (3)195–203.
[7] Naskar N, Debnath SC, Basu DK 2001 Novel method for preparation of carboxylated nitrile rubber-natural rubber blends using bis(diisopropyl)thiophosphoryl polysulfides J. Appl. Polym. Sci 80 (10) 1725–36.
[8] Nasir M, Choo CH 1989 Chemical modification of natural rubber latex with peracetic acid Polym. J 25(4) 355–9.
[9] Wang Y, Tai BL, Yu H, Shih AJ 2014 Silicone-Based Tissue-Mimicking Phantom for Needle Insertion Simulation J. Medical Devices - Asme 8 117-123.
[10] Ayers F, et al. 2008 Fabrication and characterization of silicone-based tissue phantoms with tunable optical properties in the visible and near infrared domain Proc. of SPIE 6870 1-9.
[11] Pogue BW, Patterson MS 2006 Review of tissue simulating phantoms for optical spectroscopy, imaging and dosimetry J. Biomed. Opt 11 041102.
[12] ASM International 2004 Tensile Testing Second Edition.
[13] ISO 37 2011 Methods of test for vulcanized rubber, Part 1 determination of tensile stress-strain properties (Third Revision).
[14] Sakranii S 2009 Mechanical Properties and Testing, Open course ware (University Teknologi Malaysia).
[15] Gedney R 2002 Guide To Testing Metals Under Tension Advan. Mat. Process. pp. 29–31.
[16] Kaku M 1982 Hand book of composites (Van Nostarnd: New York).
[17] Manik SP, Banerjee S 1979 Determination of chemical cross-links in rubbers Macromol. Mater. Eng 6 (71) 171–8.
[18] Cassagnau P 2003 Payne Effect and Shear Elasticity Of Silica-Filled Polymers In Concentrated Solutions and in Molten State Polym 44 (8) 2455-2462.
[19] Egorov VI, et al. 2002 Mechanical Properties of The Human Gastrointestinal Tract J. of Biomech 35 (10) 1417-1425.
[20] Agache PG, et al. 1980 Mechanical Properties And Young's Modulus Of Human Skin In Vivo, Arch. Dermatol. Res 269.3 221-232.
[21] Armstrong CG, Mow VC 1982 Variations In The Intrinsic Mechanical Properties Of Human Articular Cartilage With Age, Degeneration, And Water Content J. of Bone and Joint Surgery 87-94.
[22] Itoi E, et al. 1996 Tensile Properties of The Supraspinatus Tendon J.of Shoulder and Elbow Surgery 5 (2) S28.
[23] Wren TAL, Yerby SA, Beaupre GS and Carter DR 2001 Mechanical properties of the human Achilles tendon Clinical Biomech 16 245–251.
[24] Butler DL, Kay MD and Stouffer DC 1986 Comparison of material properties in fascicle-bone units from human patellar tendon and knee ligaments J. of Biomech 19 425–432.
[25] Butler DL, Grood ES, Noyes FR, Zernicke RF, Brackett K 1984 Effects of structure and strain measurement technique on the material properties of young human tendons and fascia, J.of Biomech 17 579-596.
[26] Nachemson AL, Evans JH 1968 Some mechanical properties of the third human lumbar interlaminar ligament (ligamentum flavum) J. of Biomech 1 211–220.
[27] Pierre RKS, Rosen J, Whitesides TE, Szczukowski M, Fleming LL, Hutton WC 1983 The tensile strength of the anterior talofibular ligament Foot Ankle 4 83-85.
[28] Akizuki S, et al. 1986 Tensile properties of human knee joint cartilage: I. Influence of ionic conditions, weight bearing, and fibrillation on the tensile modulus J. of Orthop. Research 4 379–392.
[29] Edwards M, et al. 2005 Mechanical Testing Of Human Cardiac Tissue: Some Implications For MRI Safety J. of Cardiovas. Mag.Reson 7 (5) 835-840.

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