Using shape memory effect to obtain a new polymer for the manufacture of complete dentures

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Abstract. Currently, polymeric materials represent a very important place in all areas of human activity, taking part more and more in life, day by day. Of these, synthetic polymeric biomaterials - simple or composite - constitute a very trendy topic and with a great dynamic, given to the diversity of their use in medical and pharmaceutical fields. In this respect the study aims improving the quality of acrylates used for removable dentures, by incorporating vitamin B12 into the structure of acrylic polymer for the treatment of the oral aphthae, as well as for prophylactic purpose. Structural characteristics of researched polymer indicates that a large number of factors that contribute to complex sites with affinity for the template does exist.

1. Introduction

Last century (XX) was marked by use large-scale, industrial macromolecular materials synthetic, in the form of plastics or in the form of rubber or synthetic filament. At present, polymeric materials occupy a very important place in all areas of activity human, taking part more and more in life day by day [1-2]. Of these, polymeric biomaterials synthetic - simple or composite - constitute a very current topic and with a great dynamic, given the diversity of their needs medical and pharmaceutical. Improving the quality of implants and minimally-invasive assay devices increase the biocompatibility and corrosion resistance of materials that are to come into direct contact with biological tissues, the development of performance vectors, leading to the target organ different biologically active principles, improvement of controlled drug delivery systems in the body [3-5]. Aim: Removable acrylic dentures are solutions most commonly used in the case of complete dentures. Complete dentures are the most commonly used solution in the case of complete edentation which will endure thanks to the technology constantly advancing, improvements with the purpose of alleviation this serious mutilation of the stomatognathic system as well as to reduce negative effects on the intraoral imbalance [6-9]. Although the stomatognathic system has a remarkable adaptation capacity, insertion of dentures into the oral cavity can have adverse consequences on oral balance, generating side effects...
with impairment of the integrity of oral tissues. Therefore, even if the dentures solve much of the problems of the edentulous patient (restoration of oral functions) yet wearing dentures does not remain without repercussions on oral tissues [10]. In this respect the study aims improving the quality of acrylicates used in the complete denture’s fabrication [11]. An important trajectory is the incorporation of vitamin B12 into the acrylic polymer structure for the treatment of the oral aphtha as well as prophylactic by releasing it in the saliva of the patient and reembracing it through immersion of dentures in B12 [12].

2. Materials and methods

Molecular memory is a technique used for obtaining high-capacity recognition materials. This method involves cross-linking polymerization of monomers in the presence of organic template molecules (template molecules) or ionic radicals, followed by extraction of the target molecules. Polymers with high selective memory thus obtained will bind to the molecules template or ions they will recognize from any mixture of chemical compounds. Great advantage of this method is the formation of memory sites, a method successfully applied in the production of synthetic polymers such as nucleotides, steroid hormones, etc.

The polymerization method used in this study is a new method called surface template polymerization where we used the monomer and polymer of Superacryl Plus by Spofa Dental with the following composition:

- polymethylmethacrylate powder;
- liquid methyl methacrylate;
- liquid ethylene glycol dimethacrylate.

As template molecule we used cyanocobalamin, which is the form of vitamin B12, with use on large scale clinically because of its availability and stability. It's transformed in active factors inside the body. Samples of polymers based on polymethacrylate methyl crosslinked with ethylene glycol dimethacrylate were performed under different working conditions, as in Table 1. The polymer: monomer ratio was preserved constantly following the classic polymerization recipe indicated by the manufacturer. In the same table is noted the amount and introduction way of vitamin B12, used as template molecule. Samples completed were obtained by blending monomer-polymer with the regular steps of forming the acrylate paste.

| Table 1. Samples of polymers based on methyl polymethyl methacrylate crosslinked with ethylene glycol dimethacrylate. |
|---------------------------------------------------------------|
| Sample | PMM (g) | MM+EGDMA (ml) | Vit.B12 (µg) | Observation |
|--------|---------|---------------|--------------|-------------|
| 1A     | 11      | 5             | 100 (vit in polymer) | Initial temperature =22°C Setting time in 15 minutes |
| 2A     | 11      | 5             | 100 (vit in monomer) | Initial temperature =28°C Setting time in 5 minutes |
| 3A     | 11      | 5             | 100 (Vit in water 2ml vit -1l distilled water) | Initial temperature =24°C Setting time in 10 minutes |

Figure 1 a, b and c represent temperature variation in time in the polymerization bath.

To highlight the amount of vitamin B12 retained during synthesis, the samples were subject to extraction. The extraction of vitamin B12 was carried out by three methods as follows:

a) Extraction of vitamin B12 by means of a SOXHLET extraction apparatus. The product from which the extraction is extracted is dried, ground, weighed, and then inserted into a filter cartridge.
Insert the extractor cartridge into the extractor without exceeding the siphon height. Refrigerant is mounted, cooling water is started, and the solvent is placed on the top of the shelter through a funnel until the level of the extractor liquid exceeds slightly the siphon height. The cartridge and siphon are soaked with solvent. Apply the siphon so that the solvent penetrates the distillation flask. By heating the flask, the solvent is distilled in the refrigerant. The condensate drains into the extractor over the product in the cartridge and extracts the soluble component. When the liquid reaches the siphon, the siphon is added again, passing the liquid into the distillation flask. At the end of the extraction, heating is usually stopped, usually before a siphoning, for easier recovery of the solvent, and cooling is continued for vapor condensation and cooling of the plant. The extraction was done with "synthetic saliva" and water. The synthetic saliva used was Safnor according to French standards with the following basic components: NaCl 0.70 g / l, KCl1.20 g / l, Na2HPO4 0.26 g / l, NaHCO3 1.50 g / l, KSCN 0.33 g / urea 1.35 g / l and the samples were taken from 5 to 5 extraction cycles until the extractant concentration in the evaporator vessel remained constant. The duration and effectiveness of extraction depend on nature and degree of shredding of the product, the nature of the chosen solvent and circulation rate of the solvent.

![Graphs](image.png)

Figure 1. a) sample 1A; b) sample 2A; c) sample 3A.
b) Extraction of vitamin B12 in boiling water. Synthesized polymer samples, dried under vacuum for 12 hours at 400°C, are weighed, placed in a bottle of distilled water to be boiled. For the determination of extraction kinetics, samples taken from the beaker, hour by hour, are analyzed by ultraviolet-visible absorption spectroscopy using a Spectrophotometer UV-See SPECORD 200 Analytik Jena. In the Figure 2 below are the adsorption spectra of various B12 solutions, the absorbance being measured at 361 nm.

![Figure 2. UV spectra of vitamin B12 solutions.](image)

Depending on the absorbance value, the concentrations of the solutions analyzed were read from the standard curve (Figure 3).

c) Extraction of vitamin B12 in water at 370°C. The simple retention conditions of vitamin B12 considered the way of dentures storage during sleep, namely in water glasses. Therefore, the sample was left for 8 hours in -a glass beer B12. The B12 release-retention process is a physical process that has been highlighted by obtaining ultraviolet-visible absorption spectra using a UV Spectrophotometer SPECORD 200 Analytik Jena.

![Figure 3. Standard curve for vitamin B12 solutions.](image)

To identify aspects of the supramolecular structure, a Quanta 200 scanning electron microscope with EDAX composite analysis system was used. It can be used to obtain surface topography information; surface modification due to physical and chemical treatments; identifying aspects of
supramolecular structure (micellar, fibrillated, lamellar, spherulitic structure); elementary qualitative and quantitative sample analysis

3. Results and discussions

In order to determine the release mechanism of template molecule, as well as to determine what it is the amount retained on the polymer during synthesis, studies have been conducted that involve the extraction of vitamin B12 by three methods. To determine the amount of vitamin B12 residual in the synthesized samples, was applied the method of total extraction of template. All the amount of vitamin B12 was extracted from the copolymer synthesized by the water boiling method, for 5 hours. Reintroduce the sample of the polymer into another recipient with water and resume the boiling after the initial 5 hours no longer extracts B12. Results obtained are listed in the Table 2 below.

### Table 2. The amount of vitamin B12 extracted from the samples.

| Sample | Sample weight g | Quantity of B12 extracted µg | Quantity of B12 obtained from synthetic/g polymer (µg/g) |
|--------|-----------------|-----------------------------|------------------------------------------------------|
| 1A     | 4.683           | 88.738                      | 18.94                                               |
| 2A     | 7.7645          | 13.11                       | 4.3                                                 |
| 3A     | 3.72            | 40.865                      | 10.98                                               |

The release of the polymer template has been studied under milder conditions of temperature. Extraction of vitamin B12 by the extraction method in Soxhlet implies washing the sample with cold water (160°C). As shown in Figure 4, the release of vitamin B12 under these conditions is insignificant.

![Figure 4. The kinetics of the extraction of vitamin B12 by Soxhlet method.](image)

Instead, the increase in the temperature of the extraction water at 370 changes the template release rate, so as can be seen in the Figure 5 below.

A different behaviour of polymers is observed in case of the release of the template due to its internal structure conferred by make cross structures, depending on the conditions of synthesis. After the complete removal of the template, the smart polymers have increased affinity for substances which have a template-like structure, and its retention can be done in much greater quantity than that used in synthesis [13]. The retention of vitamin B12 was made under easily practicable conditions for patients:
in a glass with water and vitamin B12 was added the sample of the polymer and leave for 12 hours. In experiments we used an initial concentration of vitamin B12 in water of 250 μg% [14]. The results of the retentions are listed in the Table 3.

| sample | Sample weight (g) | Initial concentration μg% | Final concentration μg% | Amount of B12 retained μg/g sample |
|--------|------------------|--------------------------|-------------------------|----------------------------------|
| IA_e   | 0.2512           | 250                      | 66.525                  | 730.39                           |
| IIA_e  | 0.1560           | 250                      | 13.771                  | 1514.28                          |
| IIIA_e | 0.3232           | 250                      | 67.858                  | 563.556                          |

It is noted that the highest amount of vitamin B12 is retained by sample IIA, and the template was mixed with the monomers. Considering the fact that in monomers the B12 solution mixes much more intimate with the participants in the polymerization than in the case of IA sample when the PMM barely dries the surface outside with the temple. Synthesis IIIA containing vitamin B12 dissolved in the polymerization bath retains an intermediate amount of temple thanks to high dilution of the B12 solution in water [15]. In many cases, particle morphology has an important contribution to the characteristic parameters of the products obtained, causing polymer performances.

![Figure 5. Kinetics of vitamin B12 extraction by the method static at temperature 370C.](image)

![Table 3. Retentions of vitamin B12.](image)

Figure 5. Kinetics of vitamin B12 extraction by the method static at temperature 370C.

Figure 6. The spectroscopic image of the copolymerization process.
Photographs made by electronic spectroscopy give a physical image of the copolymerization process. In accordance with the proposed scheme, the entities microscopic globe points out the wide variety of crosslinked copolymer structures. SEM data provided - EDAX: I b (sample I, statically extracted first, then retention of B12 as follows: 10 ml water + 0.5 ml B12) II b (sample II, statically extracted from the pot, then retention of B12 as follows: 10 ml water + 0.5 ml B12) II a (sample II statically extracted). In many cases, particle morphology has an important contribution to the characteristic parameters of the products obtained, causing polymers performance [16].

The ratio of surface microanalysis performed by the EDAX method reveals that the total extracted samples do not contain nitrogen, whereas after the retaining of vitamin B12, the occurrence of nitrogen brings another argument that retention of template is easily done. The samples below, the second column, were submerged for an hour in vitamin B12 solution.

4. Conclusions
The performance of the synthesized crosslinked polymers depends on the network structure and is closely dependent on the modification of the synthesis parameters. It has been observed that the polymers obtained in the presence of templates have a selective memory, preferentially retaining products with a template-like structure, in our case retaining an amount of vitamin B12 greater than that used in the synthesis.

It was found that the largest amount of vitamin B12 is retained by sample IIA in which the template was mixed with the monomers. Considering that in monomers the B12 solution mixes much more intimately with the polymerization participants than in the case of AI when PMM barely dampens on the outer surface with the template. Synthesis IIIA containing vitamin B12 dissolved in the
polymerization bath retains an intermediate amount of tempered due to the high dilution of the B12 solution in water.

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5. References
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