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Discrete Element Method to Predict the Mechanical Properties of Pigmented Coatings

Dan Varney[1,3], Martti Toivakka[2], and Doug Bousfield[3]

1) OMYA Inc. Inc., Proctor, VT 05765 USA
2) Laboratory of Paper Coating and Converting, Åbo Akademi University, Turku, Finland
3) Paper Surface Science Program, Dept. of Chemical and Biomedical Engineering University of Maine, Orono, ME 04469 USA (bousfld@maine.edu)

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Abstract

The mechanical properties of pigmented coating layers are important in a variety of applications. However, the large number of parameters that influence these properties as well as the numerous type of deformations challenges the prediction of the performance of these systems. A discrete element method (DEM) is proposed to predict the mechanical properties of paper coating layers that have a range of starch and latex content. The model is developed in both 2D and 3D and is adapted to tensile and flexural deformations. The model predictions are compared to experimental results in the literature. The predictions are generally good for the moduli and the strain to failure of the systems, but under predict the maximum stress. This result may be caused by the complex particle size distribution of the experimental systems or by the impact of the brittleness of the starch when making the free standing films.

Introduction

The mechanical properties of coatings are important in a number of applications. In paint applications, scuff or rub resistance is important (Kirsch *et al.* 2001). In the production of lithium ion batteries, the coating layers must resist deformation without cracking (Su *et al.* 2014, Hu *et al*. 2010). For coated papers, the resistance to "picking" during the printing operation is critical as well as the ability for the sample to be converted or folded without cracking of the coating layer (Sim *et al.* 2012, Barbier *et al.* 2012). The influence of binder content, binder type, and particle shape on paper coating cracking during the fold has been studied by a number of groups for example (Oh *et al.* 2016, Rättö and Hornatowska, 2010, Rättö *et al.* 2011).

If the coating layer is a homogenous material, such as a specific polymer, the mechanical properties of that layer can be estimated from the bulk properties of that material. However, when the coating layer is a composite of pigments and binder, the mechanical properties are difficult to predict. Finite element methods can be used to predict the deformation of coated paper by treating the coating layer as a continuum (Barbier *et al.* 2005, Alam *et al.* 2009). The compressive and tensile stresses during bending can be predicted. However, the elastic modulus and the Poisson ratio are inputs of the model; these would need to be measured for each coating formulation because they would depend on the latex type, starch loading, and the paper fiber properties. In addition, the basic mechanisms of crack formation and failure are not well understood if the coating layer is considered a uniform material.

Some continuum type models have been explored by modeling groups of particles connected by polymeric bridges (Rättö, 2004). When the number of particles increase and the distance between particles is small, numerical analysis of this nature are costly. While some insight into mechanical properties of porous composites has been obtained with a mesh-free continuum mechanics simulation (Toivakka *et al.* 2015), an understanding of micromechanical behavior pigment coating layers in various industrially relevant situations is lacking.

Discrete element methods (DEM) are models that are based on the particle length scale and have been used to describe granular flows, concretes, and geological materials (Donzé *et al.* 2009, Ketterhagen *et al.* 2009, and Vu-Quoc *et al.* 2000). These methods have potential to reveal particle level mechanisms in the study of coating layers that are a combination of a polymer and a pigment such as paper coatings. Toivakka and Bousfield (2001) proposed a simple DEM model to predict the dynamic mechanical properties of a pigmented coating layer in tension and compared the simulation results to experimental data. DEM has been used to study the compression of paper coatings during the calendaring event (Azadi *et al.* 2008). Tensile results and predictions have also been reported previously by Varney and Bousfield (2018) for 2D systems. These models have been applied to simple compression and tensile modes of deformation, but not complex behavior like picking during printing and bending during a folding event. Also, most of these models are two dimensional in nature except Azadi *et al.* (2008); a good comparison between 2D and 3D models has not been reported.

Here, we propose to use a particle level model to understand the tensile and bending behavior of coating layers that contain pigments, latex and starch. The results are compared with experimental data of Zhu *et al.* (2014) and Najafi *et al.* (2018). Latex and starch mixtures were used as a binder between ground calcium carbonate pigments in these systems and the mechanical properties of these starch-latex mixtures are inputs into the model. The predictions of two and three dimensional forms of the model are compared along with the experimental values.

Model Description

When two pigments move relative to each other as in Figure 1, a restoring force is calculated to pull them together based on the local strain of the polymer between them. The force equation used here takes on the non-linear form

$$F = A(1-e^{-B\varepsilon})\pi R_b^2 \tag{1}$$

where F is the tensile force between particles, A and B are parameters that depend on the pure binder properties, ε is the local strain between particles, and R_b is the radius of the binder bridge between particles. The bridge radius and the spacing of the particle depends on the pigment volume fraction (PVC) that is defined as the ratio of total volume of pigments to the volume of pigments plus the volume of binder. When the local strain between particles is larger than the strain-to-failure of the binder, the binder is assumed to fail cohesively and the force is set to zero. This non-linear form is selected because it resembles the behavior of the tensile tests of the binder films, but a linear form based in Hooke's law would give similar results.

The mechanical properties of the binder films are possible to measure from tensile tests. Zhu *et al*. (2014), Chen *et al.* (2014), Najafi *et al.* (2018) and Najafi (2019) report the mechanical properties of mixtures of starch and latex and are given in Table 1; the complete set of data for the pure binder film is in Najafi's thesis. The maximum stress at failure is the parameter A in Eq. (1). The elastic modulus divided by A is the parameter B in Eq. (1) because the initial slope of Eq. (1) is the product of A and B. As is well known, as starch is added to these systems, the elastic modulus of the binder increases but the strain at failure decreases.

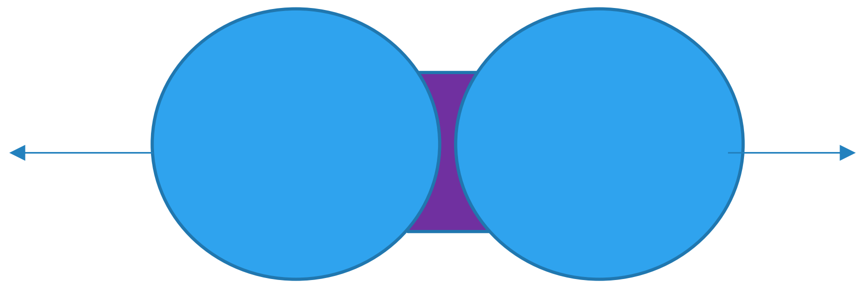

Figure 1. Idealized system of two spherical pigments connected together by a polymer binder bridge. The binders of interest here are mixtures of starch and latex.

Table 1. Mechanical properties of particle free films composed of mixtures of starch and latex.

	Weight fraction Latex	A (MPa)	B	E (MPa)	STF (%)
Najafi *et al.*	100	1.5	2	3	200
Najafi *et al.*	80	4.9	15	73.5	80
Najafi *et al.*	60	4.8	35	168	22
Najafi *et al.*	40	11	60	660	5
Zhu et al.	100	3.75	3.2	12	355
Zhu et al.	77	9.4	24	221	200
Zhu et al.	58	15.5	29	448	41
Zhu et al.	38	32	36	1156	13

If particles move closer to each other compared to the initial gap, a repulsive force is applied to keep the particles from overlapping. This repulsive force is assumed to be linear and depends on the compressive strain as $F = C\varepsilon$, where C is some constant. The value of C is found to not influence the results as long as it is large enough to prevent particles from overlapping. The model in the current form neglects the viscous effects and shear effects, but these can be incorporated in a straight forward way if needed.

One parameter in the model is the distance between two particles to consider them neighbors and have a connection. At the Critical Pigment Volume Concentration (CPVC), every particle should be close to several others. However, it is not clear at what distance particles should be considered connected by a binder bridge. In Figure 2, if the gap between the particle of interest and the other particles, is less than one radius, the particles will be considered neighbors and be connected. If they are too far away, then no connection is assumed. For all of the results here, the value of R_n=1.0 is used.

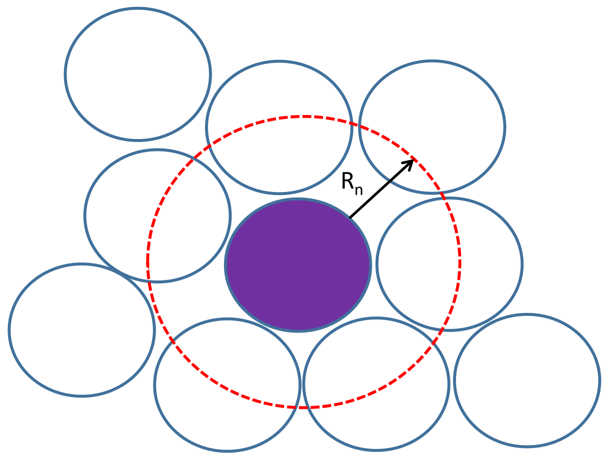

Figure 2. Near neighbor criteria with R_n=1.0. Particles closer than the criteria are assumed to be connected. As R_n increases, more particles are connected together.

For the 2D model, spheres are assumed to be confined to a monolayer, as depicted in Figure 3. Spheres are "pressed" into the region during the initial packing, keeping the minimum separation of spheres to be around 0.5% of the radius. In the 3D case, depicted in Figure 4, spheres are packed into the structure using a Brownian motion type simulation, where particle motion is accepted for minimizing the gap between particles; this packing scheme is described by Alam *et al.* 2009, Vidal *et al.* 2009 and Byholm *et al.* 2009. In either case, the particles are packed into a structure that would represent the coatings at low binder content, where most particles will have a number of near neighbors. For low pigment volume concentrations, the initial packing should result where particles are well separated from others. These cases can be calculated by using the same packing, but assuming that the particles have a radius less than what is used to pack the structures near CPVC.

To simulate a tensile event, particles in the grip region on the right of the figure are set to a velocity of one dimensionless unit value to the right. Particles in the left grip region are assigned to no velocity. This causes the particles on the right to pull on other particles in the middle of the structure and transmit forces throughout the structure. The up zone is not used in tension. The results presented here are for slow motions relative to the inertia of the particles. Therefore, the forces are near equilibrium during the deformation event and the rate of deformation is not important.

To simulate bending tests, particles in the "pull-up" zone are assigned an upward velocity. For the results here, the up zone has a width of 20 units which is smaller than depicted in the figure. Similar conditions are imposed for the 3D case. The sizes of the holding zone and pull up zone have minimal influence on the results as long as the distance between the zones is large compared to the zones themselves. Similar conditions are set for the 3D model: the bending of a 3D case is shown in Figure 4. Spheres on the two sides, called the grip zones, are not allowed to move in the vertical direction, but they are allowed to slide in the horizontal direction or deflect downward.

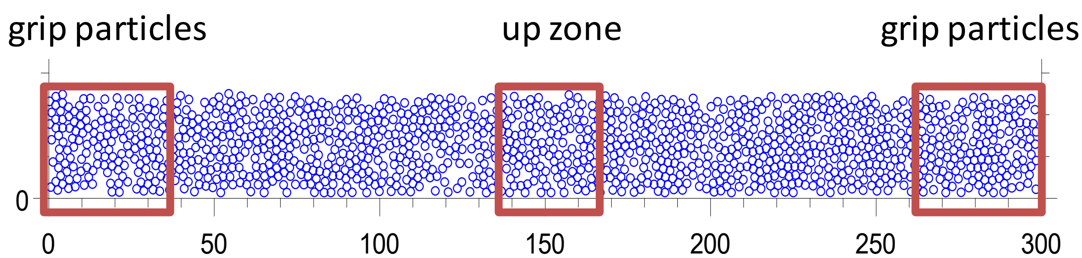

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Figure 3. Simulation set up for the 2D model for the three point bending case for 30x300 case.

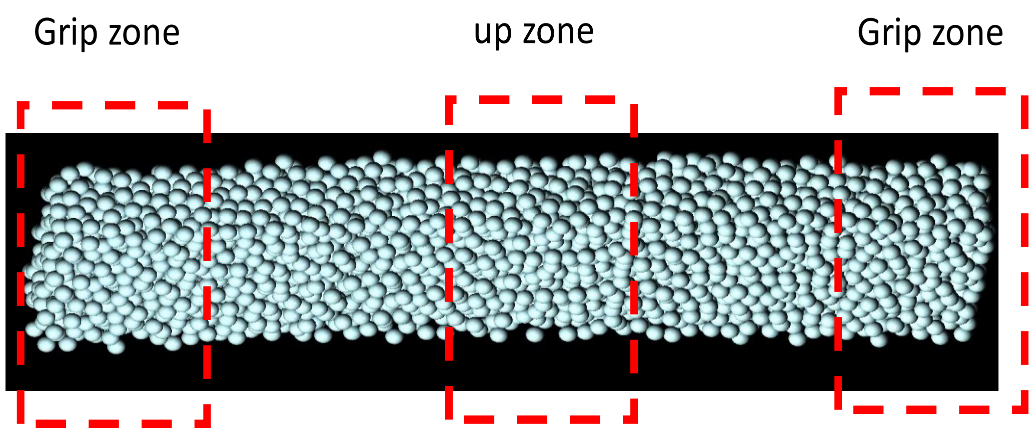

Figure 4. Three dimensional situation for uniform spheres packed in a 10x10x100 cell. Particles here have undergone some upward deflection. Particles are packed to a PVC of 64%.

In both cases, as some particles are forced to move from their equilibrium position, a force is calculated from Eq. (1), in vector form, on neighboring particles. The net force on every particle is calculated based on its position and the position of all of the neighbors. This net force is used to update particle velocities and positions with a numerical integration using a predictor-corrector method. In the results presented here, the motion is slow and the inertia terms are small; time or rates do not influence the results, but these effects are straight forward to include. The sum of forces on the particles that move related to the force a mechanical tester would record; these forces balance the sum of the forces on the particles that are not allowed to move. In tension, the stress is the sum of the forces on the grip particles divided by the cross sectional area. In 2D, the distance into the paper is assumed to be one particle diameter. The flexural stress and strain can be calculated as

$$\sigma_f = \frac{3PL}{2bd^2} \tag{2}$$

$$\varepsilon_f = \frac{6Dd}{L^2} \qquad (3)$$

where P is the sum of the forces on the grip particles (or the load force), L is the distance between grips, D is the displacement of the upward moving particles at the center of the sample, b is the width of the sample and d is the thickness of the sample. The goal is to predict the bending behavior and the crack propagation of these systems.

In the experiments, samples that are tested are often in the dimensions of millimeters. Therefore, the experimental samples have well over a million particles if the particles are pigments with a scale of micrometers. In the model, a much smaller region is explored that may have 1000 to 10,000 particles. While the model does run fine on a typical personal computer for up to a million particles, the hope is that the deformation of a small region will be that same as the bulk sample. This assumption should be true as long as the bulk experimental samples do not have flaws or larger defects.

A typical bending result is shown in Figure 5. As a group of particles moves from the initial position, the forces are transmitted through the particles to generate a force throughout the sample. At some point, the local strain of the sample exceeds the strain to failure of the pure binder, a crack propagates, and the sample breaks. This general behavior and the shape of the response are quite similar to the experimental data. The model predicts the elastic modulus of the coating layer from the initial slope of the response as well as the maximum stress and the strain to failure.

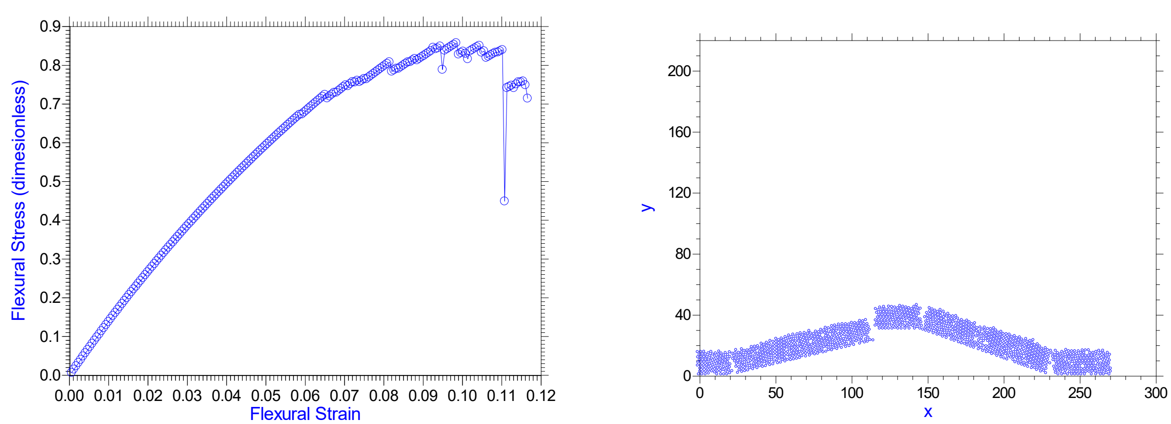

Figure 5. Flexural strain and stress predicted by the simulation (left) and crack of the coating layer (right).

The deformation and local forces in the 3D case are shown in Figure 6 for a typical case. In the region that is forced upward, a tensile force is generated. Also, near the region where particles are only allowed to slip in the horizontal direction, a tensile force is generated between particles.

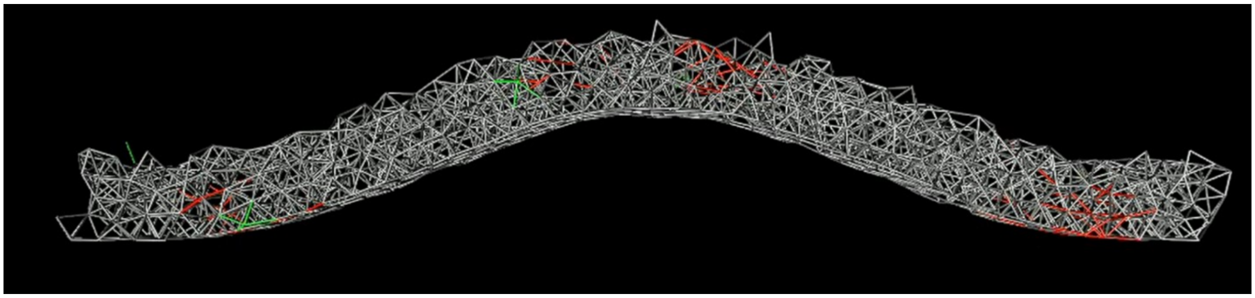

Figure 6. Bending deformation in 3D mode, showing the connections between particles for a typical case.

Results

The predictions of the models are compared to the tensile experimental data of Zhu *et al.* (2014) in Figures 7 – 9 for the PVC near the critical value or around 63% by volume pigment. The model predictions are for R_n=1.0 and R_b=1.0. The different ratio of latex and starch results in different values of A and B in Eq. (1) as well as a different strain to failure of the binder itself. Both the 2D and 3D models predict the elastic modulus well considering the assumptions of the model. The elastic modulus is on the order of 20 times larger than the pure binder films, given in Table 1. As the binder contains more latex, the elastic modulus decreases, mirroring the pure binder behavior.

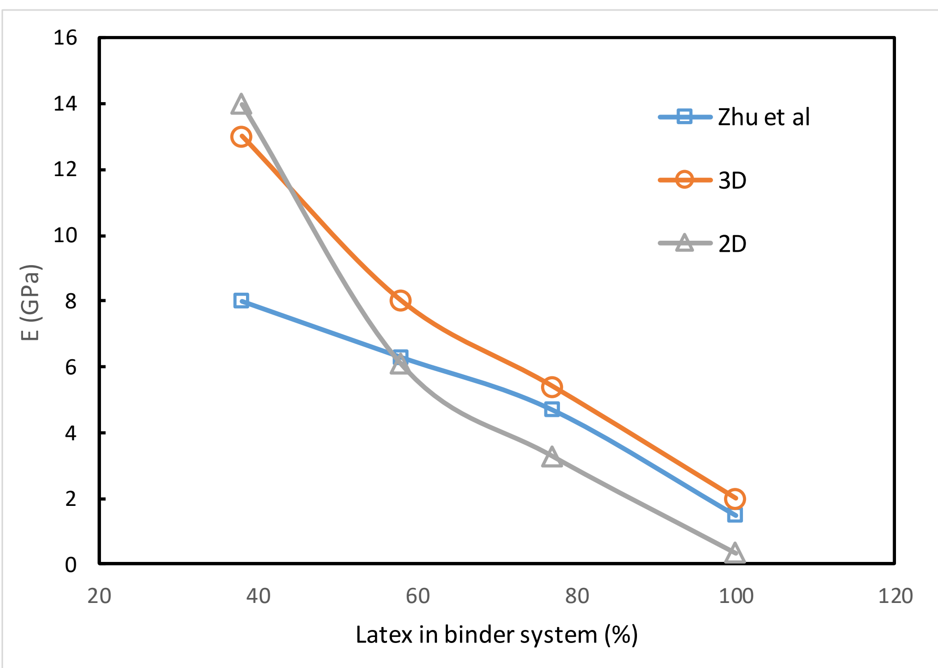

Figure 7. Elastic modulus of coating layers for PVC = 63% for various values of the starch and latex content in the binder.

The maximum stress is under predicted by both the 2D and 3D models as shown in Fig. 8. The experimental data shows a maximum value at middle values of latex content. It is possible that the decrease in maximum stress at low latex content could be caused by issues related to mounting a brittle sample into the tensile test, as discussed by Zhu *et al.* (2014). The predictions of the strain at failure are shown in Figure 9. The 3D model picks up the experimental results quite well, but the 2D predictions are quite low. The potential for a crack to form in tension comes from a weak region in the model system. In 2D, the probability of a weak area increases because of the fewer numbers of particles and the lower connectivity to neighboring particles when compared to 3D case.

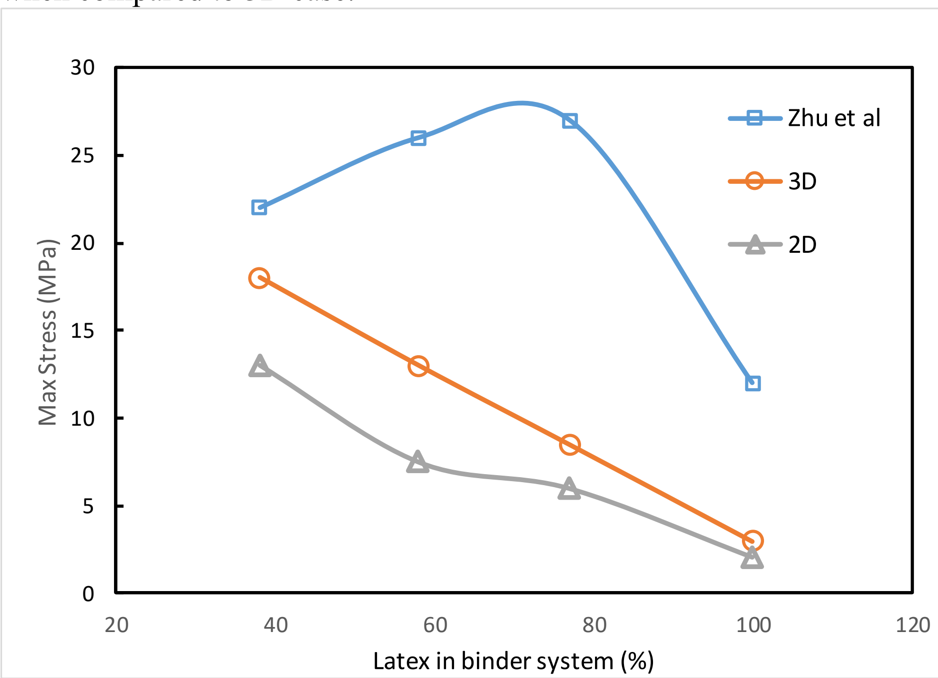

Figure 8. Predictions of the stress at failure for the coating layers in tension for PVC = 63% for various levels of latex and starch in the binder system.

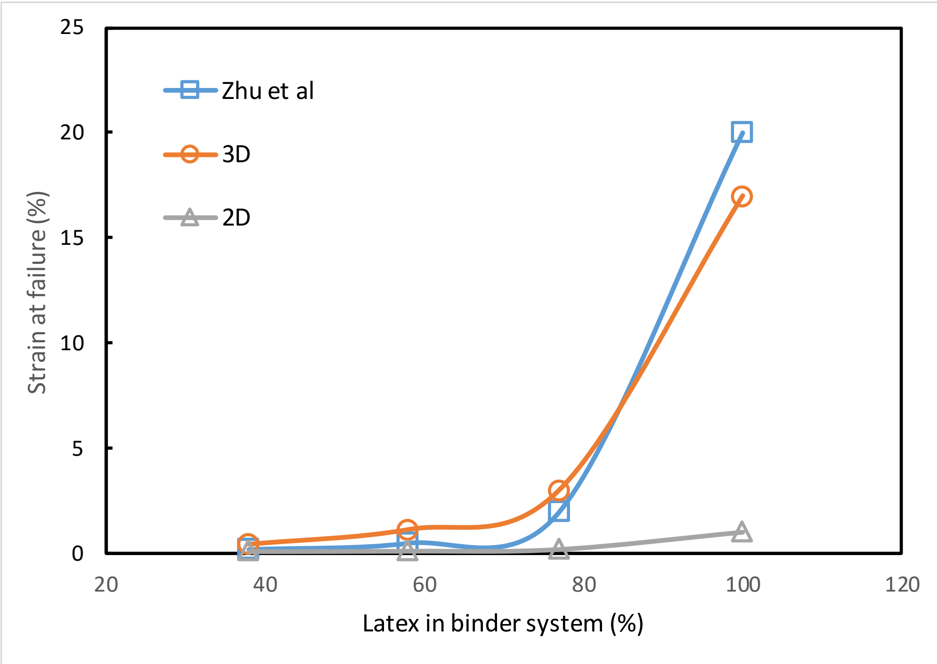

Figure 9. Predictions of the strain at failure for the coating layers in tension for PVC = 63% for various levels of latex and starch in the binder system.

The predicted flexural modulus, maximum stress, and strain at failure are shown in Figures 10 – 12 for the 2D and 3D cases, as well as the experimental data for various latex content of the binder system (for a PVC of 63% in all cases). Both the 2D and 3D models predict the correct trends: as the latex content decreases, the coatings become more brittle. The 2D model under predicts the elastic modulus and the maximum stress to some degree, but the predictions are in the correct range. This difference may be in the method within the code to determine the particles that are considered connected by binder bridges or by the way the particles are packed within the initial structure. Both models over predict the strain to failure, in Fig. 12; this may be due to minor imperfections in the coating layers in the experiments causing the sample to failure earlier than they would in theory. Considering assumptions in the model and the simple interactions between particles, these predictions are encouraging.

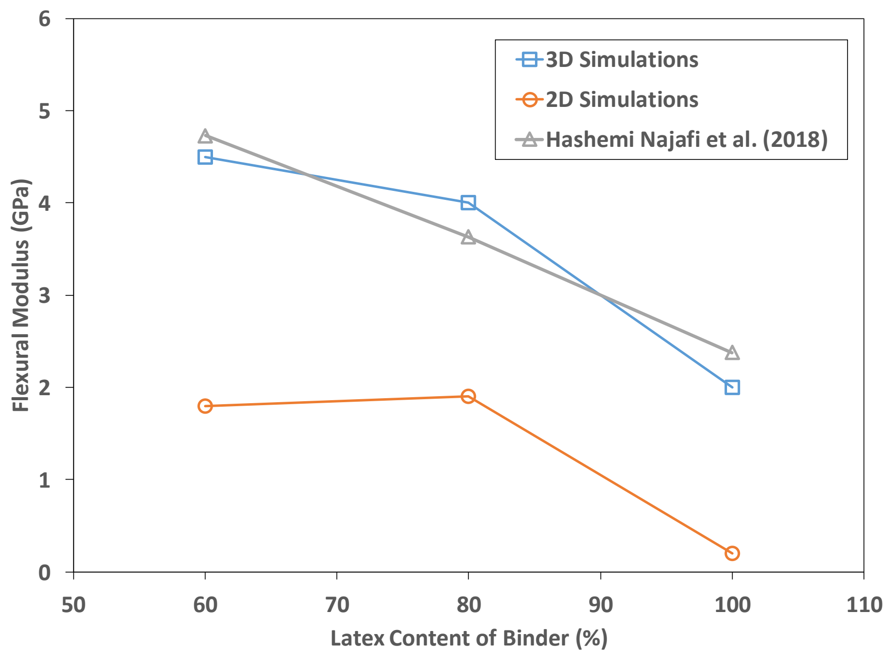

Figure 10. Predicted and measured flexural modulus for the coating layer near PVC of 63% for binder components of various levels of starch and latex.

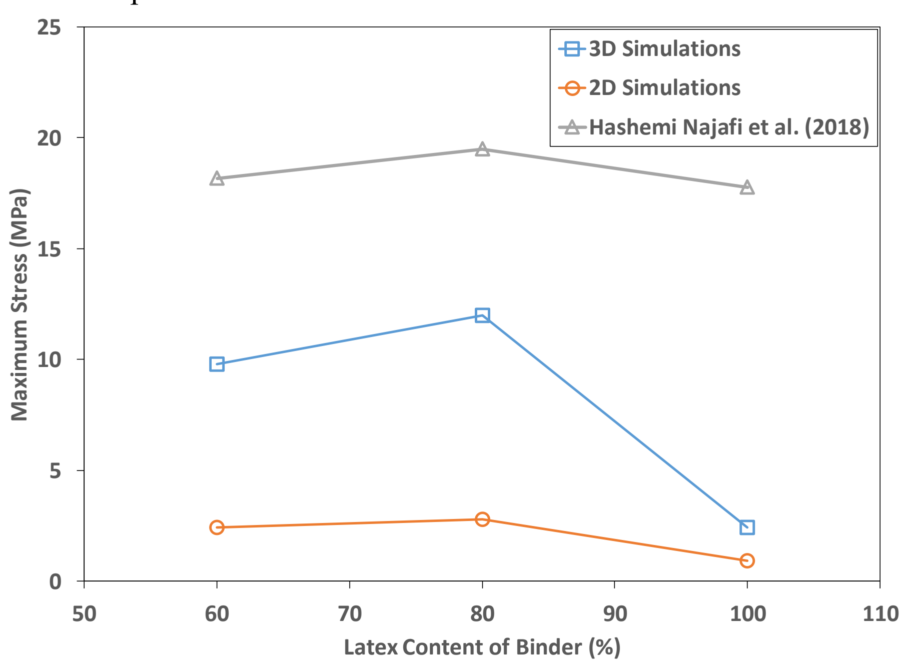

Figure 11. Maximum stress at failure for coating layers near PVC of 63% for various levels of latex and starch in the binder composition.

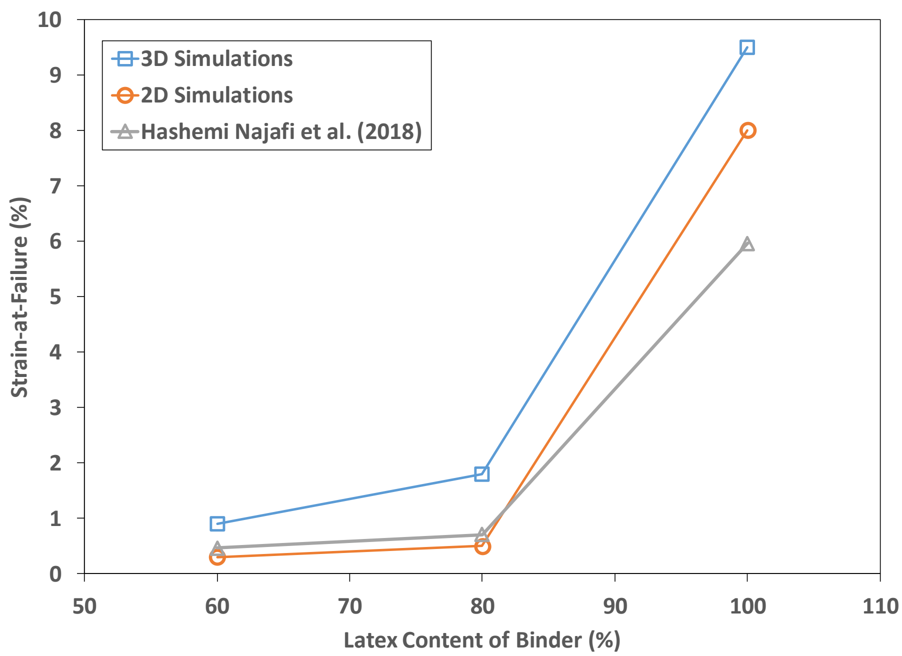

Figure 12. Predicted and measured strain at failure for coating layers near PVC of 63% for various levels of latex and starch in the binder composition.

A number of assumptions are used in these simulations, such as perfect adhesion between the binder and the pigment, the initial packing of the particles is similar to that of the real case, and that the starch and latex are forming a uniform material. In addition, these results are for a uniform spherical case while pigments in the experiments have a wide size distribution.

In both tension and flexural deformation, the model under predicts the maximum stress or the stress at failure. This under prediction is hard to explain, especially for the 3D case. The maximum stress between each particle pair summed across the cross section would control this prediction. In some way, the real system seems to make more connections than predicted with R_n=1.0. In a system with a broad particle size distribution, as in the experiments, it is possible that the particles can make more connections. The inclusion of a broad particle size distribution is straight forward. If the value of R_n in increased, the results in Figure 13 are obtained. In this case, the maximum stress prediction is improved except for the low latex case. The elastic modulus and the strain at failure, for this value of R_n, are over predicted by around 15%.

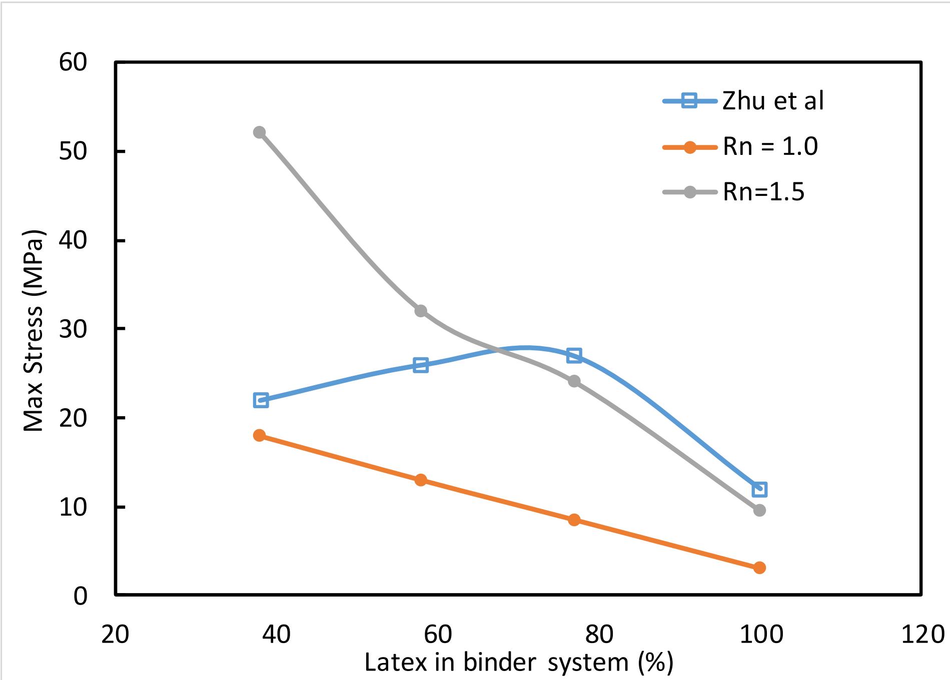

Figure 13. Predictions of tensile maximum stress for the 3D model with two values of R_n at PVC of 63% at various levels of starch and latex in the binder system.

The model is flexible for other situations. If a normal load is applied to the top layer of the particles, a calendering event would be modeled. If a load is applied vertically to a layer of the particles, the tensile event during printing could be simulated. If multiple coating layers are of interest, the parameters for each layer could be specified. The inclusion of particle inertia is natural to model high speed events. Even complex processing, such as slitting could be modeled.

Concluding Remarks

A discrete element model is developed to predict the mechanical properties of pigmented coating layers. The model parameters are the mechanical properties of the binder and the pigment volume concentration. The model gives reasonable predictions in both tensile and flexural tests. Including a full particle size distribution may improve predictions of real systems.

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