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New formulations of -cyanoacrylate for biomedical applications

Abstract

- * Introduction
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ABSTRACT

Currently, new formulations of -cyanoacrylic tissue adhesives, are being studied for the repair of soft and hard tissue in order to improve properties such as: biodegradability, biocompatibility bone flexibility (in the soft tissue applications) and ease of handling. This paper presents a review of scientific literature related to new formulations of -cyanoacrylic adhesives and medical applications.

Keywords: Tissue adhesives, -cyanoacrylate, biodegradability, biocompatibility and medical applications.

INTRODUCTION

Monomers of the family of -cyanoacrylic esters are compounds widely used as surgical adhesives, due to the property which have to adhere instantly to polar substrates, including living tissues without the intervention of other substances co-catalysts for polymerization [1] [2]. Specifically, the -cyanoacrylate alkyl were obtained for the first time in 1949 by A. E. Ardis and the end of the decade of the 50 H. W. Coover et al suggested its possible use as surgical adhesives. Currently, the most widespread use of tissue adhesives is -cyanoacrylate in the treatment of skin incisions and lacerations and, in particular, is recommended for use in pediatric emergency rooms [3] [4]. Back in the 80s, from the work of the group P. Couvreur [5], are beginning to use the polymers

obtained from the -cyanoacrylate nanoparticles as drug carriers, although this work focuses on new formulations monomer and its applications.

Initially, the -cyanoacrylate used for sealing wounds and other medical applications were the methyl and ethyl. Soon, however, were taken off the market as tissue adhesives, due to rapid degradation in vivo, resulting in significant inflammatory responses in tissues. Currently, adhesives – iso-butyl cyanoacrylate (Bucrylato (R)), – n-butyl cyanoacrylate (Indermil (R), Liquiband (R), Histoacryl (R), Tisuacryl (R), Glubran (R)) and – cyanoacrylate, n- octyl (Dermabond (R), Liquid Bandage (R)) have been approved for medical use by health authorities in different countries. These products have a slow rate of degradation, so they are used mainly for external use [6], although they have been studied and applied in internal treatments where the relationship between risk and clinical benefit has proven to be negligible. Among these applications are the use of -cyanoacrylates as embolitic material in the vascular system [7], endoscopic treatment of esophageal varices [8] [9], reinforcement of the suture in the gastrointestinal tract anastomosis [10] [11] and others. In Cuba, the use of Tisuacryl (R) (Biomaterials Center, University of Havana) is widespread, fundamentally, to seal traumatic and surgical wounds of the oral mucosa [12], [13], [14] and as a dressing periodontal, but have made important applications in general surgery [15] and gynecology [16].

PHYSICAL AND CHEMICAL PROPERTIES OF -cyanoacrylate

The -cyanoacrylates are colorless liquids of low viscosity, highly reactive, which have characteristics of homopolymer at room temperature, so it can be dispensed as pure monomers with defined properties. These compounds have two strong electron acceptor groups (CN and COOR), which makes the double bond is very susceptible to attack by weak bases (Figure 1) and this is what gives them their property to bind rapidly with polar substrates forming strong adhesive bonds. While most commonly used -cyanoacrylate were the alkyl side chains (R) containing from one to eight carbon atoms, have also synthesized other derivatives such as alkoxy-alkyl (R1-O-R2) [17].Figure 1. General structure of – cyanoacrylate

The preferred method for the synthesis of -cyanoacrylate is Knoevenagel condensation between -cyanoacetate and formaldehyde in the presence of a basic catalyst [18]. The polycyanoacrylate product of this synthesis is depolymerized to obtain the reactive monomer. The density of monomers is in the range of (0.90-1.10) g/cm³ at 20 °C and its viscosity is low, 2-4 cP at 25 °C for -cyanoacrylates not very long linear chains.

-cyanoacrylic monomers can set three different curing mechanisms: the radical, anionic and zwitterionic, the last two being the most favored way. Anionic polymerization initiators can be CH₃COO-anions, OH-, I-, etc., Weak bases such as alcohols and water and amino acids present in living tissues.

As areas for improvement in oral cyanoacrylic tissue adhesives are the following:

- o the low biodegradability of the compounds of longer alkyl chains makes it difficult to use in internal applications;
- o the low viscosity of the monomer may produce shifts of the product during its implementation;
- o the lack of flexibility of polymer is not suitable for use in soft tissue
- o the poor adhesive strength and bone support for hard tissue applications.

The following refers to new formulations of -cyanoacrylic adhesives reported in the literature and its medical applications.

NEW FORMULATIONS AND APPLICATIONS

Some authors have observed that when the -cyanoacrylates are used in small quantities without adverse effects on adjacent fracture healing and do not cause inflammatory response in the surrounding viable bone or adjacent soft tissue, B. Lu and colleagues noted that two weeks after fixation of fractures in the tibia of mice, internally with Kirschner wires of 2 mm and reinforced in the fracture surface with -n-octyl cyanoacrylate, begins in vivo degradation of the adhesive. Chondrocytes and fibrocytes grow gradually in the areas surrounding the material, which breaks down completely between 10 and 12 weeks without observing any barrier effect affecting the healing of the fracture and reported better results in the setting with respect to the control group where only internal fixation was performed with wires [19].

M.A. Shermak and colleagues compared the use of microplates and screws for fixing bone craniotomies in mice, with the application of -cyanoacrylate n-butyl. They found a normal scar, no trace of adhesive on the skulls studied. Bone healing and inflammatory response were similar in both study groups [20]. However, the low viscosity of the pure monomers difficult to use. On the other hand the use of adhesives, as the sole means of fixation does not report the same strength that the fixation with plates and screws, either stable or biodegradable, so it is undesirable for use in areas subject to continuous muscle movements.

M.C. Harper and colleagues evaluated the efficacy of -cyanoacrylate, isoamyl (-cyanoacrylate, 3-methylbutyl) viscous fix an osteotomy of the femoral condyle in rabbits by applying the adhesive on the edges of the fracture and freeing central the fracture surface to minimize mechanical barriers that could interfere with the healing. In this study, which used each subject as its own control, it made a profit of 45% effective in treating the adhesive [21].

E. Gonzales and colleagues evaluated the effectiveness of -cyanoacrylate adhesive for fixing ethyl bone flap craniotomy operations. Although this product is not recommended for medical use, the results in terms of fixation were satisfactory in the 100 patients included in the study with clinical and radiological follow-up 3 months after surgery without were apparent treatment-related complications. The authors believe that this method is safe, quick and easy, providing immediate stability of bone flap and excellent cosmetic results [22].

S. Bhat and colleagues demonstrated the ability of -cyanoacrylate adhesive for filling bone cavities, noting that the -cyanoacrylates methoxy isobutyl and has better mechanical properties in this application that the -cyanoacrylate, isoamyl [23].

F.J. Papatheofanis studied the tensile strength of adhesive bonds in bone with several -cyanoacrylate and using a reinforcement of hydroxyapatite particles. He observed that the -cyanoacrylate, isobutyl shows a tensile strength of the adhesive bond greater than that of methyl and ethyl and the addition of 10% hydroxyapatite increase this parameter, which then decreases with the addition of 15% filling [24].

Recently, S.B. Lee and colleagues studied the addition to -cyanoacrylate adhesives for ceramic particles biocompatible -tricalcium phosphate in the formulation of composite materials with a possible degradation of control, with potential use in the repair of cranial bone defects and maxillofacial [25].

For its part, C.L. Linden and S.W. Shalaby -made adhesives methoxypropyl cyanoacrylate and isobutyl, adding plasticizers to increase the viscosity of the product and better manage their implementation. Used as an additive the trioxietileno polioxalato of high molecular weight. These authors concluded that an important factor in the strength of adhesive bonding is that the modules of the adhesive and substrate are similar. For the skin, be expected to possess an adhesive elastic properties result in a stronger bond, in contrast, high modulus of cortical bone is closer to the polymer without additives of -isobutyl cyanoacrylate [26].

S. W. Meskin and colleagues have demonstrated the efficacy and safety of the use of Liquid Adhesive Bandage -n-octyl cyanoacrylate with parabens (para-hydroxybenzoate) in the lining of the wounds in the cornea after cataract surgery to prevent ocular fluid entry into the wound. The adhesive was applied in a thin layer over the wound using a micro-sponges soaked with a drop or two of them [27].

M.T. Duffy and colleagues [28] have studied how to improve the clinical behavior of the -cyanoacrylate in sutureless ophthalmic surgery, using as carrier a copolymer of poly-L-lactic and polyglycolic. The study was conducted in eye muscle and sclera of mice. The bonding was done with small patches of material support, prehydrated in saline, to which were added two drops of -n-octyl cyanoacrylate. Support the use of adhesive prevents runoff of surgical site and improves adhesive bonding.

A biodegradable cyanoacrylate has been developed in recent years by the Corporation Closure Medical Surgical Sealant Study Group, which is composed of a mixture of -cyanoacrylate n-octyl -cyanoacrylate butilolactolo. This adhesive has been used in prospective randomized clinical trials for vascular reconstruction and as a hemostatic agent and sealant vascular suture line [29], [30]. Previously, Y.C. Tseng and colleagues [31] had developed a product of ethoxyethyl -cyanoacrylate, for use in arteriovenous embolization, adding a biodegradable copolymer of poly (lactide-caprolactone), lipiodol and a radiopaque compound.

M.M. Eskandari [32] and colleagues have evaluated in vivo biodegradable system for the controlled release of vancomycin, using gelatin sponge support and the -n-butyl cyanoacrylate as a carrier of the therapeutic agent. K.M. McNally-Heintzelman et al [33] evaluated adhesive systems, porous scaffolds for soft tissue repair with promising results.

As conclusions of the review conducted found that the new adhesive formulations are obtained by adding compounds, such as thickeners, plasticizers, inorganic filler particles (in bone repair materials), [biodegradable materials](#) and other support. However, the inclusion of additives in the formulations of -cyanoacrylate is a complex task, as the monomer is capable of reacting with any polymerization initiator substance which decreases the stability and formulations.

-cyanoacrylate New Formulations for Biomedical Applications

SUMMARY Nowadays, new Formulations of -cyanoacrylic Are Being Studying tissue adhesives, Which Are Used for repairing of soft and hard tissues. They Improve adhesive properties Such as: biodegradability, bone biocompatibility, flexibility – when Applied on Soft Tissue-and manipulation. A review of the current scientific publications related to the new -cyanoacrylate Formulations and Its medical use, is presented.

Key words: Tissue adhesives, -cyanoacrylates, biodegradability, biocompatibility, medical applications.

Data from the author:

Dr. Rosa Mayelin War Britain

PhD in Chemistry

Senior Researcher Center for Biomaterials

Havana

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