

Nanoparticles Based Biolatex: Application In Coating

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ABSTRACT

Biobased emulsion polymers were first adopted in 2008. These new binders are made up of deformable water swollen cross linked biopolymer nanoparticles and tend to shrink less upon coating consolidation during drying. In addition to that self lubricating effect for better blade run ability, higher effective solids for improved coating hold out and higher gloss are other advantages.

With new high brightness grade developed by co-extruding TiO₂ particles better brightness and opacity can be achieved compare to SBR latex.

Lab evaluation results confirmed that 27 % synthetic binder can be replaced with better properties i.e. Gloss & PPS

Since the biobased latexes are made from renewable raw materials the carbon footprint is significantly less than common synthetic binders.

INTRODUCTION

Nano technology and its uses in the industry is still in early stages with significant areas open for research and applications development. It might be possible through the use of nanotechnology to eventually produce paper without any pollution and less cost. Natural starch consists of microscopic granules and starch solutions have high viscosity at low solids which limits their use in industrial applications. New nano particles are developed by reducing the granular structure of 30 micron to 0.1 microns. The process converts starch into an agglomerate of dry cross linked biopolymer nanoparticle. This dry product can be shipped directly to customer and eliminates cost of shipping water as in the case of synthetic latexes. (Fig.1)

Bio based latex and bio polymer based micro gels can be broadly defined as a special class of latexes whose particle

are made up of water swollen cross linked hydrophilic polymers. Biobased latex binders currently used in paper Industry are water swollen cross linked starch nano particles, their wet and dry properties mainly depend on their particle size and cross link density. Cross link density is especially important because it controls the extent of water swelling. Varying swell ratios of water swollen starch nano particles differentiate them from conventional starches and Latexes with respect to rheological behavior and coating performance. The unique properties of nano particle based biopolymer which are of importance for paper making perspective are discussed in this paper.

De swelling as a function of Concentration.

Cross linked bio polymer nanoparticles have very unique wet properties. First their swelling under conditions of extreme dilution with water achieves maximum swelling values that is balanced between their elastic constraint due to their cross linked net work and osmotic pressure.

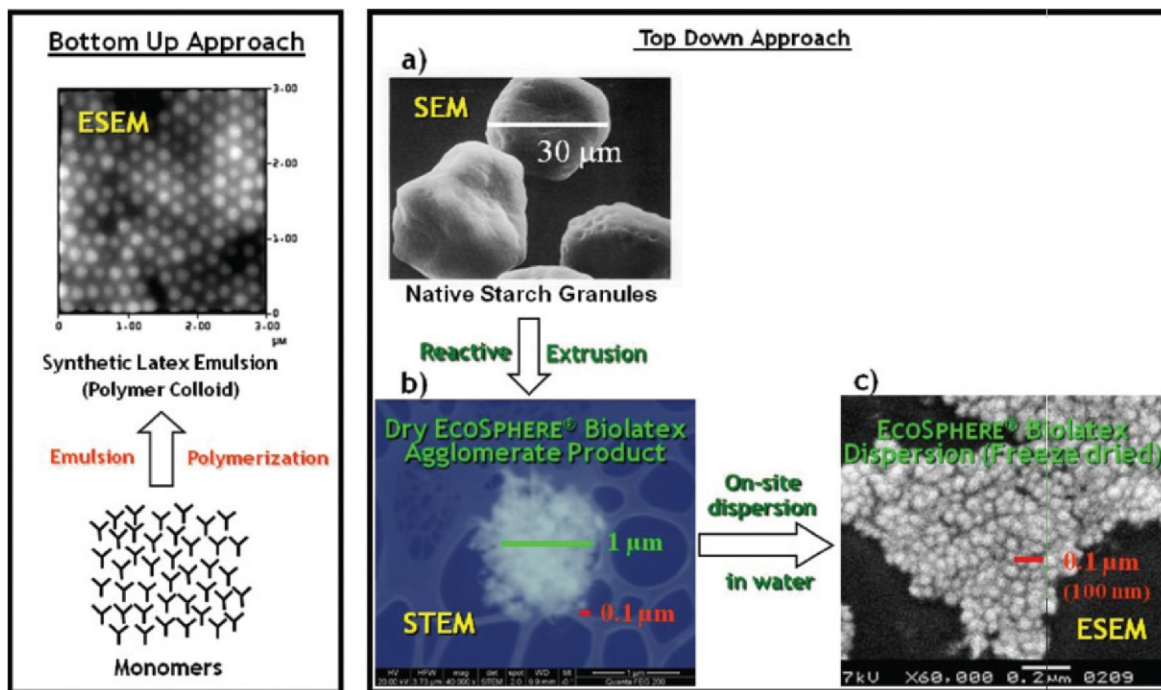


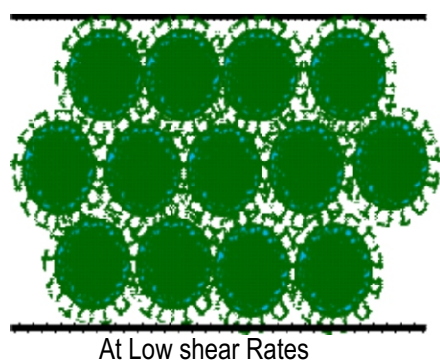
Fig. 1 Manufacturing process of Biolatex

Secondly they de-swell by addition of water miscible solvents such as alcohols and many other water soluble species such as electrolytes. Lastly they also Deswell with increasing solids so that their dispersion can be made at higher solids. Therefore de-swelling will take place when the concentration of dispersion exceeds that of starch concentration of the dispersion exceeds that of starch network in nanoparticles, which is equal to reciprocal $1/SR(W)$ of the weight swell ratio, $SR(W)$.

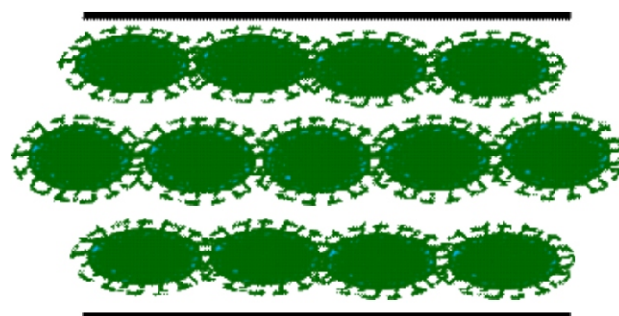
The deformation of Water swollen Cross linked Biopolymer Nano particles under shear and pressure.

Water swollen nano particles would deform and Deswell under shear and pressure

This behavior is quite unique because the water swollen nanoparticles are not only deformable under high shear and pressure, but also Deswell and release water and then may be able to lubricate jammed solid particles i.e self



At Low shear Rates



At High Shear Rates

Fig. 2A. Deformation of water swollen cross linked bio polymer under high shear rates.

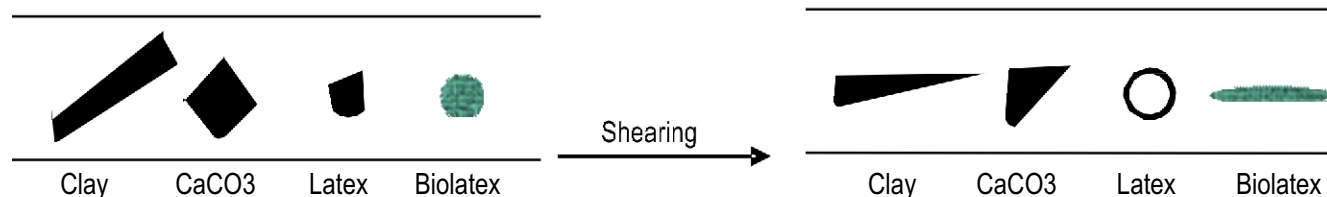


Fig. 2A. Deformation under high shear rates of biolatex in presence of pigment and latex particles.

lubricating. Biolatex exhibit high shear rheology and less dilatancy.(Fig 2.) While synthetic latex tend to be non deformable and dilatant under high shear high solids conditions (Under the blade they dewater quickly and cause blade instability.

Influence of Higher % effective solids and Volume voids of water swollen Biobased Nanoparticles on Coating immobilization and coating hold out

Cross linked hydrophilic nanoparticles in dispersion exist in form of water swollen nano particles their effective solids and volume solids will be higher than their actual solids and volume solids as compared to typical cooked starch and synthetic latex. The increase in effective coating solids enables paper coating colors containing bio based latex binders to get close to their immobilization solids so that they exhibit excellent coating hold out resulting in excellent fibre coverage and coating smoothness.

The influence of of less shrinkage of Biobased latex binder on coating gloss, porosity and opacity.

One of the most important characteristics of bio latex binders is that they shrink less than conventional starches upon coating consolidation during drying. This is because the cross linked starch nano particles maintain their swollen structure during drying. While conventional starch normally has the density of about 1.6 gm/cc it has postulated the virtual density of biobased binder within the dried paper approaches to 1.0 gm/cc similar to SB latex.

The low degree of coating shrinkage and the nano cellular void like structure of biobased latex binder containing paper coating are responsible for more open structure and better opacity.(Fig.3)

New TiO₂ extruded Biobased latex for Improvement in brightness.

It is observed that efficiency of TiO₂ can be increased significantly with very less amount of TiO₂ co-extruded with biolatex Latex binder in comparison to post addition of TiO₂. There is no improvement in brightness with post added TiO₂ while with same amount of TiO₂ used co-extruded with biolatex brightness' gain observed. This is due to uniform distribution of TiO₂ in dry coatings (Fig 4).However increasing TiO₂ to 3.2 PPH resulted in drop in Brightness with UV due to QBA Quenching effect.

Experimental

A lab study was conducted by replacing the existing synthetic Latex 18 27 % in Pre-coat and 12 20 % in top coat. Processing conditions Table .1 & Test results Table 2 are given above ;

Discussions

- By using the Bio Based latex the gloss is improved in the final product.
- The Surface roughness will be reduced after usage of Biobased latex due to particle size is less.
- The Bio based latex will improve the Print gloss and linting due to inbuilt cross linking nature along with pigment and binder.

Environmental Impact - Carbon Neutrality

Plant and animal hydrocarbons in the biosphere are transformed to atmospheric carbon dioxide. and then fixed by storage during plant growth over a 1-100(10²) year cycle.

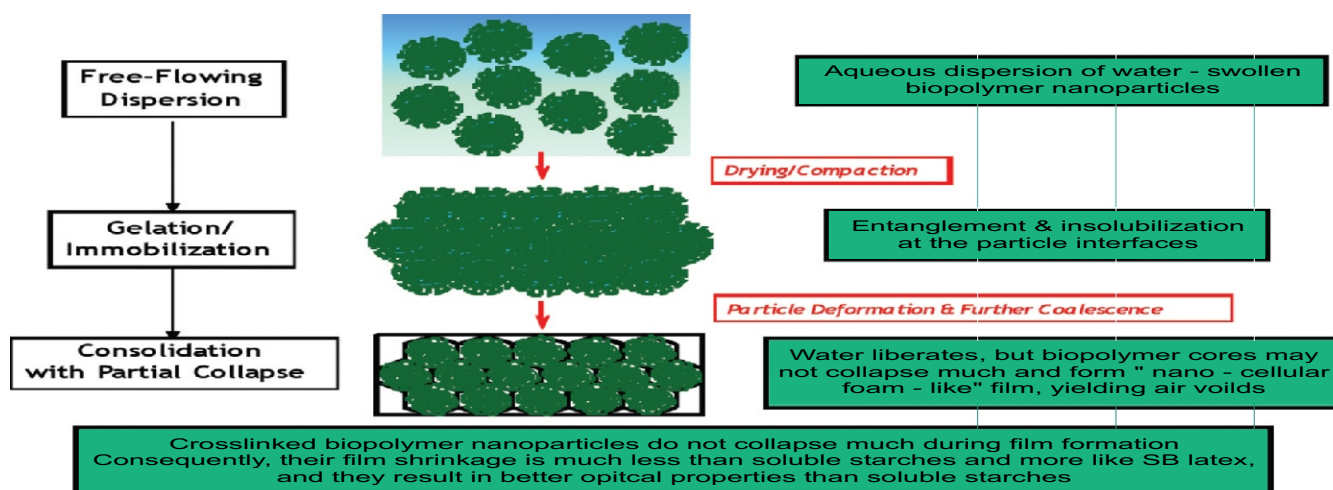


Fig 3 . Drying process of biolatex particles.

Table 1

Lab study with Ecobinder								
S.NO.	Parameters	Units	Chemical Test Results					
	Chemical Name		Bio Based Binder		Bio Based Binder		Existing Binder	
			Specs	Results	Specs	Results	Specs	Results
1	Solid	%	90	90	90	90	-	50.0
2	p H		5.6	5.5	7.3	6.8	-	6.7
3	Viscosity #2@100 rpm at 30°C	cps	-	80	-	60	-	145.0
Properties of Pre Coat Coating Solution Prepared with mentioned part of Chemical								
			Bio Based Binder Set I		Bio Based Binder Set II		Existing Binder	
Coating Chemical quantity	Bio Based Binder	%	2.0		3.0		0.0	
	Existing Binder	%	9.0		8.0		11.0	
	Fixlink		0.370		0.370		0.370	
	Caustic Flakes		0.225		0.225		0.225	
	Part of Sterocoll on Pigment		0.150		0.150		0.150	
4	Solid	%	63.000		63.500		62.000	
5	p H		9.300		9.500		9.400	
6	Viscosity #3@100 rpm at 30°C	cps	890.000		910.000		860.000	
Properties of Top Coat Coating Solution Prepared with mentioned part of Chemical								
			Bio Based Binder Set I		Bio Based Binder Set II		Existing Binder	
Coating Chemical quantity	Bio Based Binder	%	1.500		2.000		0.000	
	Existing Binder	%	11.000		10.000		12.500	
	Part of LB 50 on Pigment		1.250		1.250		1.250	
	Caustic Flakes		0.200		0.200		0.200	
	Part of Sterocoll on Pigment		0.225		0.225		0.225	
	Part of Cartabond HRZ on Pigment(As such)		0.600		0.600		0.600	
7	Solid	%	62.5		63		62	
8	p H		9.4		9.6		9.5	
9	Viscosity #3@100 rpm at 30°C	cps	1060		1100		1046	

Table 2

Properties of Board after coated with this Prepared coating Solution					
			Bio Based Binder Set I	Bio Based Binder Set II	Existing Binder
10	Gloss	%	34	35	33
11	PPS	micron	3.1	3.18	3.36
12	Dry Pick	m/s	2.10	2.10	2.00
13	Print Gloss	%	80	80	78
14	Linting	-	OK	OK	OK

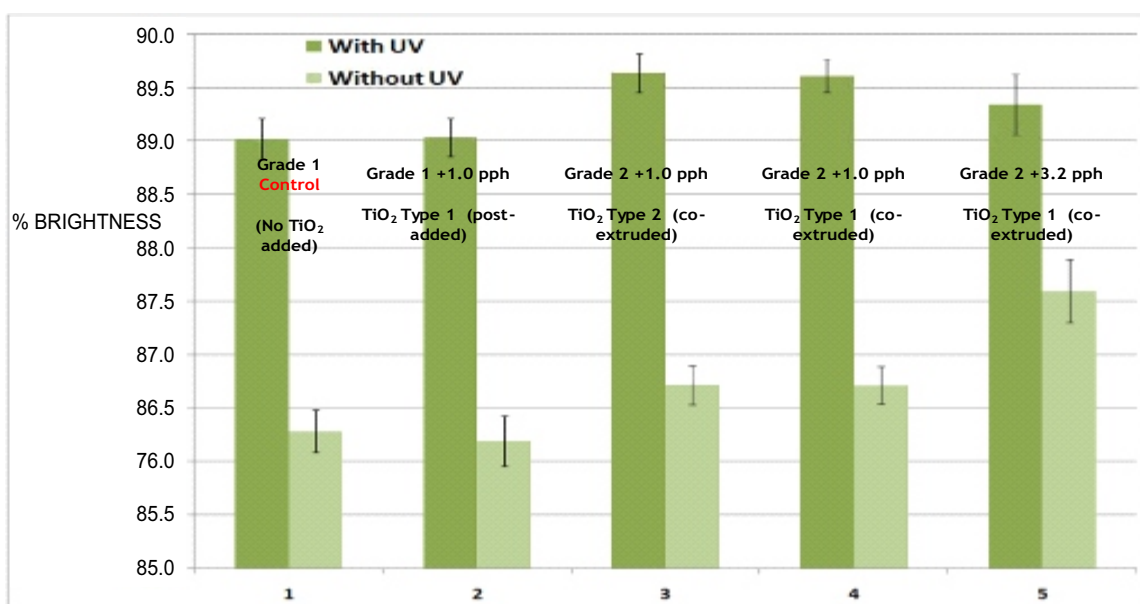


Fig. 4. % Brightness of paper coatings containing a series of biobased latex binders co-extruded with 1 part TiO₂ each of two types (Type 1: Hydrophilic and Type 2: Hydrophobic) and 3 parts TiO₂ of Type 1 plus two biobased latex binder controls

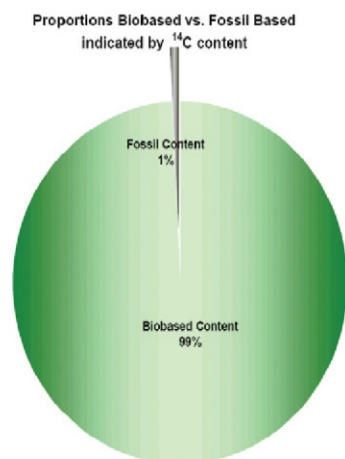
Conversion of plant animal and hydrocarbons into fossil fuel however involves a cycle of more than (10⁶) years .Therefore natural cycle is disrupted by petrochemical products and atmospheric storage becomes carbon positive, because a disproportionately long time is required to establish equilibrium.

The type of carbon used in paper coating binders can be determined an established methodology using ASTM D-6866 .This test measures the amount of radiometric carbon therefore the amount of fossil based carons versus biogenic (crop based **carbon**).**This test** has shown that synthetic binders such as SB latex contains 99 % fossil carbon since

they are produced from monomers that are derived from fossil based resources such as oil and gas.By comparison biolatex shown 1 % fossil carbon.(Fig 5)

At the end of its useful life cycle coated paper will be burned ,land filled, composted or recycled. During recycling the coated paper will be separated during various paper recycling, screening and floatation steps into reusable fibre and ink, pigment and synthetic binder residues are disposed off. Eventually this disposed residue will decompose and release CO₂ in the environment. Synthetic binders therefore have a positive carbon foot print which in case of

Mean Biobased Result: 99% *



Mean Biobased Result: 1% *

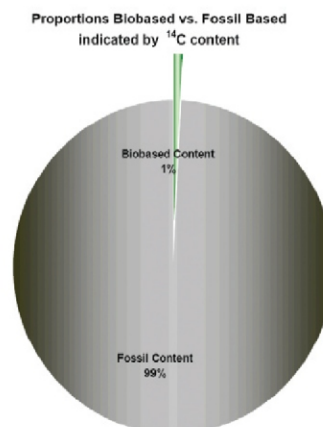


Fig. 5. Analysis of Bio based Carbon

SB latex is equivalent to 7.4 kg CO_2 per Kg of latex binder. The biobased latex are therefore have significantly lower carbon foot print 2.0 kg CO_2 per kg of bio latex.

Summary

The advantages and similarities of Biolatex vis-a vis Latex can be summarized as below.

1. Biopolymer nanoparticles form colloidal latex dispersions (as synthetic latex).
2. Using the Einstein equation, the swelling characteristics of typical SB Latex and biolatex colloids were compared. While petroleum-based synthetic SBLatex binders typically consist of colloids with a non-swollen core with an anionic repulsion layer, biolatex binders consist of cross linked water-swollen nano particles that are stearily stabilized.
3. Synthetic latex and pigment particles end to be non-deformable and dilatant under high shear-high solids conditions (under the blade they dewater quickly and can cause blade instability). Biolatex colloids are "shear deformable" (self-lubricating) and exhibit unique high shear rheology and less dilatancy.
4. The biolatex exhibits less binder migration, quicker immobilization, more open coating structure, and smoother coating surfaces.
5. The biolatex appears to resist shrinkage upon drying resulting better gloss and other paper and print properties.
7. Other direct benefits may include freight saving (dry form instead of 50 % solid emulsion) and energy saving (higher solids coating formulations)
8. Finally the use of bio based latex binders has the ability to reduce carbon dioxide emission significantly as compared to the use of petroleum based latex

9. Lab scale study results are encouraging.

Acknowledgments

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