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New Developments of Adhesives and Sealants Contributing to Environmental Sustainability

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Abstract

The demand for Sustainable Products continues to grow in an attempt to reduce the harmful impact on the environment. Many industries are placing increased emphasis on identifying environmental consequences prior to developing new products, processes or services and thus "sustainability" has become a strong driving force for innovation. For example, recent developments within the adhesive and sealant industries, have led to new environmentally friendly products. This article presents some of the latest accomplishments in the area of producing adhesives and sealants with sustainable features.

Key words: *sustainability*; *environmentally friendly products*; *adhesives and sealants with sustainable features*

Background

The accelerated rate of the Environmental destruction in the last 20 years made the "Sustainability" an urgent issue. It is world widely agreed that certain economical growth factors are responsible for the current environmental destruction.

With the actual rhythm of natural resources and energy consumption and the environmental pollution generated, our planet will become unsustainable for human life. The process of resources replenishing is much slower and certain recourses, like petroleum and gas, can not be regenerated. The long term results of degradation will be unable to sustain human life.

Brundtland Report, released in 1987 by the United Nations/ World Commission on Environment, defines the Sustainable Development as the "Development that meets the needs of the present without compromising the ability of future generation to meet their own needs.

After the release of *Brundtlant Report* also known as *Our Common Future*, *Sustainability development* concept has become very popular in the recent years, reaching un international level. Numerous national organizations and agencies from many countries also international commissions are looking for strategies to grow economically in equilibrium with the ecological system. In other words, when industries are using the Earth's resources (water, forest, minerals, oil, gas, gemstones, etc.) people decisions must take in considerations the global environmental impact: the amount of resources left for future, the health of human population and of the wildlife, the changes that they may produce to the quality of the air, water, soil, the ecosystem in general.

Sustainability requires that industrial processes and all human activities will only use nature's resources at the rate at which they can be replenished naturally. Products generated will need to be Sustainable or *Green*.

Science and Technology play in important role in achieving Sustainable Development.

Multi-disciplinary Science research may be able to solve the sustainability problems.

The Environment Protection Agency, EPA, an US governmental agency, has created in 2007 the Sustainability Research Strategy, in order to contribute to the global effort of solving current and future environmental problems. EPA's Research and Development Office has defined six sustainability research themes [1]:

- Natural Resources Protection (Air, Water, Ecosystem)
- Non Renewable Resources Conservation (Energy and Materials)
- Long-Term Chemical and Biological Impacts (using Non Toxic Materials)
- Human-Built Systems and Land use
- Economic and Human Behavior
- Information and Decision Making

Protecting environmental and human health from chemical toxicity is central to EPA's mission. Chemical pollutants released to the environment at a rate greater than he environment ability to recycle, absorb or render it, is considered to be persistent. Chemical that are persistent or bio accumulative can crate high level of exposure. The substitution of benign chemicals through green chemistry and the use of new technologies and innovative processes are key to eliminating or minimizing the level of toxicity.

The following are Priority Research topics and guidelines for Researchers provided by EPA/ORD [1]:

- Develop and apply innovative chemical transformation utilizing green chemistry and sustainable chemistry and engineering
- Improve the yield, safety and specific chemical processes by identifying appropriate solvents, controlling thermal conditions and purity, catalysts or byproducts recovery.
- Formulate products that reduce environmentally benign .
- Develop life cycle tools to compare the total environmental impacts of products generated form different processing routs and conditions.
- Develop improved or accelerated method for understanding toxicology, kinetics and persistence of chemical substances.

Elements of Sustainable Development Concept

Development of Sustainable products encompasses many aspects, such as:

- Type of raw materials used; most industries consider sustainable materials to be based on renewable sources rather than petroleum or natural gas feedstock. Bio-based products like bio-polymers are of great interest.
- Type of process used; environmentally-friendly processes that conserve energy and are safe and harmless for environment such as low temperature, use of solar energy or UV, with no or minimum of generated wastes, are highly desired.

Schematically, these aspects could be arranged as shown below, Fig. 1.

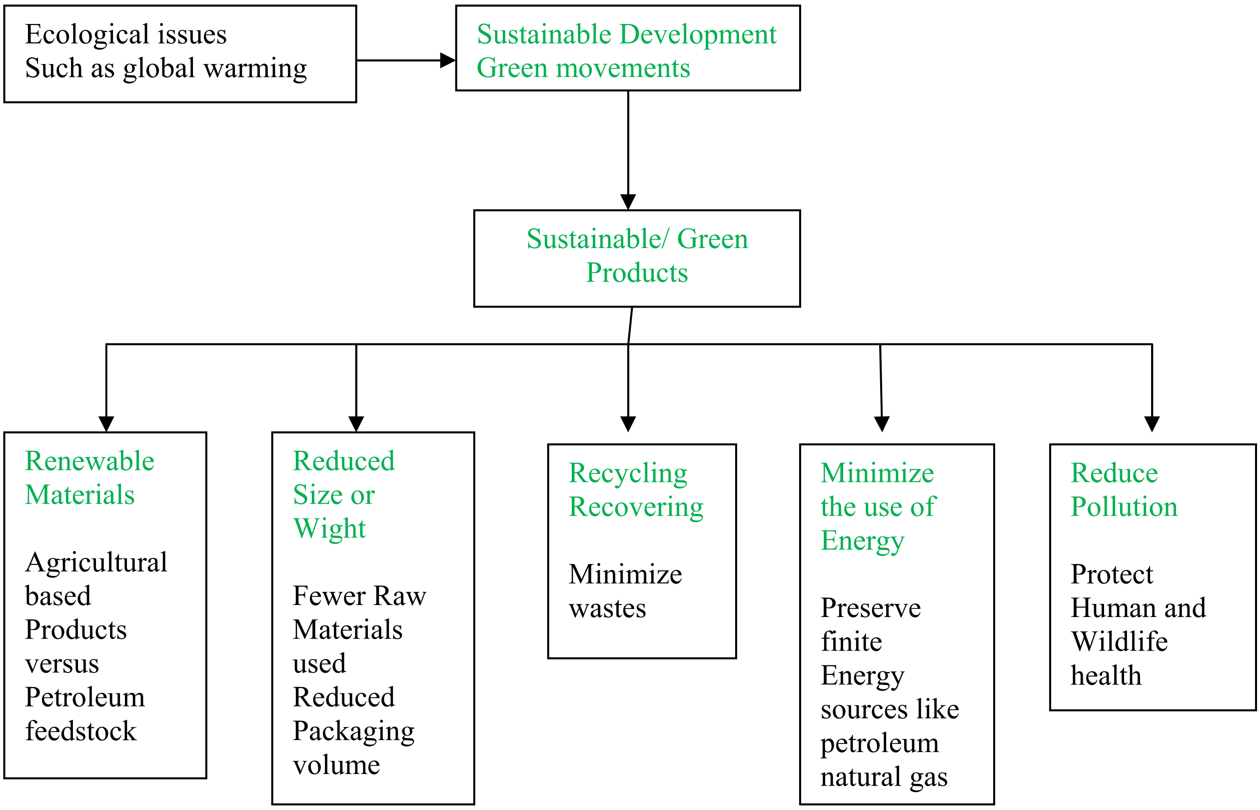

Fig. 1. Elements of Sustainable Development

As a method of measuring environmental impact, **Carbon footprints, expressed in units of CO_2 (Greenhouse gas)** emitted annually, has become the most popular one. Also known as Environmental impact can be reduced directly at each stage or indirectly at multiple stages thorough the product's life. A new term also very popular is ***life cycle analysis,* LCA.**

Besides the elements that were captured here, there is also a social aspect involved, even thought some products have only an indirect effect on society. Ultimately, human health is critical for a sustainable society.

Sustainable Adhesives and Sealants

Synthetic Adhesives and Sealants are chemical products with direct or indirect impact on the environment due to the products made with them. Synthetic polymers/plastics are used on a large scale in adhesives and sealants compositions as main raw materials and these materials are not biodegradable. Adhesives and Sealants are complex combinations of polymers with different ingredients, tackifiers, plasticizers, and a variety of additives such as: fillers, adhesion promoters, antioxidants, colorants, etc. Some of these chemicals are less safe to the environment.

In the adhesive industry Green Adhesives have a broad meaning involving many aspects: raw materials, technology/processes, size/weight, type of energy used, recyclability and others. So, sustainable adhesives are more than just recyclable/renewable, there is a complex of sustainable features that need to be considered. Graphically, these features could be represented as the below diagram shows, Fig. 2:

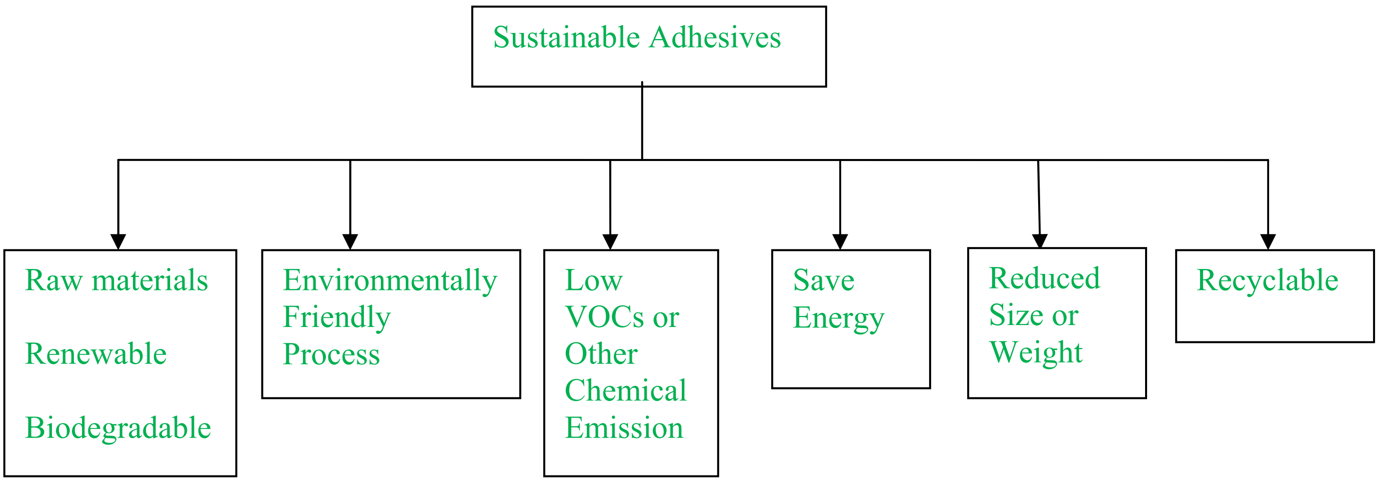

Fig. 2 Features of Sustainable Adhesives

The features presented above are also seen as criteria that need to be met for an adhesive or sealant to be recognized as sustainable. Sustainable adhesives should have at least one of the following properties:

- manufactured from a renewable raw materials such as agriculturally based feedstock or they have renewable raw materials incorporated in their formulations thus reducing the amount of petroleum based raw materials.
- manufactured through an environmentally friendly processes, harmless to nature and people, based on energy saving technologies.
- low in chemical emission like VOCs (volatile organic compounds).
- if part of a finished product, should contribute and improve somehow the sustainable features of a finished structure (automobile, building, furniture, hygiene product, packaging, etc.

There are more requirements for products to be considered *Green*. For example, they need to be fully biodegradable, release zero measurable VOCs, contain and release zero formaldehyde, contain less than 100 ppm heavy metals (cadmium, zinc, mercury) and other requirements imposed by regulations specific to different countries or regions (e.g., Directive EU).
This article is focused on the development work recently conducted by researchers on how new environmentally friendly adhesives/sealants can be created or to improve the existing ones in the direction of making them more sustainable.

Research Concerned with Development of Sustainable Adhesives and Sealants

There is a great amount of development work conducted recently by scientists from all over the world, trying to develop biodegradable or compostable products, resource-saving technologies, reduced size or weight needed, reduced VOCs or other emissions or achieve other green performances. According to the *British and European Standard BS EN 13432* [2], if a material is considered biodegradable, it can be transformed into compost. As it was mentioned before, many polymeric materials are being used in adhesive in sealants compositions. Plastics are not biodegradable; their wastes can be around for hundreds of years. Consequently, synthetic petroleum-based adhesives are generally not degradable.

Biodegradable Plastics

Synthesis of plastics consumes about 270 millions tons of fossil fuel each year [3], part as feedstock, part as process energy. Finding renewable alternatives to polyethylene, polypropylene and polystyrene becomes a priority; they are not biodegradable and the price is constantly rising.

Natural polymers, produced directly by biological systems, such as **Polysaccharides, Proteins, Poly(hydroxialkanoate)/PHA** and indirectly, using biological systems like **Polylactide/PLA,** can lower the green house emission and save the fossil feedstock.

Cellulose is the most abundant and most widely used biopolymer. It can be used as a raw material for plastic production especially in the form of cellulose acetate. **Chitosan,** highly purified chitin, is also a potential candidate. **Starch**–based plastic is starting to be used in polymer markets [3]. All these are polysaccharides.

PHAs are polymers produced by many bacteria.. They are moldable, water-insolubile, thermoplastic. The most common PHA, poly(3-hydroxibutyrate)/PHB, is stiff , high-melting point aliphatic polyester similar to industrial polyolefins. PHAS can be synthesized by microorganisms entirely from glucose [3, 4]. Resulting Physical properties depend on the bacterial species used. One such microbial polymer, PHBV, has been used to make plastic bottles and to coat paper. The process is not economical but remains in attention and it's still being investigated.

Polylactide/PLA is a new polymer [3, 4] on the commercial market**.** Manufacturing is a three step process: conversion of carbohydrates (dextrose from starch or glucose from corn) to lactic acid, conversion of lactic acid to lactide and the polymerization of lactide to polylactide.

Cargill started production in 2001 and currently the market demand is so strong that Cargill estimates to commercialized millions of tones by 2020 [5]. This is biodegradable polymer used in many applications such as: plastic films, plastic bottles, fabrics, carpet and foams, commercialized under the name **NatureWorks™**.

Shimadzu of Japan and Mitsubishi Plastics have also been producing PLA at pilot scale.

The adaptation of PLA as a component into adhesive systems has started recently in hot melt pressure sensitive and no sensitive grades due to its excellent blending capabilities with plasticizers, tackifiers and other polymers, mostly for packaging applications.

Recent developments have found that certain additives can reduce the brittleness and improve the toughness of PLA based adhesives. Also the hybrids with caprolactone have excellent performance. Other applications are being pursued such as medical/surgical area. Due to biodegradability, threads and screws will re-absorb by the body and low toxicity makes PLA a good candidate for surgical adhesives [5]. A new adhesive based on PLA and plasticizer made at University Osaka was recently disclosed [6].

Algae–Based Biopolymers are considered a very promising generation of bioplastics. Marine algae grow fast; they need seawater, sunlight, CO_2, and with the right nutrients can be cultivated in abundant amounts. Algae biomass can be converted into high quality monomers and polymers. According to recent statements from **Cereplast Inc.,** the company is close to introduce a new family of algae-based plastics for injection moulding and thermoforming [7].

Alginates are used so far in water based adhesives as hydro swelling, gelling and thickening additives.

Degradable adhesives, based on natural resources like starch, cellulose, seeds, soy and corn proteins, are not new, but they are currently being explored again. These natural resources are low in cost, environmentally friendly, do not required hazardous waste disposal, do not release harmful volatiles. The obtained adhesives have in some cases comparable performance as with those based on synthetic polymers.

Modern Soybean Based Adhesives

Many Technical Papers describe the use of soy bean proteins in adhesives, primarily in water based systems [8-11]. First the oil is extracted with hexane, than the protein is isolated, and concentrated [8]. Concentrated proteins can be used as the main polymeric component, as extenders for phenolic resins or blended with casein. Treatment with soluble alkaline material is necessary to improve dispersion in water. Soybean adhesives have limited water resistance, but they can be strong again after drying. High temperatures and (>150^0 C) and pressure are necessary for rapid production of assemblies [8].

Development work is currently done to improve soy products properties as water resistance, heat resistance, curing time, microbial resistance, in order to achieve an overall performance comparable with synthetic polymers. New methods are based on crosskicking with reactive agents.

Soy based adhesives can be combine with fiber wastes (paper) and crate hard composite products such as plywood, boards, laminated veneer lumber [9]. These adhesives are considered to be alternative for phenol and urea formaldehyde based adhesives. This way, consumption of formaldehyde (carcinogenic) in the wood industry can be significantly reduced.

Several Soy Polymers are commercially available [9]:
- Pro-Cote (manufactured by DuPond) recommended to use in adhesives for bottle labels, wood and textiles.
- Soy Seal for Gaps & Cracks (BioBased Insulation) for home improvements, used to spry around pipes and vents; Soy Seal for Windows & Doors.
- Soyad (Hercules and Heartland Resources Technologies) for panel board products
- NutraSoy 7B (Archer Daniels Midland) used in foamed plywood adhesives.
- Pure bond (Columbia Forest Products) entirely formaldehyde- free adhesive for hardwood plywood for interior use.

Modern Starch Based Adhesives

Starch and Dextrin conventional adhesives are notorious for their ability to bond paper products.

Corn, potatoes and wheat are the main sources for starch granules extraction. When heated with water, starch granules burst into a gelatinized, tacky paste. Initial viscosity and solid concentration can be later optimized with uncooked starch dispersions. Heat is necessary after the application to activate the dispersed starch particles (150-175^0 C). Once cured, the adhesives provide a good heat resistance but they are not thermoplastic. Also, the resistance to water is limited and biocides are needed to prevent mold growth. Some of these limitations can be improved by combining starch with other polymers (polyesters, polyvinyl alcohol) fillers (clay, calcium carbonate), thermosetting resins (urea formaldehyde).

Most of the current developments are directed to improve conventional starch adhesives limitations and to crated new, modern products. For example, due to the plenty hydroxyl groups along the molecular chain, starch molecules can react with isocyanates to form **Starch - Polyurethanes** [12]. New technologies are transforming regular size starch particles (~ 30 microns) into nanoparticles (50-150 nm) with huge increase of surface area. Thus, the amount of water needed for application is reduced and drying can take place faster, at lower temperatures.

A commercial nonostarch material is produced by **EcoSynthetix** and commercialized under the name **EcoSphere** delivered as a powder to be dispersed in water. The results is a latex with similar properties with a synthetic latex, superior then a cooked starched solutions. **EcoSphere** advantages over the conventional starch [13]:
- Typical size range of 50-150 nm; it can mix into a liquid that contains less water.
- Higher solids, lower viscosity.
- Reduced water content means less energy and time required to dry the adhesive.
- Produces stable latex-like dispersions; nanoparticles remain stable in liquid longer and the dispersions can still be used the next day.
- First biobased high-solids “Cold Glue”.
- Dramatically lower activation temperature; no gel point.

Manufacturing technology is based on a chemical-mechanical process involving a special equipment and glyoxal as reacting agent.

Biobased Additives

Many natural additives can be used in adhesive formulations. Among them, plasticizers are an important category. Their role is to soften rigid polymers, in order to improve final product rheology. New plasticizers are made from vegetable oils such as **Dow Ecolibrium™** or **Hallgreen** products, others are blends of vegetable oils and safe chemicals like citrates such as **Citrofol** product [14].

A plasticizer from vegetable oils was developed to improve PVC polymers properties [15], composed from epoxidized bioesters of vegetable oil fatty acids.

There are considerable R&D efforts conducted to develop biofillers to be used as reinforcing additives for plastics composites. Different cellulosic fibers are being investigated to be incorporated into polyolefins for improved mechanical properties [16, 17].

Nanoclay additives exihibit the potential to be use in many polymers as reinforcing fillers to create polymers-nanoclay composites with enhanced mechanical properties, durability barrier properties, electrical and thermal conductivity and flame retardation. Natural montmorilonit/nanoclay is already utilized on a large scale [18].

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Contribuţia noilor cercetări din domeniul adezivilor şi izolanţilor la protejarea mediului

Rezumat

Cererea pentru produse durabile continuă să crească în încercarea de a reduce impactul distructiv asupra mediului. Datorită preocupării crescânde a industriilor de a identifica consecinţele asupra mediului înainte de a dezvolta noi produse, procese sau servicii sustenabilitatea a devenit o forţă inovatoare. De exemplu, cercetările recente în domeniul adezivilor şi izolanţilor au condus la apariţia unor noi produse cu caracte recologic, durabil. În cadrul acestui articol sunt prezentate şi discutate câteva din aceste noi produse.