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The bio-touch: Increasing coating functionalities via biomass-derived components

V. Montano[a,*], A. Smits[b], S.J. Garcia[a]

[a] Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands
[b] Croda, Coatings & Polymers Business, Buurtje 1, 2802 BE Gouda, The Netherlands

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A B S T R A C T

The global increase of the environmental consciousness led to a rapid interest of the scientific community in the exploration of novel bio-based materials. To date several high-quality reviews on the topic of bio-based polymers in general and coatings in particular have been published. However their main focus has been on reporting different raw organic materials used, specific application fields or particular final products. Due to that approach the existing reviews nearly or completely fail in identifying and analysing the potential uniqueness of bio-based raw materials to implement new or better functions to polymeric coatings. The current review offers an overview of the peculiar effect of the bio-based raw component on different coating properties, a characteristic that we like to call the "bio-touch". The review highlights the relation between the bio-based element and the property achieved. The aim is not to report all the approaches and advances existing, but to critically analyse the main and most successful approaches pointing out possible intrinsic weakness.

1. The *bio* material world: a coatings perspective

The prefix "bio-" stems from the Greek word *bios* originally used to describe one's life or simply used as definition of life. Nowadays, the prefix bio- is used in many different areas, from food science to architecture and materials, in general to make reference to some form of connection to biological, organic life [1]. Nevertheless, its use when combined with the word "materials" can lead to multiple misunderstandings as different research fields use similar nomenclature. The term "biomaterials" in the medical world refers to materials to be used in living species such as humans (e.g. artificial hips or polymeric porous scaffolds), even when the materials pointed at are purely synthetic. Possibly a more suitable word in this case would be "bio-compatible" materials. In most other scientific and technological areas the word "biomaterials" refers to materials fully or partially derived from bio-sources. The latter is the main topic of this work, in which we focus in particular on the use of such materials for coatings.

The current dimension of a field and its rate of development can be roughly estimated from a basic search using an online indexing search engines for the scientific literature such as Web of Science or Scopus. When the keywords "bio" AND "material" NOT "fuel" are combined > 15,000 citations can be found, including articles, conference papers and patents. The number of records grew quasi-exponentially in the last two decades from 100 in 1999 to the 2000 + records for 2016.

In Fig. 1a simplified classification scheme for bio-based coatings is proposed. Although the classification scheme proposed is intended for the particular case of bio-based coatings we believe it can be easily extrapolated to other areas. "Bio-principles" refer here to two subclasses: (i) materials, derived or not from traditional sources, which are developed after a deep understanding of a biological model and aim at mimicking the main underlying natural principles to give new technological solutions [2] such as drug delivery [3], surface structuring [4] and structure integrity [5] (i.e. Bio-inspired); and (ii) materials designed and/or containing elements directly derived from renewable natural sources (i.e. Bio-based). Bio-based is then subdivided according to the treatment (chemical or mechanical) applied to extract the raw material from the biomass source as it happens in the case of specific bacteria, vegetable oil derivatives, algae, seed, exoskeletons and shells [6,7]. The review presented here primarily focuses on the effect of *organic* bio-mass derived raw materials on the modification of coating properties or implementation of new functions. Therefore, the use of minerals or derivatives thereof (e.g.: silica, montmorillonite, zeolites), often classified as green alternatives to achieve advanced properties in coatings, will not be part of the review.

Up to date several high-quality reviews have been published on bio-based materials. However, their focus is mainly on reporting the many different raw organic materials used such as vegetable oils derivatives [8,9], or a very specific application field such as packaging [10,11] or a

* Corresponding author.
E-mail address: v.montano@tudelft.nl (V. Montano).

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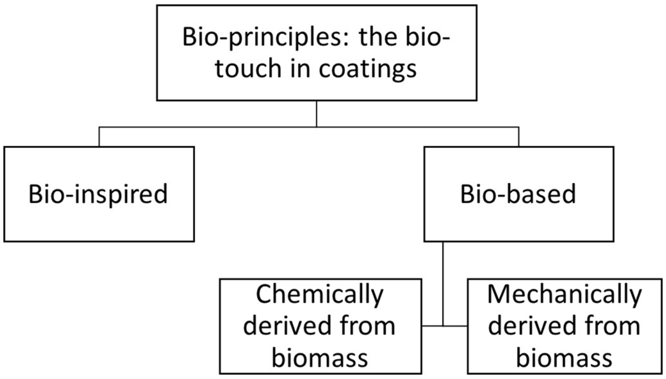

Fig. 1. Classification of the material principles in coatings: the bio-touch.

particular final product such as polyurethanes and vinyl polymers [12,13]. Although these works very well describe the properties of the natural building blocks and the possible synthesis and processing routes there is little to no focus on analysing the potential uniqueness of bio-based raw materials to create new or better functionalities. The current review is an attempt to offer an overview of the specific effect of bio-based raw materials on different coating properties; what we here call the *bio-touch*. The review strongly stresses the relation between the bio-based element and the foreseen property achieved, but also points out intrinsic weaknesses of the approaches used.

2. Driving forces for bio-based materials in coatings

Coatings can be defined as all kind of thin (organic) solid planar structures mechanically or chemically attached to a much ticker substrate in order to add a certain functionality such as protection against contaminants, wear resistance, electrical isolation and other properties not addressed by the substrate material itself. The major components of organic coatings are: (i) the polymeric binder that forms a continuous phase and gives the main characteristics to the coating; and (ii) the fillers, which are the discontinuous phase giving additional or improved properties or simply lower the material costs. In this paper we focus on bio-based organic coatings, in which one or both the components contain at least one compound chemically or mechanically derived from bio-mass.

The conversion from the current oil-based polymer industry to a bio-based industry and economy is a major challenge requiring joint efforts from industries, research centres, governments, consumers and users. Two main driving forces lead the conversion to green bio-based economy. First, the increasing demand of energy for transport and electricity and the correspondent reduction of fossil fuel feedstocks. Secondly, environmental concerns aiming to reduce the carbon footprint. For coatings, these traditional driving forces are not strong enough to attract major investments into the research of bio-based alternatives. On the contrary, it is the possibility to bestow new functionalities to coatings due to the unique behaviour of the bio-based components, which has drawn the attention of both companies and the scientific community. So, herein we propose the bio-touch as the main driving force for the conversion to bio-based coatings.

3. Coating functionalities using bio components: the bio-touch

Bio-based raw materials have demonstrated their potential to implement and improve several advanced properties in coatings, as schematized in Fig. 2 and summarized in Table 1. Unlike traditional reviews [9,14–17], Table 1 offers a different perspective focused on the property achieved thanks to the bio-touch. Considering the approach by which the bio-based concept is incorporated in the coating we propose an alternative classification as being used in the field of self-healing materials [18,19] where the approach is classified as 'extrinsic' or 'intrinsic'. 'Intrinsic' concepts are those where the bio-based component is an (inseparable) part of the (in)organic network forming the coating (i.e. the coating matrix or binder). In contrast 'extrinsic' concepts are those where the bio-based material is added as a discrete phase to the polymer binder. A particular coating functionality can be therefore implemented by either of the two approaches (extrinsic and intrinsic) but the guiding principles are rather different. In Table 1 we also include some key references to orient the reader on some basic literature to be followed in order to more deeply understand one or the other concept developed so far. In the remaining of the chapter we critically analyse if and to which degree the different targeted properties have benefitted from the use of a certain bio-based concept or material.

3.1. Barrier properties

Barrier related properties (oxygen permeation rate, water vapour transmission rate) are key properties for coating in applications such as food packaging, electronics, construction and heritage conservation.

In the food industry the problem is of high relevance: few days, or even few hours of food exposure to open environment can permanently compromise its quality, creating a health risk for the customers [34]. Water vapour and oxygen are the two main deteriorating permeants reported in food packaging applications. The intrinsic small volume allows them to easily permeate the plastic barrier and reduce the food shelf life [35]. Thereby to extend lifetime it is important to increase the barrier properties against these species. According to *Food Packaging Forum*, 37% of food packages are currently made out of plastics, mainly compounded commodities, such as PE, HDPE, PTFE, or PVC. Nowadays, there is a growing demand for bio-based plastics to fully or partially replace traditional plastics in packaging due to increasing environmental concerns related to the use of petroleum-based resources and waste disposal. Several bio-based strategies have been explored in an attempt to decrease oxygen and water diffusion through films and coatings [20–22], nicely demonstrating the added value of bio-based strategies and therefore the bio-touch. Relevance in packaging developments for coatings relies on the relative ease to extrapolate the concepts derived in films into coatings, thereby requiring special attention in this review despite not too many works have specifically focused on coatings.

3.1.1. Bio-based topcoat

Whey proteins, a by-product of the cheese industry consisting of a complex mixture of globular proteins, have attracted significant interest in recent years both as coating binder material and as additives of commodity plastics to reduce oxygen permeation rate (OPR) while keeping intact their aesthetical appearance [36–39]. The barrier property against oxygen is accounted by whey's tertiary structure schematized in Fig. 3. The long hydrophobic amino acid chains point towards the protein while the polar hydrophilic amino acids are bound outwards. The outermost layer may act as a very effective barrier against oxygen but the partial hydrophilic character of the molecule along with presence of polar groups and hydrogen binding capacity increases the sensitivity to environmental moisture, inducing unwanted plasticization and poor barrier property against water vapour. Hong et al. applied transparent whey protein coatings, plasticized with selected amounts of glycerol, on LDPE [37] and polypropylene [36] films verifying, for low and medium relative humidity (RH) conditions, an additional oxygen permeability rate (OPR) decrease of three and two orders of magnitude respectively. As previously reported by Rogers [40] for several polymers the OPR followed Arrhenius temperature dependence showing a strong reduction of OPR for whey coated polymers with respect uncoated systems at all service temperatures (from 15 to 50 °C). Due to the intrinsic partial hydrophilic character of whey proteins at mild and high RH, moisture has a plasticizing and/or swelling effect that may result in increased film permeability to gases and vapours (e.g. oxygen and