Int J Pharm Bio Sci 2013 July; 4(3): (P) 524 - 533

Review Article **Polymer sciences**

International Journal of Pharma and Bio Sciences

ISSN
0975-6299

ECO- FRIENDLY BIOPOLYMERS AS ADHESIVES – AN OVERVIEW

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ABSTRACT

Over the past 25 years significant advances have been made in the development of different biodegradable polymers. These polymers are eco-friendly and can be tailor-made to a variety of forms like films, sheets, resins, adhesives and waxes. With increasing environmental concerns and need for advancement in medical technologies, biodegradable polymers have been developed to tackle such problems. The natural biopolymers (e.g., starch, cellulose and soy protein) extracted from plants or animal tissues were used for various industrial purposes. Several synthetic polymers of biodegradable and biocompatible nature have been extensively used in the medical sector such as surgical sutures, drug delivery systems, internal fixation devices, and tissue engineering scaffolds. This review summarizes on biodegradable polymers used as adhesives in both industrial and medical applications. In a broader aspect, biodegradable polymers play a dual role as potential solution to waste management and best sealing agent for various applications.

KEYWORDS: Biodegradable polymers, Biocompatible, Adhesives, Poly-lactic acid, Poly-glycolic acid

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INTRODUCTION

Bio-adhesives are not of recent origin, but have been dated back to 2000 BC itself. There is archeological evidence which suggested that the ancient Egyptians used resinous adhesives at least 6,000 years ago. Typical examples of bioadhesives include birch-bar tar to red ochre, hematite and goethite that were used for various purposes[1]. In later years, the significance of these natural adhesives was lost due to the advent of synthetic adhesives. Synthetic adhesives are cheap and have good mechanical and tensile strength. Another advantage is that it can be easily moulded into any shape and has high resistance to corrosiveness. The major drawback is its non-biodegradability and toxicity which is reviewed in detail by Chiang Hung-Lung [2]. Toxicity of these adhesives is mainly due to the solvent used in adhesive preparation. Some of the solvents used are toluene, n-hexane and acetone; these have been classified as volatile organic compounds and are hazardous. The health risk, chronic toxicity and carcinogenicity of different solvent based adhesives were reviewed by many researchers [3, 4]. Recently Bin Yuan *et al* 2010 [5] reported that the ozone formation potential is highest for solvents used in paints. Altogether these issues have urged a need to develop a specific legislation which governs the maximum solvent exposure limits. However, the guidelines vary from country to country, in UK the limits are set under control of substance hazardous to health (COSHH) while in USA limits are set by the occupational safety and health agency (OSHA). In addition to these legislations a holistic approach is needed to completely replace the solvent based adhesives. Every year tonnes and tonnes of non-biodegradable wastes are dumped in the environment leading to environmental pollution. Therefore, it has necessitated the need to formulate bioadhesives with good mechanical properties. Numerous biodegradable polymers both natural (Table 1) and synthetic biodegradable polymers (Table 2) have been developed for the past two decades. These biodegradable polymers serve as the backbone for bioadhesive formulation.

Table 1
Different types of biodegradable adhesives from natural sources

Adhesive Type	**Sources/Properties**	**Common Uses**
Protein based adhesives [6,7,8]	zein (corn) gluten (wheat) soy protein isolates (SPI) peanut proteins	Bookbinding, box making, paper converting, packaging and laminating applications. Bonding of plywood layers and particle board, interior-type plywood.
Starch based adhesives [9]	Derived from different sources (*i*) Cassava and potato starches (*ii*) Corn and rice starches and (*iii*) Cereal starches- wheat.	Adhesive for non paper substances such as charcoal in charcoal briquettes, mineral wool in ceiling tiles and ceramics before firing.
Cassava starch adhesives [10]	Derived from the roots of many plants	Widely used as a tub size and beater size in paper manufacturing. Adhesive for postage stamps, envelope flaps, and labels.
Corn starch [11]	Corn plant (*Zea mays*)	Adhesives used for glass and for plywood
Cereal starches [12]	Rice and Wheat starch	Paper bag industries

Table 2
Types of biodegradable synthetic polymers (Available from Polysciences, Inc.)

Biodegradable synthetic polymers	Application
Poly (caprolactone) (PCL)	drug delivery
Poly (glycolic acid) (PGA)	drug matrices and sutures for Cataract surgery and for repairing inguinal hernias
Poly (dl-lactic acid) (P dl-LA)	Biocomposites
Poly (l-lactic acid) (P l-LA)	sutures, implants and controlled release systems
Poly (lactase-co-glycoside) (PLG)	Biocomposites

Recently biodegradable synthetic polymers (Poly lactic acid, Poly glycolic acid) are becoming very popular. Rohm and Haas is one of the leading companies that have introduced two new adhesives systems with the sustainable resin PLA. Robond™ PLA-WB water-based adhesive and Adcote™ PLA-SB solvent-based adhesive have been tailored for various applications. Poly glycolic acid is mainly used as surgical sutures and it is currently marked as Polyglactin 910. The Polyglactin 910 mesh is composed of threads, woven into a mesh with pores. These materials are known to be effective in reducing postoperative adhesions [13, 14]. Currently companies including Cargill Inc.'s Nature Works LLC, Proctor & Gamble Co., Johnson & Johnson, Inc., and Paper Mate are manufacturing products made from these synthetic biodegradable polymers.

BIO-ADHESIVES USED IN INDUSTRIES

New promising bio-based polymers like poly lactic acid (PLA), cellulose, protein and starch-based adhesives are widely used in packaging industry. This has made an important progress towards green packaging which reduces waste and its environmental impact. PLA are generally used as packaging material, especially for garbage and shopping bags, wrappings, or fast - foods plates and cups. Other than packing industries PLA are used as adhesives mainly for various purposes. In Europe a company Dow has made significant efforts to identify adhesive solutions for bio-based packaging and products. These are now available using the company's ADCOTE™ and MOR-FREE™ technologies. The bio-film structures formulated from these new adhesive systems had met most of the requirements for dry food, meat, cheese and even coffee. In UK, according to Intertech Pira, the current market for natural adhesives makes up about 30% of the total adhesive markets. The study also predicts that in the 2007-2017 periods, the overall adhesives market will increase constantly. Nature works LLC in the United States is one of the top manufacturers of PLA and commercialized it under the brand name Ingeo, with a production capacity of 300 million pounds / year. Lately BASF Corporation have received license from Metabolix to market PLA (PolyLactic Acid) under the trade name Ecovio®. Researchers have also attempted to develop other biodegradable adhesives, a patent was developed using sulfonated aliphatic-aromatic co polyester, which contains a glycol component and 0 to 5.0 mole percent of a polyfunctional branching agent (European patent, 091735704). Hence, in the forth coming years, considerable researches are focused towards the development of low cost, biodegradable adhesives that would make significant advances in various industries.

(i) Poly lactic acid

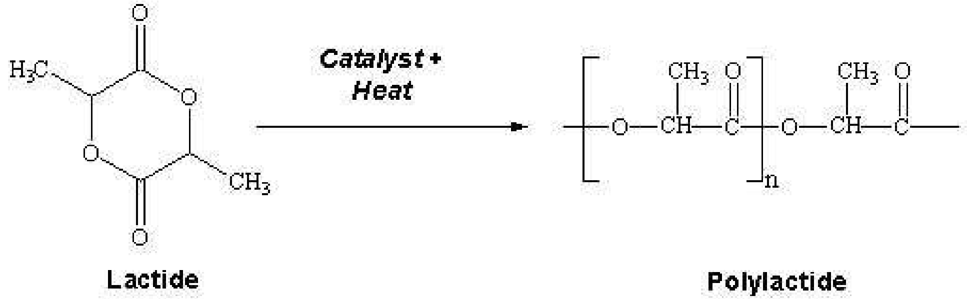
Poly lactic acid is a rigid but brittle polymer that can exist in two isomeric forms L- form and D-form. The general features of PLA are given in Table. 3. The high production cost of this biodegradable polymer can be reduced by using cheap raw materials for its production. Several such raw materials like tofu liquid waste [15], corn steep liquor as nitrogen source [16], sugar molasses [17] and wheat flour [18] have been used. Several efficient plasticers like poly (ethylene glycol), poly (propylene glycol), citrate esters, triacetate, and acetyl tribu citrate can be added in order to improve the plastic deformative ability of PLA polymers. These plasticizers easily migrate to the material surface at higher temperature thus altering the mechanical properties.

Table 3
General features of Poly lactic acid

Nature	Semi-crystalline polymer
Melting point (Tm)	180^{0}C
Glass transition temperature(Tg)	55^{0}C to 65^{0}C
Soluble in	Organic solvents like acetone, pyridine
Non soluble in	Water, alcohol & unsubstituted hydrocarbon
Blending with other polymers	Good

PLA can be produced mainly by two routes: poly condensation and ring opening polymerization. Poly condensation produced only low molecular weight poly lactic acid therefore an attempt was made by Hisham Essawy [19] to develop a melt/solid poly condensation method to produce a high molecular weight PLA. This was carried out in the presence of different concentrations of either SnCl2_2H2O/p-toluene sulfonic acid (PTSA) 1: 1 or Sb2O3 which acted as catalyst (Figure. 1). Ring opening polymerization of lactide was generally done to obtain high molecular weight poly lactic acid.

Figure 1
Poly-condensation of Lactic acid [20]



Apart from poly-condensation (PC) and ring-opening polymerization (ROP) other methods were developed like chain extension, grafting for producing high molecular weight PLA [21, 22]. PLA has wide application as biodegradable polymers and its stability can be increased by means of blending and copolymers of PLA have been reported with good stability. Several reports on blending such as poly D- lactic acid with poly L- lactic acid [23]; with PBS poly (butylene succinate) [24]; with Poly caprolactone (by dissolution in the presence of methylene chloride with a total polymer mass of 10%) [25]; with poly (ethylene-*co*-vinyl acetate) [26] and with bis (2-hydroxyethyl terephthalate) [27] were developed and various factors including its miscibility, thermal and mechanical properties were investigated. Various enantiomers of poly lactic acid viz., D- lactide, L- lactide, meso D, L – lactide and racemic D, L – lactide were blended with other oligomers to enhance the thermal and mechanical properties of adhesives.

PLA are mainly used as hot melt adhesive, typical parameters to be evaluated for hot melt adhesive are open time, setting time, hot tack development, viscosity and weight loss. Mechanical properties includes tensile strength, lap shear strength and elongation measurements. Several works on PLA and its copolymers for evaluating these parameters were done. The suitability of biodegradable copolymers poly (L -lactide) (PLLA) and poly (ε-caprolactone) (PCL) as hot melt adhesive was evaluated by Viljanmaa [28]. Copolymer consisting of poly (L -lactide) and poly (ε-caprolactone) with molar ratio 81:19, respectively was formulated. The thermal degradation of the lactic acid-based hot melt adhesive formulation for lamination process was also studied by analyzing the weight loss, viscosity, open time and molecular weight measurements. It was found, that the thermal stability of the adhesive was sufficient for the normal application process [29]. Therefore the PLLA/PCL copolymer is a potential candidate for a biodegradable hot melt adhesive for packaging application.

Saara Inkinen, [30] investigated on the stability of blends of a lactic acid-based hot melt adhesive (LHM), oxidized potato starch (dried or non dried), and polyethylene glycol (PEG) in the ratio of 70: 24:6 (w/w/w). Pure LHM was used as a reference material; during the ageing period of 56 days at ambient conditions (23± 1°C and 42 ± 4% RH) the tensile properties of the blends were close to each other. All the investigations had relatively low Young's module, compared to PLA-starch blends. Similarly in the water absorption experiment (23 ± 1°C), the blends reached significantly higher maximum values than the LHM. Recently in order to solve the problem of the inherent brittleness of PLA, which is due to poor elongation at break and impact strength, researchers at Michigan State University have recently developed biodegradable materials based on nanoscale hyper branched organic particles [31]. This innovative modified PLA exhibited an improvement in elongation at break of about 800 to 1000% in relation to traditional PLA grades with minimal impact on tensile strength and modulus.

BIO-ADHESIVES USED IN BIOMEDICAL FIELD

The use of synthetic biodegradable polymers for suture started in USA in the 1970's. Commercial polymers used for this purpose include polyglycolide (PGA), which is still the largest in volume production, together with a glycolide-L-lactide (90:10) copolymer. PGA is a thermoplastic, less toxic, biodegradable and biocompatible polymer approved by the Food and Drug Administration (FDA) for clinical use such as implants, resorbable sutures, drug delivery devices and scaffolds for tissue engineering. Currently other copolymers such as poly (lactic-*co*-glycolic acid), poly (glycolide-*co*-caprolactone) and poly (glycolide-*co*-trimethylene carbonate) are also widely used. The sutures made from these polymers are of braid type processed and are the next largest consumption in surgery, for hemostasis, sealing, and adhesion to tissues [32]. Nowadays PGA and various copolymers such as poly-D, L-lactide-coglycolide (PDLLA-co PGA) can also be used as as scaffolds for tissue engineering and as controlled/sustained release drug delivery vehicles [33]; implants for bone fixation [34] and fixation of 1-4 anterior cruciate ligament (ACL) grafts to overcome the problems such as graft and suture laceration, imaging interference, and difficulties with revision surgery inherent seen in case of metallic implants [35, 36]. PGA was the first synthetic polymer produced successfully and approved by the FDA for biomedical applications.

(i) Poly glycolic acid

Glycolic acid (HOCH2COOH) is known to be the simplest kind of hydroxyl carboxylic compounds which can be produced from glycolonitrile hydrolysis by mineral acid, such as sulfuric acid [37]. Polymerization of glycolic acid leads to the formation of polyglycolic acid (PGA). PGA was the first synthetic biodegradable polymer produced successfully.

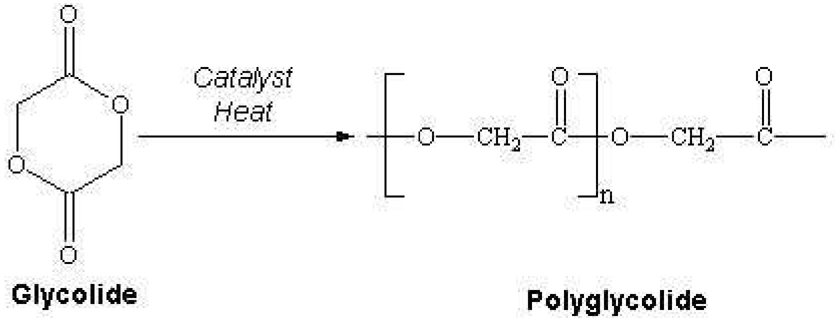
It has superior properties, partly due to its greater stereo regularity as shown in Table 4. It also has a higher strength and modulus of 7 GPa[9], in spite of its low solubility, this polymer can be fabricated into a variety of forms and structures.

Table 4
General features of Poly glycolic acid

Nature	Crystalline
Melting point (Tm)	225-230^{0}C
Glass transition temperature(Tg)	35-40^{0}C
Soluble in	Highly fluorinated solvents
Non soluble in	Water & organic solvents
Blending with other polymers	Good

Simple poly condensation of glycolic acid is the simplest method for synthesis of PGA but an inadequate method to obtain high polymer (Figure 2). PGA can also be prepared by melt/ solid polycondensation of glycolic acid using zinc dehydrate as catalyst. In this method a high molecular weight of 91kda was obtained similar to that of PGA prepared by ring-opening polymerization. Henceforth this process has paved way for large scale synthesis of PGA [38]. Another effective way to obtain poly (lactic-co-glycolic acid) (PLGA) based copolymers is by chain- extension process which is a combination of two different reactions [39]

Figure 2
Condensation of Poly glycolide [40]



The main advantage of PGA is its biodegradability and biocompatibility with biological systems than non-biodegradable materials. It degrades at a faster rate compared with other biopolymers and the mechanism of degradation is by simple hydrolysis of the ester backbone linkage. *In vivo* degradation occurs both by random hydrolysis and by tissue esterases enzymes. Another important factor is that the degradation product, glycolic acid, is non-toxic which is later metabolized through the tricarboxylic acid cycle [41]. In this context, PGA have become very popular for medical applications as it is safe, degradable and therefore does not need implant removal [42]. They are mainly considered as needle free sutures for various medical applications. Numerous studies on this aspect was done, in case of spinal surgery repair of the dura is difficult when it is torn or fragile in such cases non-suture dural repair technique was followed using PGA mesh and fibrin glue. The efficacy and safety of using PGA mesh and fibrin glue as non-suture duroplasty was significant[43]. A comparative study between fibrin adhesive versus sutured anastomosis in the small intestine of pigs were done and it was found that PGA was as effective as sutured cases[44].

Satoi Sohei [45] worked on the PGA as potent sealant for Pancreticojejunostomy and Kazuhiro Ueda [46] also attempted to control alveolar air leaks without suturing, using polyglycolic acid mesh as artificial pleura. A study on the growth inhibition effects of a new type of biological glue composed of polyglycolic acid on cultured endometrial cells was also attempted [47]. This biodegradable glue was capable of inducing apoptosis of endometriotic cells of patients with endometriosis. Therefore this suggested that PGA in addition to adhesive nature can also have growth inhibitory effects on endometrial cells and may be useful for endometriosis therapy. Recently soft PGA felt were used to stop bleeding of a lacerated liver in two patients. This was first reported by Markus Golling [48] the main advantage of this felt was the combined effect of compressing the wound edges and PGA which acts as a strong sealant.

Resorbable scaffolds can be developed using PGA with hetero-bifunctional peptide linkers, which was termed as ‘‘interfacial biomaterials’’ (IFBMs) [49]. PGA was found to be an effective method for controlled release delivery devices for a wide range of bioactive molecules. An improved encapsulation process to produce microparticles made from poly DLGA which is suitable for rapid plasmid DNA delivery was successfully developed[50]. Porous 3D biodegradable scaffolds which served as an adhesive substrate for implanted cells was prepared using PLLA and poly DL- lactic-co-glycolic acid with controlled pore structures. Different types of method for anchoring bioactive molecules in their native form to a substrate, which can also control the release of the molecules into solution, have been developed. The copolymer of chitosan grafted with the PGA lacking additives of catalytic amounts of heavy metals was developed to be used in biology and medicine [51]. Other biomedical uses of PGA include artificial skin and to repair bone system.

CONCLUSION

In developing countries, environmental pollution by synthetic polymers and waste disposal problems has become a most important problem. Therefore biodegradable polymers with excellent biocompatibility and mechanical properties, such as poly-lactic acid (PLA), poly-glycolic acid (PGA) have been identified as alternative materials. PLA is produced from a naturally occurring organic acid that can be produced by fermentation of sugars obtained from renewable resources. PGA is the best tissue adhesives due to its biocompatibility and considered as needle-free method for wound closure that does not require local anesthetics. The amount of adhesives used may be meager but their impacts on economic and environmental concerns are wide. These biodegradable polymers therefore have wide application both in medical and industrial fields. Even though there are number of research papers reported on biodegradable polymers but still biodegradable adhesives are at infancy level. Furthermore, recent advances necessitate the modification of existing polymers or synthesis of novel polymers for specific applications.

CONFLICT OF INTEREST

Conflict of interest declared none.

ACKNOWLEDGEMENT

We are grateful to University Grant Commission, New Delhi for supporting this study under Maulana Azad National fellowship.

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