Granta EduPack White Paper

Bio Engineering Database. Part 2: Bio-derived materials and example applications

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A companion White Paper, "The Granta EduPack Bio Engineering Database. Part 1: Introduction to Biological and Bio-medical materials" introduces biomaterials comparing them with engineering materials.

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1. Introduction and Synopsis

The Granta EduPack Bio Engineering database Level 2 is described and illustrated in the White Paper Part 1, which introduces the concept of biomaterials and specifically looks into biological and bio-medical materials. It describes the data for the basic building blocks of natural materials–proteins, glycoproteins, polysaccharides, and minerals–and for the natural structures made from them–soft tissue, mineralized tissue, wood-like structures and natural fibers. It also introduces examples where man-made materials might best be used for bio-medical applications. The Bio Engineering Level 2 database was restructured, revised, and enlarged for 2014. One of the enlargements is the inclusion of bio-derived materials and of bio-medical materials. This second Bio Engineering White Paper describes the new structures and the additions and improvements to the database, specifically looking into the bio-derived materials, and illustrates its content via case studies.

2. The new structure and content of the Granta EduPack Bio Engineering database

The database contains data for biomaterials (defined in a moment) and for the standard materials of engineering. Each dataset can be accessed and used separately; they can also be used together, allowing comparisons between the attributes of biomaterials and engineering materials.

By biomaterials we could mean:

- ***Biological materials*** are natural materials, those produced by biological systems. Thus skin, bone, wood, shell, and hair are biological materials.
- ***Bio-derived materials*** are those synthesized from natural biological materials. Thus paper, plywood, twine, and rope are bio-derived materials.
- ***Bio-medical materials*** are materials synthesized for tissue engineering or to replace or support body parts; they have to be compatible with the human body. Thus bio-glass, alumina bio-ceramics, titanium grade F67(B652), silver amalgam, and ultra-high molecular weight polyethylene (UHMWPE) are bio-medical materials.
- ***Bio-inspired materials and structures*** are those that mimic nature and biological materials. Thus high performance silk, Velcro, adhesive-free ("Gecco") adhesion, and water-repellent ("Lily-pad") surface texturing are bio-inspired materials and structures.

In Granta EduPack, material records use the blanket-term ***Biomaterials*** refer to biological, bio-derived, bio-medical, and bio-inspired materials. The new Bio Engineering Level 2 includes additional of bio-derived materials and of bio-medical materials.

The Bio Engineering Level 2 database has 250 records, 177 of which are classified as biomaterials. The structure of the folder tree has changed, following Design Level 2, with the same families of materials. The top-level structure parallels that of other Granta EduPack Materials databases, with folders for Metals, Ceramics and Glasses, Polymers, Hybrids and Composites, and Fibers. The biomaterials records are contained within this structure, in the folder corresponding to their chemical nature. Biomaterials can easily be accessed by the subset of materials, read Box 1 to find out how to access these sub-groups of materials. Filters in the Browse and Select functions allow subsets of biomaterial, biological, bio-medical, and bio-derived materials to be isolated, hiding all other records.

The database inherits all the records of the earlier Bio Engineering Level 2 database, documented in the White Paper entitled “The Granta EduPack Bio Engineering Database. Part 1: Introduction to Biological and Bio-medical materials”. Its content has been expanded in ways described below. In addition a chemical structure diagram is now included in the polymer records to help students with a chemistry background to relate polymer properties to the functional groups. That for the bio-polymer polyhydroxyalkanoate (PHA) is shown in Figure 1.

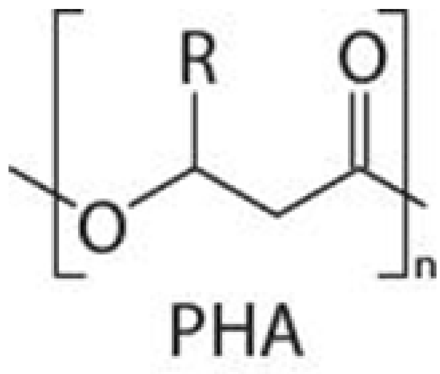


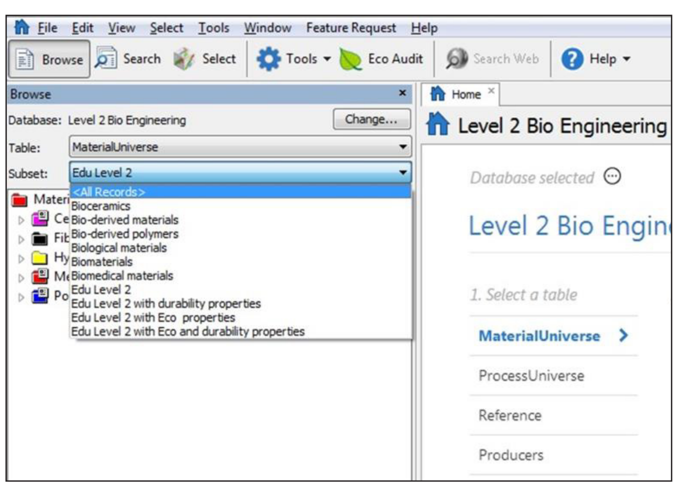
Figure 1. PHA diagram

Biomaterials subset in Bio-Engineering Level 2

Biomaterials and their sub-groups can easily be accessed by pre-defined subset of materials. Filters in the Browse and Select functions allow easy and quick access to subsets of biomaterial, biological, bio-medical, and bio-derived materials to be isolated, hiding all other records.

Access To access these subsets, in Browse mode, open the drop-down menu for Subset on the left pane, and select the relevant subset of interest.

You can now only browse the tree among the relevant materials.



Box 1. How to easily access biomaterials subsets.

2.1 Bio-polymers (Bio-plastics)

Bio-plastics are plastics made wholly or partly from resins derived from natural sources such as sugar cane, soya, castor nut, potato starch, or cellulose from straw, cotton, or wood. Some are biodegradable or compostable, some are not. The present-day production of bio-plastics is about 1m tonnes per year, equivalent to about 0.5% of the world plastic production, but it is growing at over 10% per year.

Figure 2 puts them in perspective. The common oil-based plastics are at the lower-left, neither bio-based nor biodegradable. At the lower-right are a small subset of oil-base plastics that are biodegradable and, a few, compostable. The upper part of the diagram shows bio-based plastics. Many bio-products can be broken down by fermentation processes to alcohols, which in turn can be synthesized into monomers and subsequently polymerized plastics as familiar as polypropylene and polyethylene. Others, shown at the upper-right, are uniquely bio-derived. There is a further distinction: these unique bio-plastics can be blended with oil-based polymers to make combinations such as PLA/PE that are, to a degree, biodegradable and, by having a bio-content, are less dependent on oil.

The Granta EduPack Bio Engineering Level 2 database contains 28 plastics records, including 7 bio-plastics:

- Cellulose nitrate (Celluloid) (CN)
- Cellulose polymers (CA)
- Nylon 11 (PA-11)
- Polyhydroxyalkanoates (PHA, PHB)
- Polylactide (PLA)
- Polytrimethylene terephthalate (PTT)
- Starch-based thermoplastics (TPS)

A case study in Section 3 compares their properties with those of oil-based plastics.

2.2 Bio-derived composites

Composites that use natural fibers–hemp, flax, kenaf–in place of glass or carbon are attractive as bio-substitutes for widely-used man-made materials. They have properties similar to those of conventional glass-fiber composites. Composites based on waste agricultural fiber (such as wheat and rice husk, bamboo, or sugarcane residues) bonded with phenolic resin have promise for use in places where wood is a scarce resource. They have properties and applications like those of fiberboard.

The Bio Engineering Level 2 database contains records for 5 bio-derived composites. They are:

- Agro fiberboard
- Furan-based composites
- Medium density fibreboard (MDF)
- PLA matrix/ kenaf fiber composites
- Plywood

2.3 Woods

Wood, like stone, is one of the structural materials of pre-history. It is cheap, easily machined, carved, and joined, and—when laminated—they can be molded to complex shapes. Its uses range from the built environment to transport and tools. The number of records in the database describing species of woods has been increased to 18. Their mechanical properties are compared with those of wood-like composites in Section 3.

Metallic bio-medical materials	Polymeric bio-medical materials	Ceramic bio-medical materials
Cobalt-chromium alloys (bio)	Acrylic (medical grade)	Alumina bio-ceramic
Gold	Acrylonitrile butadiene styrene (ABS)	Bioglass ceramic
Nickel-chromium alloys (bio)	Epoxies	Calcium phosphate bio-ceramic
Nickel-Titanium alloys (Nitinols), austenitic	Ethylene vinyl acetate	Glass ionomer
Nickel-Titanium alloys (Nitinols), martensitic	Natural rubber (NR)	Silicon
Precious metals implants (bio)	Nylon 11 (PA-11)	Vitreous carbon
SIlver	Polyamides (Nylons, PA)	Zirconia bio-ceramic
Silver amalgam (bio)	Polycarbonate (PC)	
Stainless steel (bio)	Polyetheretherketone (PEEK)	
Titanium (bio)	Polyethylene (PE)	
	Polyethylene terephthalate (PET)	
	Polyglycolic acid (PGA)	
	Polylactic-co-glycolic acid (PLGA)	
	Polylactide (PLA)	
	Polymethyl methacrylate (Acrylic, PMMA)	
	Polyoxymethylene (Acetal, POM)	
	Polypropylene (PP)	
	Polystyrene (PS)	
	Polytetrafluoroethylene (Teflon, PTFE)	
	Polyurethane (elPU)	
	Polyurethane (tpPUR)	
	Silicone (medical grade)	
	Ultra high mol. wt. polyethylene (UHMWPE)	

2.4 Papers

Paper is one of the oldest, and perhaps one of the most remarkable of materials made by man from natural and renewable resources, and it is one with equally remarkable properties. Its uses range from books to packaging and simple structures. The database contains records for five grades of paper, illustrated in a case study in Section 3.

2.5 Bio-medical materials

Bio-medical materials are materials synthesized for tissue engineering or to replace or support body parts. Some, like the body itself, are polymeric, others are metallic or ceramics. The Bio Engineering Level 2 database contains records for 20 bio-medical materials of which 8 are metals, 6 polymers, and 6 ceramics. They are listed in the table below. Case studies are described in the white paper Part 1.

3. Case studies

This section describes five case studies that illustrate some of the ways in which the Granta EduPack Bio Engineering database can be used. All the figures and data in the case studies derive from the Level 2 version of the database.

3.1 How do bio-plastics compare with plastics made from oil?

Bio-polymers are plastics made from hydrocarbons derived from renewable sources such as corn, soya, cellulose, and polysaccharides. They are used as packaging (NatureWorks PLA), disposable cutlery (biodegradable, Figure 3), dental care items (Cereplast), agricultural turf stakes (Telles PHA), planter pots (Novamont's Mater-Bi starch resin), and medical products. Here we compare the properties of seven bio-polymers with those of seven common oil-based plastics, listed in the two tables below.

Figure 3. Biopolymer products. (Reference: AdobeStock 385500504)

Bio-polymers	Oil-based polymers
PLA Polylactic acid	PP Polypropylene
PHA Polyhydroxyalkanoate	PE Polyethylene
CA Cellulose acetate	PET Polyethylene terephthalate
CN Cellulose nitrate	PS Polystyrene
PA11 Nylon 11	PA6 Nylon 6
PTT Polytrimethylene terephthalate	PUR Polyurethane
TPS Thermoplastic starch	ABS Acrylonitrile butadiene styrene

Mechanical properties. Figure 4 shows two mechanical properties: Young's modulus and Tensile strength. Those of bio-polymers are broadly comparable with the same two properties of conventional plastics. The mechanical properties can be adjusted through a considerable range by blending, use of plasticisers, or filling with glass, mineral, or chopped fibers. The data shown here are for unfilled, moulding-grade materials. Bio-polymers, generally, have stiffness and strengths that are comparable with those of PE or PP, but they are denser. Bio-polymers have low heat resistance and poor impact resistance, both of which can be improved with plastizers and by blending with oil-based plastics, but this inhibits recycling.

Environmental properties. Bio-polymers are widely perceived to have a better eco-character than conventional, oil-derived, polymers, but evidence does not entirely bear this out. Figure 5 (a) shows the carbon footprint and cost per unit volume of bio and oil-based polymers. The sweet spot here is at the bottom left (low carbon and low cost). Today's bio-polymers compare poorly with conventional oil-based alternatives. This is because the fermentation or processing needed to make bio-resins requires heat and thus carries an energy and carbon burden, and the subsequent polymerization step for both bio and oil-based polymers makes almost identical contributions to both. Figure 5 (b) shows a comparison of the water requirement associated with producing bio and conventional polymers. The water demand of bio-polymers is high because of the needs of the plants from which they are derived. Bio-polymer production is, of course, in its infancy; as production is scaled up and processing is refined it is expected that bio-polymers will begin to show an environmental gain.

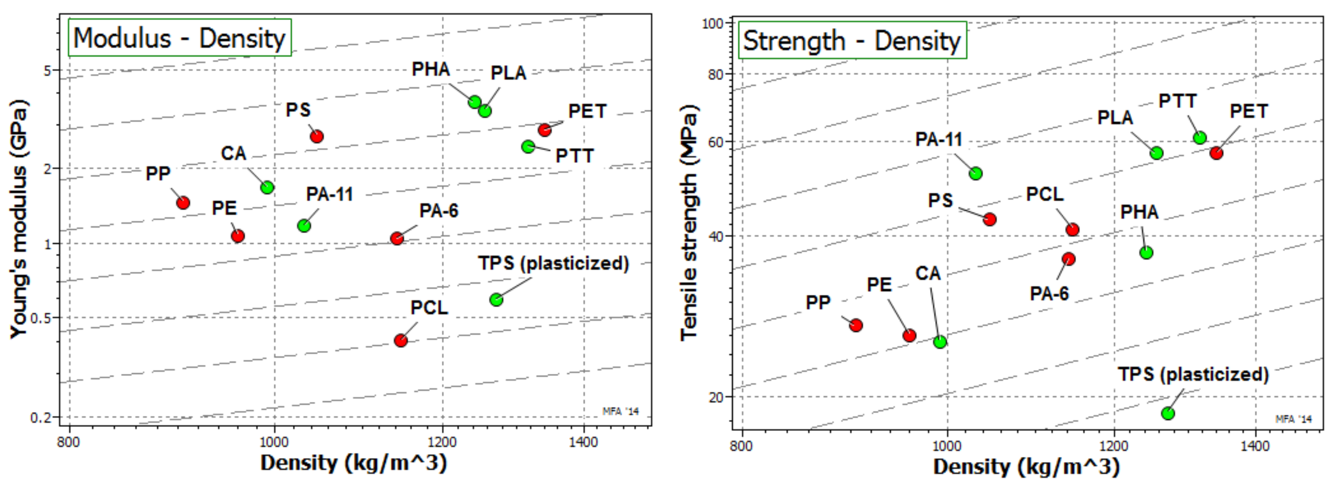


Figure 4. (a) Young's modulus, E, tensile strength, σ_t, and (b) density ρ of commodity oil base polymers (blue) bio-polymers (green) and blends of bio and oil-based polymers (aqua), with contours of E/ρ and σ_t/ρ.

Energy and carbon are not the only issues related to bio-polymers. The land area required to synthesize conventional polymers is negligible; that for bio-polymers is large, up to 5 m2/kg per year. At that level the production of 1 million tonnes of bio-polymer per year requires 5,000 square km2 of fertile land. This competition with agriculture is seen by many as the great weakness of bio-polymers; in a world in which one seventh of the population is undernourished, displacing food production to make plastics seem wrong. There is, however, a potential solution to this problem: the use of algae as feedstock. Marine algae require only seawater, sunlight, carbon dioxide, and nutrients to flourish, leaving fresh water and land for food production. Algae multiply fast, producing up to 15 times more feedstock per unit area than land biomass. Fermenting them to make ethanol and other alcohols could allow their synthesis to bio-polyethylene, bio-PVC, and bio EVA. Additionally, there is the attraction that some bio-polymers are biodegradable: they are broken down into CO2 and water by microorganisms. A distinction is drawn between biodegradability and compostablility, a purely practical term applied to biodegradable packaging that is sufficiently thin to break down by 90% in six months in a standard composter (such packaging is marked by a "Compostable" symbol).

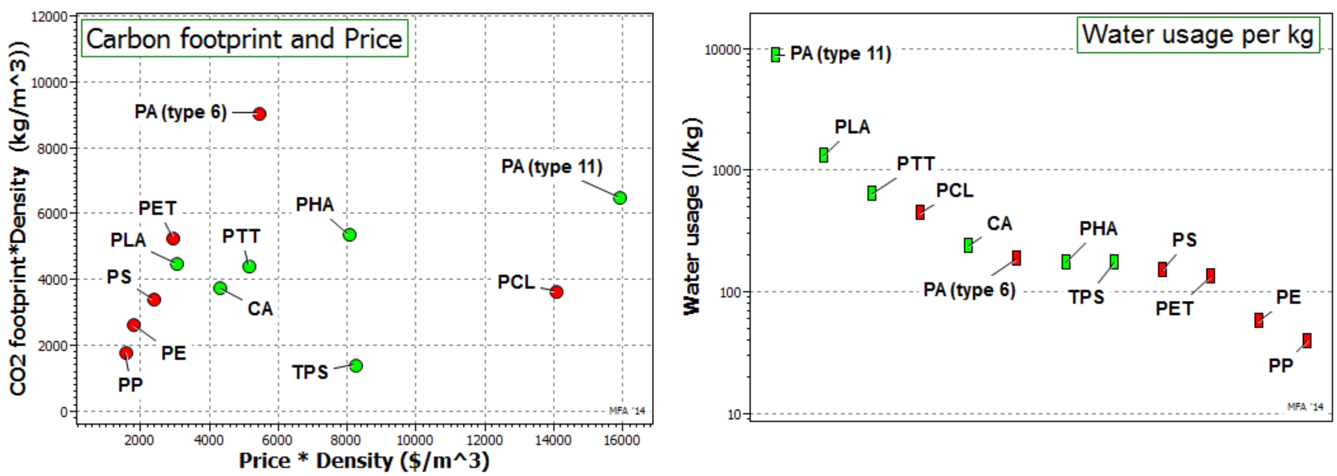


Figure 5. (a) The carbon footprint and price of commodity oil base polymers (blue) and bio-polymers (green); (b) Water usage in making the same polymers, segregated into those that are biodegradable and those that are not.

Economics. A price for crude oil of $100 per barrel corresponds to cost per unit weight of $ 0.72/kg. Commodity plastics (PP, PE, PVC, PET, PS) all have prices between $1.50 and $2.80 per kg, only about 2 to 4 times that of the oil on which they are based, making them vulnerable to rising oil prices.

Today, bio-polymers cost more than commodity oil-based polymers, like polyethylene and polypropylene. Figure 6 plots the price per kg against density on the left, and the price per unit volume (per m3) on the right. In a straight substitution of a bio-polymer for a conventional polymer, it is the price per unit volume that is significant. PLA and PPT are about 25% more expensive per unit volume than PP and PE. All the other bio-polymers are more expensive than this.

Despite their higher price, the bio-plastics market is growing at 8-10% per year and is predicted by some studies to take up to 25% of the polymer market by 20202.

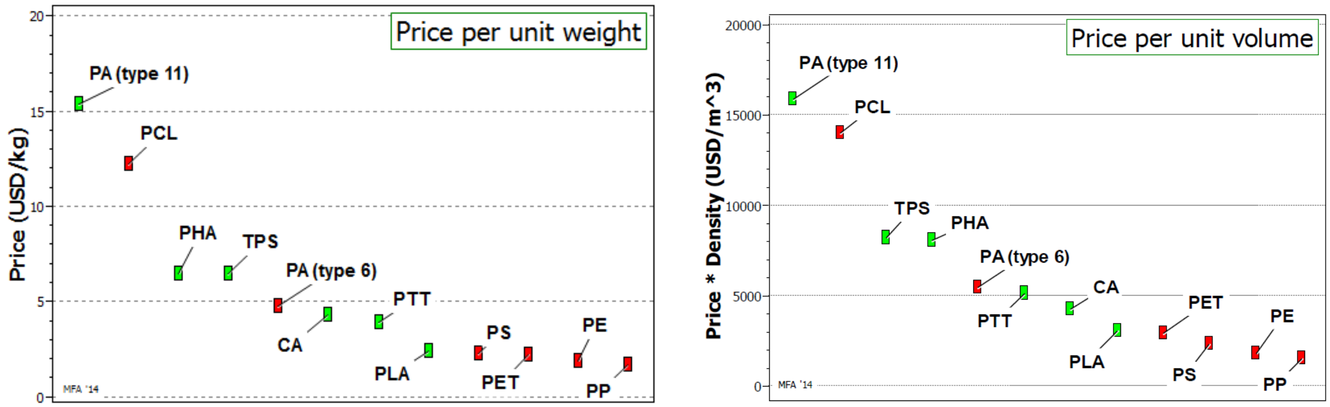


Figure 6. The price per kg (a) and the price per m3 (b) of commodity oil base polymers (blue), bio-polymers (green) and blends of bio and oil-based polymers (aqua).

3.2 The properties of woods and wood-like composites

The enlarged Bio Engineering database contains data for 18 common woods. It also includes three wood-like composites: plywood, medium-density fibreboard (MDF), and agro fibreboard–a composite made of agricultural waste fibers from wheat, rice, bamboo, or sugarcane, bonded with phenolic resin. In this case study we explore the density-dependence of the mechanical properties of woods and compare these with the properties of wood-like composites.

Figures 8 and 9 plot of the moduli and strengths of woods against their densities, respectively. The green symbols are for loading parallel to the grain of the wood; the blue ones are for transverse loading.

Cellular solids like wood are characterized by their densities, ρ. When the wood is loaded parallel to the grain, the cell edges are loaded in-plane and the modulus *E*, varies linearly with the density: $\widetilde{E} \propto \widetilde{\rho}$. The upper line on the figure shows this relationship. When instead, the wood is loaded across the grain, the cell walls bend and the modulus varies as the cube of the density: $\widetilde{E} \propto \widetilde{\rho}^3$. The lower line, a plot of this dependence, fits the relationship well.

Figure 7. Willow, and cricket bat made from willow. (Images reference: pexels.com 6057 and AdobeStock 58348948)

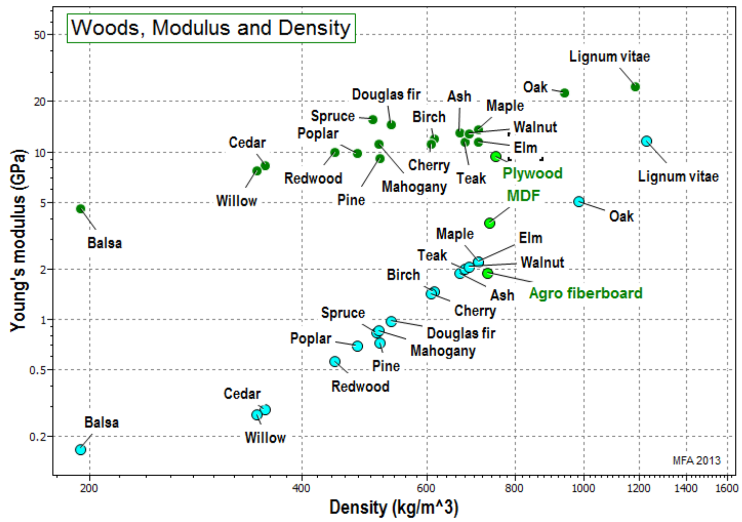


Figure 8. The moduli of woods and wood-like composites. Dark green symbols are for loading parallel to the grain of the wood, blue symbols for transverse loading. The scales are logarithmic. The lines correspond to the relationships described in the text.

The strength $\tilde{\sigma}_y$ of woods depends on their densities, $\tilde{\rho}$ in a somewhat similar way. When the wood is loaded parallel to the grain the strength $\tilde{\sigma}_y$ varies linearly with the density: $\tilde{\sigma}_y \propto \tilde{\rho}$. The upper line on the figure shows this relationship. When instead, the wood is loaded across the grain the cell walls bend and the strength now varies as the square of the density: $\tilde{E} \propto \tilde{\rho}^2$. The lower line, a plot of this dependence.

The wood-like composites have properties that lie, not surprisingly, between those of the longitudinal and the transvers properties of woods, in both comparative Figures 8 and 9.

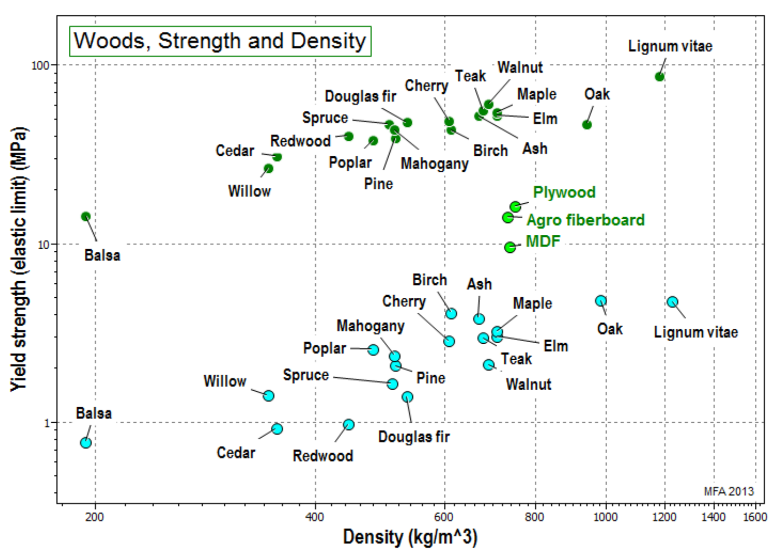


Figure 9. The strength of woods and wood-like composites. Dark green symbols are for loading parallel to the grain of the wood, blue symbols for transverse loading. The scales are logarithmic. The lines correspond to the relationships described in the text.

3.3 The properties of paper and their strange units

We use paper in quantities that exceed those of most other materials–430 million tons in 2013 world-wide, and rising. Some–about 12% of the total–is recycled; even this small fraction equates to 50 million tons per year. Most is used for packaging and for printing (see Figure 10), and for both these applications the strength of the paper plays a key role. Packaging provides protection and here the need for strength is obvious but it is equally important if paper is to be fed through printing presses and copiers. The feel of paper has to do with its density, stiffness, and surface texture. So how do paper-people describe these?

The density of paper products is measured as Grammage, R, its weight in grams per square meter, abbreviated to gsm. It is related to the bulk density ρ in the usual units of kg/m^3 by

$$\rho = R/t$$

where t is the thickness ("***Caliper***") of the sheet in millimeters. The density of paper is almost as diverse as its uses: as low as 200 kg/m^3 (toilet paper) through 300 kg/m^3 (Kleenex) to 800 kg/m^3 (copier paper) peaking at 1,200 kg/m^3 (glazed art paper). Paperboard, heavily filled, is even denser (Figure 11).

Tensile stiffness St, units kN/m, is the slope of the *force-per-unit-width* versus *tensile strain* curve. It is related to the bulk Young's modulus *E* (usual units, GN/m^2) by

$$St = Et.$$

Figure 10. Bond / copier paper(image reference: Pexels, karolina-grabowska-4464379

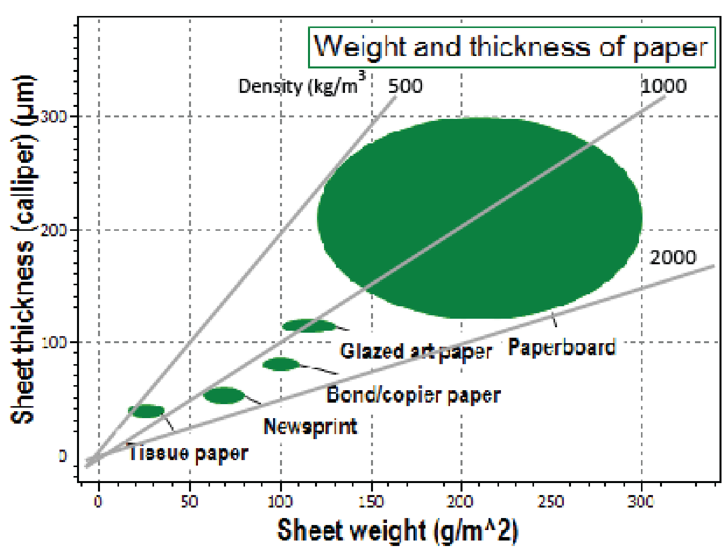


Figure 11. The calliper (sheet thickness) of paper plotted against its grammage (weight per unit area)

Tensile strength, less obviously, is measured as the ***Breaking length, BL,*** measure in meters (m). It is the length of a paper strip in meters that would be just self-supporting if hung vertically from one end. It ranges from 500 meters for extremely soft tissue to about 8,000 meters for strong Kraft bag-paper. Figure 12 shows the breaking length of papers plotted against the sheet weight.

The breaking length is related to the bulk tensile strength σ_{ts} in its more usual units of MN/m^2 by

$$\sigma_{ts} = \rho\ g\ BL = g\ BL\ (R/t),$$

where g is the acceleration due to gravity (9.81 m/s^2). The breaking lengths given above correspond to bulk tensile strength of 1.5 – 60 MPa.

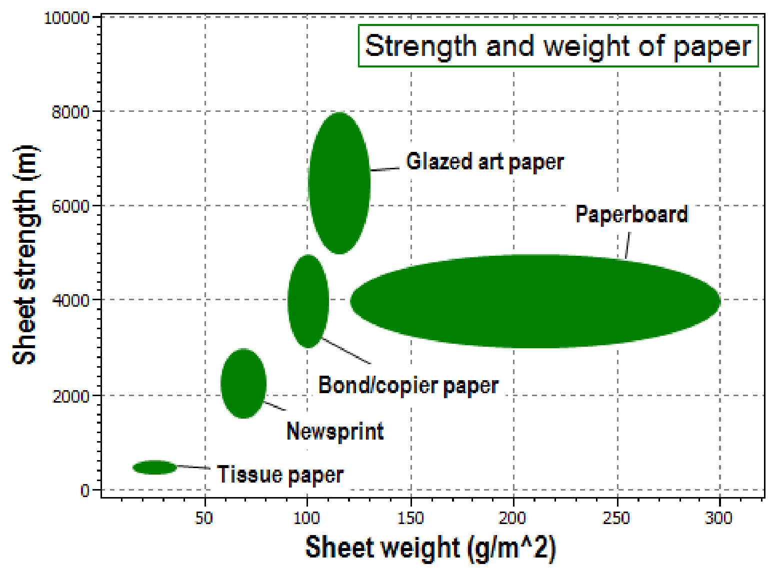


Figure 12. The breaking length of paper plotted against its grammage (weight per unit area).

4. Summary and Conclusions

The interest of biomaterials and their use expands beyond their biocompatibility attribute and their applications on bio-medical applications. Greater interest and knowledge on biomaterials for other applications that are not medical-related is growing. Mainly, due to the perception that bio-derived materials are more sustainable than other man-made materials. Also, because there is a real need that new materials fulfil the role of current more expensive, scarce, or incompatible-with-the-environment ones. Nature and biological materials provide a great source of new materials, raw materials to make new composites, or ideas on how to develop engineering materials, via biomimicry.

The teaching of biomaterials to engineering and/or non-bio-medical students, their particular material properties, and how they compare with the most commonly used materials for engineering applications is becoming increasingly of interest. The Granta EduPack Bio Engineering edition aims to support the introduction of these concepts, and in their advanced versions, to aid design in real applications using such materials. A wealth of uses is still to be applied and tested, and the case studies presented herein provides some examples to students to start learning about new possibilities. Additionally, it provides a platform to compare the sustainable and environmental advantages or disadvantages of biological and bio-derived materials when compared with man-made non-biological ones. The accompanying white paper “The Granta EduPack Bio Engineering Database. Part 1: Introduction to Biological and Bio-medical materials” expands on the concepts and case studies for bio-medical applications.

Acknowledgements

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