Chapter

Biofunctionalized Polymer Nanomaterials: Implications on Shapes and Sizes

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Abstract

Nanotechnology has been one of the most widely used tools in various industries such as pharmaceutical, food, and chemistry, among others, for the encapsulation of compounds or even microorganisms. However, an analysis of the methodologies or polymer matrices to be used is rarely generated, and these in turn contribute to the objective of the product that is intended to be designed. In addition to the evaluation of its physicochemical, optical, and rheological characteristics, and others, are a set of technological tools that allow predicting the stability of a colloid, however, some of the factors that have less importance as the effect of the synthesis process on the shape and size that a structure may have, studies have been carried out to evaluate this phenomenon, which has become a determining factor in the design of any nanoscale material.

Keywords: functionalization, synthesis, polymers, biomaterials

1. Introduction

Recently, the science of nanomaterials has gained strength, due to the wide applications as it is in the pharmaceutical, food, agricultural and other industries, since it has been a tool that allows making the objectives of each of them more efficient in comparison with the direct compound applications, because there are different processes to trap them generating this form particles resistant to biochemical oxidations, UV radiation, gastric digestion or even in some cases can be taken as transport [1, 2].

In this context, the advances in technologies for encapsulation has allowed the development and implementation of polymer matrices with enhanced properties, however, in some cases the size and amount of the materials are not adequate causing allow stability in the emulsion [3].

Due to the growing demand for these materials and the large amount of study that exists, the custom synthesis has been generated, which allows us to obtain materials in suitable sizes depending on the characteristics of the objective, through basic techniques and in some cases with the basic elements that are described below.
2. Functionalization of polymers: synthesis-controlled shapes and sizes

One of the principal objectives of nanoscience is building small structures for the design of advanced material nanodispositives of high performance. Inorganic nanoparticles are particularly attractive as construction parts for such purposes due to their unique optical, electronegative, and catalytic properties, many of those can be modulated simply by changing their shape, state, or functionality of the surface of the nanoparticle, without changing the composition of the material [4–6].

Figure 1 shows a proposed diagram for some of the sections that encompass nanoscience.

Due to their physical and chemical properties, nanoparticles are often described as artificial atoms. The advances in the processes of synthesis have allowed the precise control over the structural parameters that govern the formation of the nanoparticles which has allowed to adapt the properties of these artificial atoms according to their specific use. The synthesis and modular assembly of nanoparticles allows to exploit their unique properties, which can lead to new applications in catalysis, electronics, photonics, magnetism, as well as chemical and biological sensing.

The nanoparticles can be obtained mainly by two different ways: “Top-down” (Chemical vapor deposition, Thermal evaporation, and Ion implantation) and “Bottom-up” (Microwave irradiation, Colloidal, Solvothermal, Dendrimers, and Sol-gel), where each method exhibit its particular characteristics as described below [7].

2.1 Top-down methods

Top-down focuses on the division of mass solids in small proportions, in which operations such as grinding, chemical methods, or volatilization of a solid can be involved from individual molecules [8]. The most representative is shown below:

- **Chemical vapor deposition (CVD):** It consists of the decomposition of one or more volatile compounds, inside a vacuum chamber, to produce products of high purity and yield in solid materials. It is used for the design of mono and polycrystalline materials, amorphous and epitaxial in titanium nitride, carbon nanotubes, silica dioxide, carbon fibers, and others [6].
• **Thermal evaporation**: It consists of heating until the evaporation of the material that is to be deposited. It is carried out in a vacuum chamber in which the vapor is condensed on a cold sheet, requiring always an accurate control of the growth conditions so as not to produce a modification of the morphology of the deposited layer [9].

• **Ion implantation**: The process consists in the interaction of the ion of a solid material when implanted in another, changing therefore its physical properties. It is used in the manufacture of coating devices for some metals used as semiconductors, as in research in the science of nanomaterials, due to its versatility and ease of control, which allows the synthesis of a wide range of nanocrystals. The ions cause chemical and structural changes in the matrix of origin, since they can be of an element different from the one that composes it, which can be damaged by the glass or even destroyed [10].

2.2 **Bottom-up methods**

Bottom-up synthesis requires complex, and expensive instrumentation, the most used are under chemical procedures; which is based in the reduction of metallic ions to metal atoms, consequently the aggregation of the atoms in controlled. On the other hand, the nanoparticles obtained by this method exhibit uniform and small structures as described below.

• **Microwave irradiation**: Microwave irradiation produces nanoparticles, which have a low size dispersion without precise control in morphology, as it happens in most “bottom-up” techniques. This method creates a high-frequency electric field, any material can be heated, containing electrical charges such as polar molecules in a solvent or conductive ion in a solid. The polar solvents are heated, and their molecular components are forced to rotate with the field and lose energy in collisions. The conductive and semiconductor samples are heated when the ions and electrons contained in them form an electric current, and the energy is lost due to the electrical resistance of the component. In recent years, given that it is a uniform, effective, and fast method, it has been used as an attractive alternative for the synthesis of nanometer-scale materials. Colloidal nanoparticles of Pt, Ru, Ag, and Pd stabilized by polymers have been prepared by microwave heating, from the metal precursor salts dissolved in ethylene glycol solutions [11] (Figure 2).

• **Colloidal**: Colloids are individual particles; they are larger than atomic sizes, but small enough to produce Brownian motion. When the particles are sufficiently large, their dynamic behavior in suspension as a function of time is governed by the forces of gravity and will cause the phenomenon of sedimentation; it is attributed to collective bombardments of a multitude of thermally agitated molecules in a liquid suspension when they are small enough to be colloids. This method is efficient due to the size range that the nanoparticles are produced, which oscillates below 300 nm depending on parameters of elaboration [12, 13] (Figure 3).

• **Solvothermal**: It is an efficient method of production of materials consisting of the conjugation of substances that are reacted in a hermetically sealed container at low temperatures (generally at 200°C) and controlled pressure. The objective of the technique is to mix immiscible compounds with each other under normal conditions (aluminosilicates, titans, sulfides, etc.).
environmental pressure inside the system is exceeded since it occurs in a closed system, in which solvents surpass boiling points, generating a state of “critical” fluid in which certain chemical reactions that not occur under usual conditions. Once the system is cold, the structures reach the crystalline phase. Low energy, accelerated interactions between species, controlled stoichiometry, the greater power of dissolution and transport of reagents, better control of morphology, and a reaction yield close to 100% are some of the advantages of this technique. It is currently used to synthesize a variety of compounds of scientific and industrial interest [14].

- **Dendrimers**: It is a method based on the intervention of micelles, emulsions, and dendrimers, which allows defined shapes and sizes; however, it is a technique that requires a long process to obtain good results in addition to intervening variables
such as time, temperature, pressure, speed of homogenization, and molecular weight, among others, to obtain good results [15].

The most suitable dendrimers for the synthesis of hybrid and monometallic nanoparticles are of different generations with some functional groups. The poly(amidoamines) are the most popular dendrimers used to synthesize gold nanoparticles oscillating between 1 and 3 nm; studies with palladium and platinum with nanometric characteristics inferior to gold have also been highlighted [16, 17].

- **Sol-gel**: Chemical process in wet phase starts from the synthesis of a precursor (alkoxide, salt, or other inorganic chemical compounds) with alcohol or water under mild thermal conditions. With the help of a catalyst (base or acid), it is hydrolyzed, forming a hydroxide of the metal used, thus constituting the “sol.” Subsequently the groups generated condense, obtaining a three-dimensional structure that forms the “gel” of the metallic oxide. During both processes the oxidation and reduction intervene and these in turn in its aging [18].

Figure 4 shows the diagram of the products and sizes that can be obtained in each of the stages of the sol-gel method.

### 3. Biomaterial characterization

Through the characterization it is possible to define the structure of biopolymers and materials, with the purpose of explaining and relating the behavior of these with their properties dependent on their structure. Once a polymer and its known properties have been characterized, it is possible to optimize and control the microscopic factors including chemical composition, molecular size, topology, microstructure, the morphology of the aggregates, and transition structure affect the properties of a biopolymer.

From the various tools that enable the characterization of biopolymers, it is possible to classify or divide them according to spectroscopic, physical, mechanical, thermal, and physicochemical properties.
Due to the composition and characteristics of biopolymers, some tools become more related to a certain group of materials; that is why the following are the most commonly used tools for most biopolymers, in order to show an overview general.

### 3.1 UV-Vis spectroscopy

This technique is very used for quantitative analysis; however, in the qualitative analysis, in the determination of structures; it is surpassed by other techniques, such as infrared spectroscopy and nuclear magnetic resonance. Ultraviolet and visible radiation is characterized by being absorbed by valence electrons of molecules and atoms, which are excited at higher energy levels.

The absorption of electromagnetic radiation by valence electrons is normally within the ultraviolet region of the spectrum; this means that, commonly, matter is opaque to radiation somewhere in this region. In the case of electrons that participate in double bonds, the characteristic absorption frequencies can extend in the visible region, originating color in many organic substances, and in special cases in the near-infrared region [20].

### 3.2 Infrared spectroscopy (IR)

The vibrational analysis of polymeric materials through Raman and infrared spectroscopy is an appropriate experimental method to obtain information on structural parameters of the same. Thus, besides being able to analyze the chemical species present in the compound, it is possible to obtain, among others, data on the state of order of the polymers (chain orientation, crystallinity, crystalline phases, etc.).

This method is fast and sensitive and does not present great difficulty of interpretation. It is based on the vibration of the atoms of an organic molecule due to thermal energy. Each molecule has a resonant point, analogous to the resonance vibration of mechanical structures. Therefore, the electromagnetic radiation incident on a material is absorbed only in frequencies corresponding to molecular vibrations, if the intensity of radiation-transmitted frequency plotted against the absorption bands of the material (absorption spectrum) is obtained. IR spectroscopy allows to measure the vibrational energy levels of the molecules [21]. Because the levels of vibrational energy are different for each molecule (as well as its isomers), the IR spectrum can be considered as a fingerprint of each molecule.

The parameters of the characteristic bands, measured in IR spectroscopy, are frequencies (energy), intensity (polar character), shape of the band, and polarization in several ways, that is, the transition moment direction of the molecular system. Since the levels of vibrational energy are different for each molecule (and its isomers), the IR spectrum can be considered as the fingerprint of the molecule. However, the identification procedures are based on the purity of the compounds; therefore, it is necessary to verify the purity prior to an IR spectrum analysis.

The interpretation of IR spectra, the wave number \( \nu \), which is the number of waves per centimeter, is commonly used; the ratio between \( \nu \) and \( \nu \) and the wavelength \( \lambda \) is defined by the following equation:

\[
\nu(cm^{-1}) = \frac{10^4}{\lambda}(mm)
\]
The said formula can also be expressed as follows:

\[ \nu(\text{cm}^{-1}) = 3 \times 10^{10} \text{Hz} \]  

(2)

The wavenumber scale is directly proportional to the energy and absorbed vibrational frequency, which corresponds to the positions of the characteristic infrared bands of some functional groups in polymer chains. Table 1 presents characteristic wave numbers for some functional groups [22].

### 3.3 Raman spectroscopy

This is a very useful technique to identify chemical compounds. Their results are equivalent to the fingerprint of the compound to be identified. Unlike most other analytical techniques, a chemical or physical pretreatment is not necessary to obtain a Raman spectrum. Hydroxyl groups and silicates have a weak Raman dispersion which means that water and glass do not influence the spectrum obtained. In this technique, the change in wavelength is observed because the molecule disperses the incident radiation inelastically. The gain or loss of energy due to dispersion represents the energetic differences between the vibrational and rotational states of the molecules. This interaction depends on the nature of the polarization ellipsoid of the molecule and the electric dipole moment [23].

Generally is preferable to use Raman spectroscopy to characterize the polymers by the bands associated with the vibrations of the polymer chain which are more intense in the Raman spectrum than in the IR spectrum. The polymers and their reaction mechanisms can be characterized using Raman spectroscopy, from

| Group                      | Frequency range (1/cm) |
|----------------------------|------------------------|
| Stretch vibrations CH      |                        |
| \( = \text{CH} \)         | 3280–3340              |
| \( = \text{CH} \)         | 3000–3100              |
| \( \text{C} \equiv \text{CH}_3 \) | 2872.2962 (+/-10)     |
| \( \text{O} \equiv \text{CH}_3 \) | 2815–2832             |
| \( \text{N} \equiv \text{CH}_3 \) (aromatic) | 2810–2820            |
| \( \text{N} \equiv \text{CH}_3 \) (aliphatic) | 2780–805              |
| \( \text{CH}_2 \)         | 2853–2926 (+/-10)     |
| CH                         | 2880–2900              |
| Stretching vibrations C=O  |                        |
| Not conjugated             | 1700–1900              |
| Conjugate                  | 1590–1750              |
| Amides                     | 1650                   |
| CH flexing vibrations      |                        |
| \( \text{CH}_2 \)         | 1405–1465              |
| \( \text{CH}_3 \)         | 1355–1395, 1430–1470   |

Source: Serrano and Mendizabal [22].
which qualitative and quantitative information is obtained such as stereoregularity, chemical nature, orientation, conformation, and three-dimensional order in the polymer [24].

3.4 Differential scanning calorimetry (DSC)

Calorimetry allows to see very subtle changes in the structure of biopolymers compared to other materials when they are subjected to a processing with elevated temperatures, but that does not undergo any transition; that is why the physical transition temperatures are important in the characterization of biopolymers.

Differential scanning calorimetry (DSC) determines the amount of heat required to maintain the temperature of the sample at a value given by the temperature program. The said technique is measured by determining the heat of the sample through an external thermocouple. In turn measurements are compared to a reference material with a known specific heat; also the specific heat of the sample is determined by comparing the reading obtained from the instrument, corrected with the target, at a constant temperature, and then obtained at a constant rate of heating or cooling. It is said that the glass transition temperature occurs when the movement of the polymer segments begins [21].

3.5 Light scattering

The dispersion density and refractive index of light appear dissolutions and mixtures of liquids, that due to fluctuations in composition [21]. The calculation is determined by Debye, with which the effect of these fluctuations is obtained by relating them to the change in concentration \( c \) associated with the osmotic pressure \( \pi \) per mole of solute, the turbidity (\( \tau \)—Greek letter “tau”) You can describe how:

\[
\tau = \frac{32 \pi^3 R T c}{3 \lambda^4 N_0} n \frac{dn}{dc} / \frac{dn}{dc}
\]  

(3)

where \( n \) is the refractive index, \( \lambda \) is the wavelength, \( R \) is the universal constant of gases, \( N_0 \) is the number of Avogadro; and \( T \) the absolute temperature. Inserting the relationship between osmotic pressure and molecular weight gives the Debye equation:

\[
\frac{K}{R_{90}} = \frac{H}{\tau} = \frac{1}{M} + 2 A_2 c + ...
\]

(4)

\[
K = \frac{2 \pi^2 n^2}{N_0 \lambda^4} \left( \frac{dn}{dc} \right)^2
\]

\[
H = \frac{32 \pi^3 n^2}{3 N_0 \lambda^4} \left( \frac{dn}{dc} \right)^2
\]

where \( M \) is the molecular weight and \( A_2 \) is the second coefficient of the virial. This equation lays the basis for the determination of molecular weights by scattering light.
3.6 Ebulloscopy and cryoscopy

These methods based on Raoult’s law depend on the sensitivity of the available thermometry [22]. The average numeral molecular weight is based on the Clausius-Clapeyron equation using the boiling point elevation and the freezing point decrease, as shown below:

\[ M_n = \frac{RT^3Y}{\Delta H} \frac{C}{\Delta H} c \to 0 \]  

3.7 Osmometry

The osmotic pressure (\( \pi \)) of closely colligative properties therefore depends on the number of particles, measuring the osmometric pressure \( p \) applied to the determination of the osmotic pressure of solvent relative to polymer solutions [21]. An automatic membrane osmometer measures the non-limited capillary rise of a polymer solution using the modified Van’t Hoff equation:

\[ \pi = \frac{RT}{M_n} C + BC^2 \]

According to Figure 5, the inverse of the arithmetic mean of the molecular weight \( (M_n - 1) \) is the cutoff of the curve \( \pi/cRT \) as a function of \( c \) when extrapolated to zero concentration.

3.8 Size exclusion chromatography

This technique can be used to determine the molecular weight by means of polymeric analytes, such as natural molecules (polysaccharides, starches, etc.) and synthetic polymers (polyethylene glycol or polyethylene). To obtain information on the distribution of molecular weights in polydispersed polymers, there is a specific software. It requires a selection of appropriate columns for a correct analysis. Columns packed with polymeric absorbers are often used for polymer molecules with a wide molecular weight distribution, such as heparin, starch, or cellulose [25].

![Figure 5](image-url)  
*Obtaining \( M_n \) through osmometry, the value at zero concentration is extrapolated from the experimental measurements.*
3.9 Scanning electron microscopy (SEM)

The electronic scanning microscopy (SEM) allows obtaining characteristics of the surface of materials, as well as the shape and size of their particles and their arrangement. The operation of this technique is that the electrons travel through the arrangement of lenses designed to obtain a convergent beam. The coils located under the array of lenses direct the beam of electrons from left to right and from top to bottom in such a way that a sweep is made on the entire surface of the sample at the base of the vacuum chamber. The electrons that hit the sample are diffracted to the detector. The latter captures the signal and sends it to a processor where it is converted into an image [26].

3.10 X-ray diffraction (XRD)

The depth of penetration of laser radiation in the visible region is only several hundred Angstroms, so Raman spectroscopy is an excellent method to perform a structural description of surface areas of the compounds and a good complement to the structural information obtained by X-ray diffraction; this allows to make a spectroscopic map of the surface of the compounds. Each component has its characteristic signal region; therefore, X-ray diffraction works as a fingerprint identification. In the same way, it is possible to determine in addition to the morphology of biopolymers its stability, observing changes in the ranges and intensity of the signals with respect to time, using this technique for periods after the analysis in an initial time [27].

3.11 Thermogravimetric analysis (TGA)

Thermogravimetry is used in the study of primary reactions related to the decomposition of solid and liquid materials; this technique allows analyzes desorption processes and adsorption and decomposition reactions in an atmosphere of inert gas or in the presence of oxygen [28]. However, this technique does not allow knowing the chemical composition of the material under study or identifying the thermal changes that are not associated with mass variations such as crystallization or glass transition. Basically, a thermogravimetric analysis consists of the continuous recording of the variation of the mass of the material according to the variation of the temperature at a constant thermal rate. This type of thermogravimetric process is known as dynamic analysis. There is the option of doing an isothermal thermogravimetric analysis, in which the constant temperature is maintained for a set period. As a result of the thermogravimetric analysis, the mass change data are obtained with respect to temperature or time and a thermogram, which graphically represents the percentage variations of the mass. This type of technique is widely used in the quantitative characterization and kinetic characterization of polymers, coal, and clays, among other materials. Even in Costa Rica, this technique is applied to the analysis of soils, food products, and crops, among other areas [29].

4. Conclusion

At the moment countless equipment have been generated that allow the encapsulation of different organic and inorganic materials; however, there are different basic tools for the development of new materials. However, important factor for the development of these structures is the method used with which we can manipulate its shape and size through the study of the different variables that constitute it with the aim of obtaining a material that meets the needs to eradicate their problem.
References

[1] Shen Y. Rice husk silica derived nanomaterials for sustainable applications. Renewable and Sustainable Energy Reviews. 2017;80:453-466

[2] Gu M, Zhang Q, Lamon S. Nanomaterials for optical data storage. Nature Reviews Materials. 2016;1(12):1-14

[3] Khademolhoseini S, Talebi R. Green synthesis and characterization of cobalt aluminate nanoparticles and its photocatalyst application. Journal of Materials Science: Materials in Electronics. 2016;27(3):2938-2943

[4] Daniel MC, Astruc D. Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis and nano technology. Chemical Reviews. 2004;104:293-346

[5] Medintz IL, Uyeda HT, Goldman ER, Mattoussi H. Quantum dot biococonjuates for imaging, labelling and sensing. Nature Materials. 2005;4:435-446

[6] Lu AH, Salabas EL, Schuth F. Magnetic nanoparticles: Synthesis, protection, functionalization, and applications. Angewandte Chemie International Edition. 2007;46:1222-1244

[7] Mohammad R, Navid R, Reza S, Ghazal R. Introduction to Nanomaterials in Medicine, Chapter 1. IOP Concise Physics. Morgan & Claypool Publishers; 2019. pp. 1-4

[8] Conesa-Egea J, Zamora F, Amo-Ochoa P. Perspectives of the smart Cu-iodine coordination polymers: A portage to the world of new nanomaterials and composites. Coordination Chemistry Reviews. 2019;381:65-78

[9] Wang X, Gong Y, Shi G, Leong W, Keyshar K, Ye G, et al. Chemical vapor deposition growth of crystalline monolayer MoSe2. ACS Nano. 2014;8(5):5125-5131

[10] Rajput N. Methods of preparation of nanoparticles. International Journal of Advances on Engineering & Technology. 2015;7(4):1806-1811

[11] Zhu H, Zhang C, Yin Y. Rapid synthesis of copper nanoparticles by sodium hypophosphite reduction in ethylene glycol under microwaves irradiation. Journal of Crystal Growth. 2004;270:722-728

[12] de-Jong KP. Synthesis of Solid Catalysts. Wiley-VCH: Weinheim; 2009

[13] Schmid G. Nanoparticles. From Theory to Application. Weinheim: Wiley-VCH; 2004

[14] Suresh S, Aruneshan C. Dielectric properties of cadmium selenide (CdSe) nanoparticles synthesized by solvothermal method. Applied Nanoscience. 2014;4(2):179-184

[15] Karakhanov E, Maximov AL, Zakharyan EM, Zolotukhina AV, Ivanov AO. Palladium nanoparticles on dendrimer-containing supports as catalysts for hydrogenation of unsaturated hydrocarbons. Molecular Catalysis. 2016;440:107-119

[16] Kim Y-G, Oh S k, Crooks RM. Preparation and characterization of 1–2 nm dendrimer-encapsulated gold nanoparticles having very narrow size distributions. Chemistry of Materials. 2004;16(1):167-172

[17] Zheng J, Dickson RM. Individual water-soluble dendrimer-encapsulated silver nanodot
fluorescence. Journal of the American Chemical Society. 2002;124:13982-13983

[18] Ashour AH, El-Batal AI, Maksoud MI, Sayyad GS, Labib S, Abdeltwab E, et al. Antimicrobial activity of metal-substituted cobalt ferrite nanoparticles synthesized by sol-gel technique. Particuology. 2018;40:141-151

[19] Seidel A. Characterization and Analysis of Polymers. John Waley & Sons, Inc, Publication. 2008. pp 1-31

[20] Malacara D. Óptica básica. Segunda edición ed. Mexico, FCE-SEP; 2004. (Ciencia y Tecnología)

[21] Campbell D, Pethrick RA, White JR. X-ray diffraction. In: Polymer Characterization: Physical Techniques. UK: Stanley Thornes; 2000. pp. 194-236

[22] Serrano RFL, Mendizábal ME. Introducción a la ciencia de los polímeros. Primera Edición ed. Guadalajara, México: Universidad de Guadalajara; 2015

[23] Frausto-Reyes C, Medina-Gutiérrez C, Sato-Berrú R, Saghún LR. Qualitative study of ethanol content in tequilas by Raman spectroscopy and principal component analysis. Spectrochimica Acta Part A. 2005;61:2657

[24] Rudin A, Choi P. The Elements of Polymer Science and Engineering. 3rd ed. Kidlington, Oxford, UK: Elsevier; 2012. pp 149-228

[25] Gutiérrez-Bouzán MC, Burdó-Expósito A, Cegarra-Sánchez J. La cromatografía de exclusión: análisis de la distribución de pesos moleculares en siliconas por GPC. Boletín Intexter del Instituto de Investigación Textil y de Cooperación Industrial. 2009;135(1):33-40

[26] Valero-Valdivieso M, Ortega Y, Uscategui Y. Biopolímeros: Avances y Perspectivas. DYNA. 2013;80(181):171-180

[27] Ezquerra TA, Martínez-Gómez A, Álvarez C, Alonso E, Sanz A, García-Gutiérrez MC, et al. Structure-dynamics relationship during the amorphous to smectic transition of a main chain liquid crystalline polymer. Journal of Non-Crystalline Solids. 2005;351(33–36):2768-2772

[28] Grueiro LF. Estudio cinético, dinamomecánico y termogravimétrico del sistema epoxídico BADGE (n=O)/m-XDA mediante las técnicas de análisis térmico: DSC, DMA y TGA, construcción de un diagrama TTT [doctoral dissertation]. Universidade de Santiago de Compostela; 2001

[29] Rodríguez E, Villegas E. Caracterización de polímeros aplicando el método termogravimétrico. Métodos y materiales. 2012;2(1):25-32