

Use of nanoparticle binders for paper coatings: A review

ABSTRACT

Starch is a biopolymer that is used as a co-binder alongside synthetic petroleum based latex binders for paper coating applications, though it causes production downtimes due to the problems during cooking process, such as gelling; lack of full expansion of starch granules; increase in viscosity during cooling; bacteria growth in cooked starch and difficulties in viscosity control during storage. On the other hand, synthetic binders negatively affect paper recyclability and biodegradability. To overcome these problems, a new biopolymer binder has been introduced to the paper manufacturing, being used initially as a partial replacement for petroleum based synthetic latex polymers. This study reviews the recent developments of nanoparticle biopolymer binders, referred to as biolatex binders. These binders are shipped dry and can be dispersed in water without cooking requirement while improving paper quality and reducing costs of paper manufacturing. They also provide quality benefits, coater runnability improvements and new higher solids coating formulations for future product advancements.

KEY WORDS

Binder, paper coating, biopolymer, starch, nanoparticle

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First received: 10.03.2017.

Accepted: 11.05.2017.

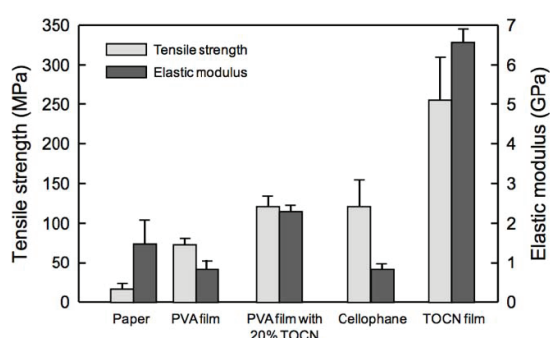
Introduction

The growing interest by many industrial segments to use sustainable materials has stimulated the development of new biopolymer materials. Some of the biomaterials that have a use in papermaking and coating industry are cellulose, coating starches (modified low molecular weight grades of the native material), chitosan, soy protein, alginate, casein, zein, lecithin and cellulose derivatives such as methyl cellulose and carboxymethyl cellulose (CMC), among others (Klass, 2011). Paper grades sometimes need to be coated with these materials to improve paper printability, surface characteristics or to add extra functional properties.

Printability is the main quality for high quality colour reproduction, increased ink gloss, uniform appearance or preventing print defects. It is greatly affected by paper porosity since the rate and depth of ink receptivity depends on it. Porosity is measured by the number and size of the voids within the coating layer. The voids can be controlled with different pigments, binder types, dispersing agents and additives in the coating layer.

Nanoparticles (within the range of 1 and 100 nm) show different properties compared to their bulk materials. Some of the recent nanomaterials in the papermaking and coating industry include nano crystalline cellulose (NCC) (Klass, 2007; Zaman et al., 2012; Cha et al., 2014),

nano fibrillated cellulose (NFC) (Martins et al., 2013; Missoum et al., 2013; Liu et al., 2015), TEMPO-oxidized cellulose nano fibrils (TONC) (Fujisawa et al., 2011; Fukuzumi, 2011; Okita et al., 2011; Fukuzumi, Saito & Isogai, 2013;) and nanoparticle biopolymer binders (Giezen et al., 2004; Helbling et al., 2004; Van Soest et al., 2004; Bloembergen, Kappen & Beelen, 2005; Helbling et al., 2007a; Helbling et al., 2007b; Figliolino & Rosso, 2009; Lee, Bloembergen & Van Leeuwen, 2010; Oberndorfer, Greenall & Bloembergen, 2011; Houze & Pajari, 2012; Shin et al., 2012; Shin et al., 2013). The studies have demonstrated that these nano materials improve various important properties of coated paper. Figure 1 represents an example for the tensile strength and elastic modulus differences between the paper, polyvinyl alcohol (PVA) film, cellophane and TOCN film.



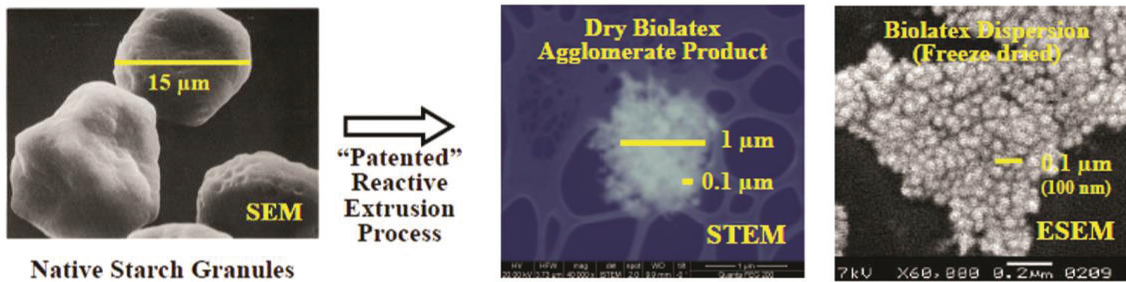
» **Figure 1:** Mechanical properties of TOCN films (Fukuzumi, 2011)

Synthetic polymers, such as styrene butadiene (SB), polyvinyl acetate and styrene acrylics, are petroleum based latex binders, therefore they are not environmentally benign and suffer from price instability with major up and down swings linked to oil prices. They have been used in paper coating applications due to their ability of increasing paper properties and mechanical strength though they reduce recyclability and can cause “white pitch” issues with deposits on calender rolls, etc. Biopolymers have an advantage of being sustainable, renewable and biodegradable, therefore they also reduce the carbon footprint. Biopolymer materials have relatively stable pricing and these advantages are driving adoption of these natural products.

When cooked, starch is a mostly soluble biopolymer produced from plant sources such as corn (maize), potato, wheat, tapioca (cassava), pea, rice. It has been used in paper coating applications as a co-binder (Klass, 2011). Conventionally, starch is purchased in dry granular powder form, either in modified (acid thinned, thermally modified, thinned/hydroxyethylated, etc.) or in its unmodified (native) form, and then cooked or chemically/enzymatically modified on site at the mill before it is used in the paper coating (Klass, 2007). Natural (unmodified, pearl, native) starch is attractive

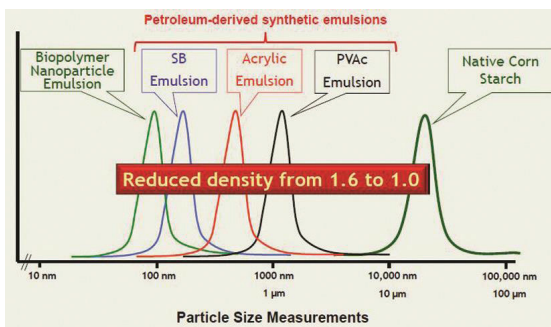
due to its low price, but poor process control frequently reduces productivity and paper quality (Mishra, 2005). Starch in its native form is an ultra-high molecular weight (MW) polymer (>300 million g/mole or Daltons) and that becomes a challenge during cooking production. When starch is cooked in solutions (to allow it to act as a binder) MW must be sharply reduced, to yield cooked solutions with sufficient substance (i.e. % solids). Modified starch usage is more common than natural starch due to added functionalities in paper industry. The typical cooking procedure is that starch must be well agitated at room temperature, then heated up to 90-95°C and held at that temperature for 20-30 minutes while maintaining good agitation for complete cook-out of the starch. Improper cooking for paper coating may cause gelling (lack of full expansion of starch granules); increase in viscosity during cooling; bacterial growth in cooked starch or difficulties in viscosity control during storage, all of which can cause quality issues and production downtimes. For papermaking, if starch granules are not ruptured completely, the size press nip will likely reject it, and later may cause viscosity changes, drying and scale problems on the paper machine.

The first starch nanoparticle biopolymer binder in the paper industry were developed, produced and commercialized by EcoSynthetix Corporation as EcoSphere™ biolatex™ binders with the intention of replacing petroleum-based synthetic latex (Bloembergen et al., 2011). EcoSynthetix has >100,000 ton/annum capacity at its manufacturing facilities in North America and Europe (Van Ballegoie et al., 2012; Van Ballegoie et al., 2013) and the biolatex has 99% bio based agricultural feedstock that makes it sustainable, renewable and biodegradable. These advantages also help companies reduce their carbon footprint. EcoSynthetix has patented the process of using a twin-screw extruder with different shear forces, upstream pressure and a crosslinking agent to generate starch nanoparticles around 100 nm (dominant size range is 20-150 nm, ideal for low viscosity biolatex dispersions). Figure 2 represent the conversion of native starch to the biolatex emulsion polymer along with TEM, STEM and SEM images of the native starch granules and biolatex particles. Unlike natural (native) and modified starch, these nanoparticles do not require cooking, and can be readily dispersed in water due to their internally crosslinked, water-swollen and deformable colloid particle nature (Bloembergen et al., 2010; Wildi, Van Egdom & Bloembergen, 2015). It is reported that starch is known as a stiff and brittle polymer while the nanoparticle biopolymer is more flexible and helps to reduce folding and scoring cracks (Klass, 2007). The extrusion process is used to bring down the starch granule diameters from micron to nano range. In Figure 3, the comparison of particle sizes between the biopolymer nanoparticles binders and synthetic/natural binders are represented. Over the past two decades, SB latex has become the dominant paper coating binder system in the industry. Its particle size has



» **Figure 2:** Native starch conversion to biolatex (Klass, 2011)

been pushed to smaller particle sizes towards an aggressive 100-120 nm target, given that smaller latex particle sizes have higher surface area, beneficial for binding performance. Biolatex emulsions do not require surfactants nor other repulsion mechanisms that help keep synthetic latex particles in stable suspensions (which inadvertently adds cost and reduces other performance requirements). The biolatex binders, on the other hand, are smaller in size, which is beneficial to binding power, and they do not contain added surfactants but produce naturally highly stable dispersions with long shelf lives.



» **Figure 3:** Particle size comparison of binders (Bloembergen, 2009)

Materials and Methods

Assessment method for this study was a literature review. Existing knowledge gathered based on the data from patents, journals, conference papers, industry magazines and pilot testing. In pilot test experiments, the coating formulation ingredients were clay, ground calcium carbonate (GCC), titanium dioxide (TiO₂), carboxymethyl cellulose (CMC), lubricant, rheology modifier and optical brightening agent (OBA). Synthetic latexes in coating formulations were replaced on a 1:1 basis with the EcoSphere bio based nanoparticle latex.

Results and Discussions

According to ASTM D6866 bio based content testing, the biolatex binder has 99+% bio based agricultural feed-stock, while synthetic latex is based on 99+% fossil. The

test indicated that the biolatex binder is a sustainable, recyclable and biodegradable binder (Figliolino & Rosso, 2009; Lee, Bloembergen & Van Leeuwen, 2010; Oberndorfer, Greenall & Bloembergen, 2011; Houze & Pajari, 2012; Shin et al., 2012; Shin et al., 2013). The research showed that 73% carbon footprint reduction is possible with biolatex binder (Lee, Bloembergen & Van Leeuwen, 2010). Overall results conducted by the researchers showed that 30 to 50% of synthetic latex replacement with biolatex binder is immediately possible in coating formulation. Further optimization can help attain higher substitution levels, coating structure, strength and optical properties were improved. The biolatex binder showed increase in brightness; equal or higher gloss and better opacity values. Brightness value would be increased further when the TiO₂ pigment co-extruded with the binder (Lee, Bloembergen & Van Leeuwen, 2010). The biolatex binder could increase solid content 1 to 3% that enables saving in dryer energy due to having less water content in the coating structure (Figliolino & Rosso, 2009; Oberndorfer, Greenall & Bloembergen, 2011; Houze & Pajari, 2012; Shin et al., 2012; Shin et al., 2013). The amount of some coating components such as CMC, polyvinyl alcohol and rheology modifier were eliminated or decreased with the biolatex binder addition (Figliolino & Rosso, 2009; Oberndorfer, Greenall & Bloembergen, 2011; Shin et al., 2013;). Runnability of the coating in the coater was increased due to better coating uniformity, better rheology and superior water retention that has been achieved by using biolatex (Oberndorfer, Greenall & Bloembergen, 2011; Shin et al., 2013). Better paper stiffness value was also reported (Oberndorfer, Greenall & Bloembergen, 2011). The experiment showed no significant effect on wet pick performance of the coating with biolatex binder, yet the IGT dry pick performance improved 7 to 31%. Lower binder migration was observed when 20% of synthetic binder replaced with biolatex binder (Figliolino & Rosso, 2009).

Conclusion

Bio based nanoparticle latex binders are successfully replacing petroleum based synthetic binders while improving paper quality. The crosslinked, water-swollen and deformable colloid particles are represented that

they can enable further cost savings for manufacturers since the biolatex binder does not require the typical starch cooking procedure and can be readily dispersed directly in water. Biolatex binder has 99+% bio based agricultural feedstock. It is sustainable, renewable and biodegradable and helps paper manufacturers to reduce their carbon footprint. Future studies need to investigate optical, mechanical and printability properties of different papers coated with bio based nanoparticle binder.

Acknowledgements

This study was supported in part by the Scientific and Technological Research Council of Turkey (TUBITAK) under the 2214-A program.

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