Modelling Polymer Particle Deformation on Mineral Surfaces - Part I: Validation of Initial Concepts

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Summary: A simple model based on elastic and attraction forces is proposed to describe the spreading of a cross-linked polymer particle on one or two surfaces. The model considers the internal elastic forces between the knots of reticulation and the external attraction forces between the particle and the mineral surface. The deformation and therefore the final shape of the particle is a resultant of the applied forces. The model is validated by fitting with experimental data of latex spreading on mineral surfaces, and the next steps towards using this knowledge to help design new particle structures and morphology are outlined.

Keywords: deformation; mineral; particle; polymer; surfaces; young modulus

Introduction

Large volumes of synthetic latex are commonly used as binder in paints and paper coating colour formulations in order to improve the mechanical properties of the dry coating layer.[1,2] These formulations are composed of mixtures of latex with mineral particles, and various additives. The primary function of the latex particles is to promote adhesion between the mineral particles and between mineral particles and the surface to be coated (for example: wood, cellulose, concrete). In addition, in paper coatings, where the coating structure is composed of a matrix of pores, the latex polymer also has an important influence on the surface energy, size and distribution of the pores.

The process of coating a substrate with a latex-mineral formulation involves complex processes of particle immobilisation, consolidation and deformation as the water or solvent in the original formulation migrates in to the substrate or is lost through evaporation. After application to form a dry coating layer, each latex particle inside the layer can be considered as a single mechanical link between one or more surfaces. This link results in the adhesion between the mineral particles, the strength of which is partially defined by the mechanical properties of the polymer.

In this dry coating layer the latex particles are deformed from their originally spherical shape in to flattened areas of polymer films. The polymer in the latex particles are classically characterized by bulk properties such as T_g and gel content, however the relationship between these bulk characteristics and the structure of the polymer network or the processes of latexes particles deformation and film formation when in contact with mineral surfaces is not well understood.

After a brief discussion of published experimental and modelling studies, this paper presents a simple model to describe the deformation of a latex particle, composed of cross-linked polymer networks, on the surface of a mineral particle. The deformation occurs as a resultant of the applied external attraction and internal elastic forces, and the final shape of the particle is the result of the balance of these forces.

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The final section of the paper then demonstrates how the model can be validated using experimental data[3] of latex spreading on mineral surfaces, and outlines the next steps towards using this knowledge to help design new particle structures and morphology.

Observations on Latex Deformation in Coating Layers

Many studies have been carried out to establish how latex particles behave during the drying process that forms the coating layer and defines the final state of the latex after drying.

Lafon *et al.*[4] used an indirect method to evaluate latex deformation during the drying process. They measured the variation of light scattered by the coating layer. The intensity of light scattered depends on the pore size (mainly due to the pigment packing) and in a lesser extent to the shape of the latex particles. Using this test, they observed that even when the coating layer is dried at a higher temperature than the film formation temperature of the pure latex, the particles do not necessarily deform and coalesce to form a film. They suggest that the deformation of latex particles in a coating layer is a combination of both the polymer T_g and the polymer bulk modulus. However, this macroscopic measurement only gives a relative view of the latex particle deformation and it does not give information on the final shape of the particles. Only microscopic investigations can give access to this level of information.

Kugge *et al.*[5] investigated the latex topology in the coating layer using SEM. They mainly focussed on the coating formulation and the only latex parameter that was varied was the T_g. They confirmed that depending on the drying conditions and the latex T_g, the latex particle can remain spherical or spread on the pigment surface. No quantitative measurement of latex spreading is possible using such a complex system since each latex particle spreads and coalesces to such an extent that it is not possible to identify the edge of the final deformed particle.

The most accurate technique used to experimentally measure single latex particle deformation or spreading on a rigid surface is the atomic force microscopy (AFM). This method clearly demonstrates that latex particles spread extensively on flat surfaces.[6] However the conditions of sample preparation have an influence on the final shape of the particle. The nature of the removal of the aqueous phase seems to play a major role. It is suggested that the residual water interacts with the chemistry of the particle surface (e.g. acidity, presence of surfactants...) and has a plasticizing effect.[7]

Engqvist *et al.*[8] worked not only on the spreading of latex particles but also studied the kinetics of this spreading. They also considered that polymer T_g and E-modulus are the principle variables that influence particles spreading. The equilibrium measurement of E-modulus is very accessible and is therefore commonly used in deformation models however Engqvist *et al.* suggest that oscillating rheological measurements maybe more appropriate due to the dynamic nature of such deformation.

Portigliatti *et al.*[9] used AFM to measure the force of adhesion of latex particles to the AFM tip. Both the deformation and the adhesion work of the latex particle depend on the surrounding environment of the particles. The presence of other latex particles increases the adhesion forces. This observation emphasizes the need of a global understanding of the latex-pigment system.

Indeed, the direct measurement of the deformation of one particle on a surface gives only a limited amount of information concerning the geometry of the latex in a coating layer and thus the mechanical properties of this coating. However, before attempting complex modelling the necessary first step is to validate models that trend to establish relationships between single particle deformation and polymer physico-chemical description.

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Modelling of Particle Deformation

The deformation of polymer particle was studied initially by Hertz.[10] In Hertz model, the diameter of the contact surface between the sphere and the plan is a function of their Young modulus and the load applied the top of the sphere. In this analytical model, adhesion phenomenon is not considered. Johnson, Kendall and Roberts[12] proposed the inclusion of adhesion force equations. It is called the JKR model. This model can be used for soft solids with higher surface energy and low or zero applied load. Derjaguin, Muller and Toporov[13] proposed a model (DMT model) that considered the adhesion forces operating over a finite distance in a region just outside the contact zone. This model can be used for hard solids with low surface energy. Maugis[14], Schwarz[16], Unertl[6] and Shull[17] extended the application range of these models.

The most appropriated model in the case of latex particles is the JKR model. This is because the latex particles used in paints and coating colours recipes are soft and have high surface energy. Experimental studies show the behaviour of latex particles on mineral surfaces. Lau *et al.*[3] worked with the JKR model to calculate the radius of the contact area between SB latex particles and silica. A reasonable agreement between the experimental data and calculation was obtained.

However, all these models consider the particles as a homogeneous solid material. Lin[15] and Sauer *et al.*[19] applied methodology of finite elements to the contact region between particle and flat surface. However, in order to describe the deformation of the whole particle in contact with one or two mineral surfaces, a more detailed model must be built. Since latex particles can present a soft shell and hard core, this model must therefore consider the possibility to describe the deformation of core-shell particles.

The Proposed Model

The model proposed in this paper considers the polymer particle as a nanomechanical entity composed of both cross-linked and uncross-linked polymeric chains. A 150 nm particle has about 15 million monomer molecules distributed in about one thousand polymeric chains. Depending on the amount of chain transfer agent and polymer composition, in one particle is possible to find from zero to about one million knots of reticulation. It is possible to imagine the particle as a spherical spring matrix (Figure 1). Each spring represents a polymeric chain between two knots of reticulation.

Therefore, a simple model was developed in FORTRAN® considering two basic forces, as being: the elastic forces between the knots of reticulation and the attraction forces between each knot and the mineral surface. This model assumes the polymer and mineral surface are charged. In the case of polymer, the charges are located just in the knots. The forces will

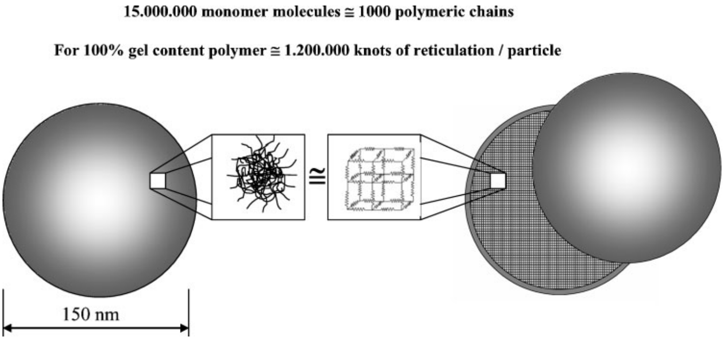

Figure 1.
Visualization of a latex particles as a nanomechanical entity composed by springs (polymeric chains).

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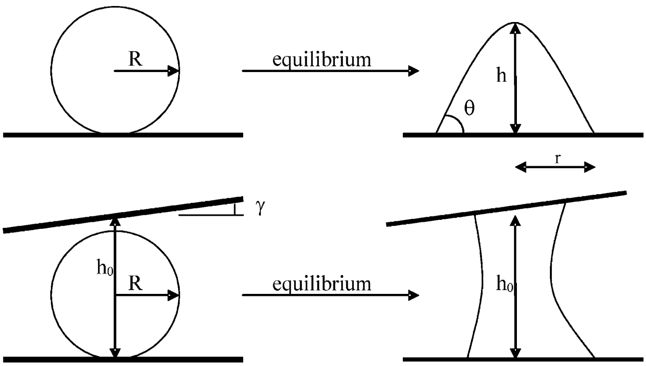

Figure 2.
Schema of latex particle deformation on the surface of mineral particles.

promote the particle deformation (see Figure 2). It is important to notice that a strong adhesion takes place when the knot touches the mineral surface. In this model, as soon as the knot touches the surface, a vertical reaction force from the surface to the knot is generated by the model to compensate the attraction force and keep the knot strongly adhered to the surface. Other simplification of this model is that the charge of each knot does not change during the mechanical deformation. This model is able to consider different charges for each knot and different distribution of knots inside the particle. This is the case of core-shell particles for instance. However, this model cannot predict changes of charge during mechanical deformation. Otherwise, in order to validate model of particle deformation and charge distribution in function of time, experimental data should be generated. This assumption will be studied in the next papers.

The elastic force $\vec{F}_E$ between two knots is described in this work by the Hooke's law (see equation 1). The spring or elastic constant k_E is a function of the polymer Young Modulus. The constant k_E can have different values for compression (k_{EC}) and traction (k_{ET}). The vector $\vec{d}$ has a modulus equal to the difference between the current and initial lengths of the polymer chain between the two knots. The values of k_{EC} and k_{ET} can be functions of the position of the point inside the particle. The distance between two points can be limited by two parameters, cf and tf. These parameters, multiplied by the initial length before deformation, define, respectively, the minimum and maximum length between each couple of neighbour points.

$$\vec{F}_E = k_E \cdot \vec{d} \tag{1}$$

The attraction force in this work is based on Coulomb's law (see equation 2). In this case, it was defined an attraction constant k_A. It is a function of the electrical charge of the knot and the charge of the mineral surface. Beside it, the distance between the knot and the mineral surface ΔZ was elevated to n (normally equal to 2). The vector $\vec{Z}$ has components in the three directions (X, Y and Z). In this work it was considered a component horizontal in the radial direction and vertical component in the direction Z, in the sense to the mineral surface (see Figure 3).

$$\vec{F}_A = \frac{k_A}{\Delta Z^n} \cdot \vec{Z} \tag{2}$$

The model makes the balance of forces for each knot in the sphere and calculates the total volume of the particle. Each point has an identity composed by three numbers (n, p and s) representing its position in the sphere. The Cartesian coordinates of each points are X(n,p,s), Y(n,p,s) and Z(n,p,s).

The incremental change of each point position in the space XYZ is made in the

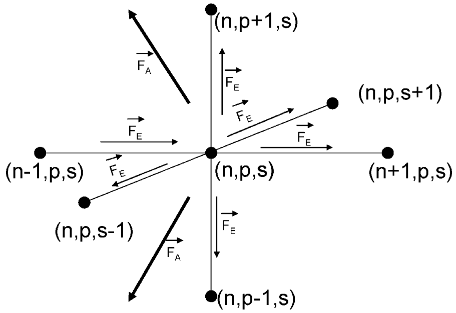

Figure 3.
Balance of forces in the point P(n,p,s) inside the sphere.

direction to reduce the resultant force modulus. The routine searches the particle shape that gives the lowest particle height (h) with a final volume equal to the sphere volume ±30%. The model considers the possibility to include a second flat surface parallel or not in relation to the first one.

Initial Results

An example of particle deformation on a flat surface as simulated by the model is shown in Figure 4. The original particle is shown in Figure 4a. The particle spreads on the flat surface by the effect of attraction forces. The points tend to be in contact with the surface, but the elastic forces try to keep them in their original position (Figure 4b to 4d).

These results demonstrate that the deformation and spreading of a latex particle on a mineral surface can be described by the sum of the attraction and elastic forces acting on individual elements of the structure. The next step was to calibrate and validate the model by identifying the elastic and attraction constants that allow prediction of experimental observations of latex deformation on mineral surfaces. In order to do this, the model was fitted to the experimental data from Lau[3]. The parameters used in this validation, and the results from simulation are listed in the Table 1.

The values of elastic constant (k_E), attraction constant (k_A) and maximum elongation between points (tf) are optimised

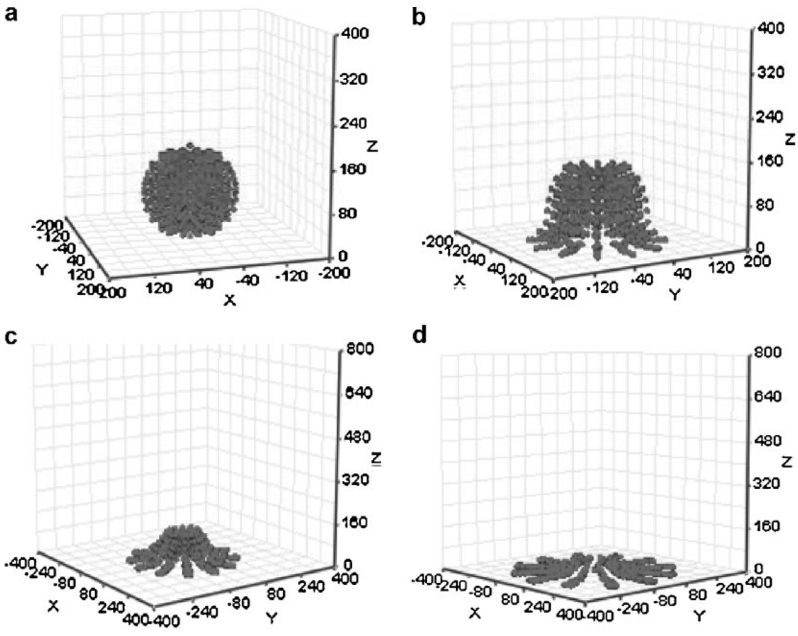

Figure 4.
Simulation results, before and after deformation, for particle with initial diameter 175 nm, $k_E = 50$ N/nm, $k_A = 1000$ N · nm, $n = 1$. The sphere was described using 720 discrete points being a) initial points, b) after 1000 interactions, c) after 1300 interactions and d) after 1700 interactions.

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Table 1.
Results of Simulation with Lau's experimental data[3] and fitted parameters.

	Lau's Data[3]							Results from this model				
	T_g	GF	N	D	E_B	h	2r	h	2r	k_E	k_A	V/Vo
SB(−2)-75	−2	75	210	175	0.63	26.0	640	34	660	45	1000	1.17
SB-(11)-75	11	75	235	167	1.35	39.0	610	37	602	48	1000	1.25
SB-(28)-75	28	75	225	167	1.92	49.5	565	50	560	55	1000	1.33
SB-(−2)-92	−2	92	310	148	0.60	46.0	398	49	396	140	1300	1.29

T_g = glass transition temperature, °C; GF = gel fraction in toluene, %; N = acidity, μmol/g; D = initial particle diameter, nm; E_B = bulk elastic modulus, MPa; h = height of the particle after deformation, nm; 2r = diameter of the contact area of the particle after deformation, nm; k_E = elastic constant, N/nm; k_A = attraction constant, N · nm; r = ratio of the contact area of the particle after deformation, nm; V/Vo = ratio between final and initial particle volume; n = 1, exponent for equation 2; cf = 0.1, minimum ratio current/initial distance between points; tf = 5 (for SB-(−2)-92) and 20 for the others, maximum ratio current/initial distance between points; Cfh = 4, ratio between modulus of componets (X + Y) and Z of attraction force.

in order to have the final results presented in Lau's data [3]. In general, the results were obtained after 1700 interactions.

These results are shown graphically in Figure 5. In this graph it is possible to see good agreement between the extent of predicted latex deformation and the experimental data. The SB-(-2)-92 does not appear in this figure because of its higher value of N comparing to the other three samples. The contact area ratio R decreases with the increase of k_E. The height h increases with the increase of k_E. In the Figure 6, the opposite effect can be seen, when k_A is increased. The model is reasonable fitted to the experimental data.

It is important to notice that the k_E is a function of the polymer T_g and GF. The multi-linear regression gave the correlation presented in the equation 3 ($r^2 = 0{,}99$).

$$k_E = (-376 \pm 7) + (0.34 \pm 0.05) \cdot T_g + (5.7 \pm 0.1) \cdot GF \qquad (3)$$

This equation is not in agreement with the values of E_B (see Table 1). The value of E_B does not change with GF. This can be explained by the nature of the measurement of bulk Elastic Modulus in films formed from the coalescence of polymer particles. Beside the elastic intra particle force, there is also a Van der Waals inter particle force that interferes in this measurement. Otherwise, the values of k_A have reasonable agreement with the values of N (see Table 1). The data cover a small region in

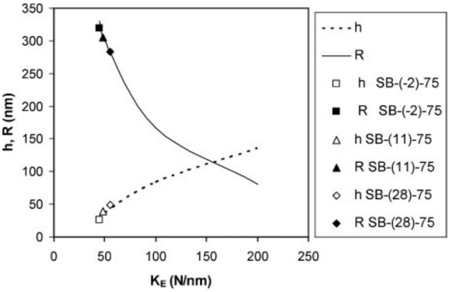

Figure 5.
Comparison between the data from Lau[3] and data obtained by the model, considering $k_A = 1000$ N · nm.

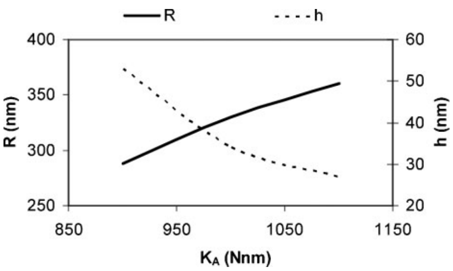

Figure 6.
Contact area ratio R and height h versus k_A for k_E = 45 N/nm.

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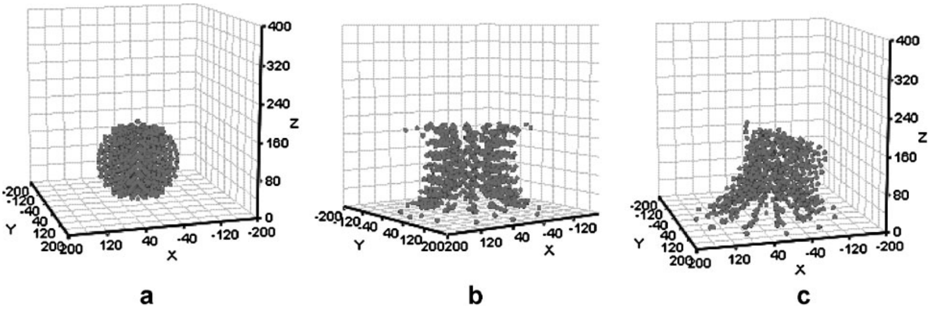

Figure 7.

Particle deformation between two flat surfaces, particle diameter 175 nm, $k_E = 50$ N/nm, $k_A = 2000$ N · nm, $n = 1$, distance between the two surfaces equal to 175 nm, (7.a) before deformation, (7.b) after deformation between parallel surfaces ($\gamma = 0°$), (7.c) after deformation between non parallel surfaces ($\gamma = 15°$).

this graphic. Therefore, in the next steps of this work, polymers in a large range of k_E and k_A will be explored.

In the Figure 7, the simulation of particle deformation between two surfaces has been made. The results show that under certain conditions, one particle can adhere to both surfaces. But there is no experimental data of measured latex morphology that is available to validate this hypothesis. This behaviour will be explored further in the next studies.

Conclusions

The mathematical modelling of polymer particle deformation has been studied since the 19th century. It is a very important tool to understand the mechanism of adhesion and mechanical deformation of coatings. However, the connection between particle design and nanomechanical properties still needs more modelling work.

In this paper it has been shown that a simple model using two basic equations (Hooke's and Coulomb's law) can predict the deformation behaviour of cross-linked polymers on one flat surface or between two flat surfaces (parallel or inclined).

The model has been validated using experimental data for deformation of latex particles on a single mineral surface, and preliminary correlations have been established between certain measured polymer properties and the spring constant of the polymer network.

The next steps include a more detailed analysis, for instance using finite element methodology, and to transform the simple model outlined in this paper in to a predictive model where the attractive and elastic forces are more precisely described in terms of standard polymer or mineral characteristics, such as polymer Tg, polymer gel fraction and different surface charges. The effect of charge redistribution during deformation must be discussed and better understood.

It is anticipated that knowledge of the ease of particle deformation and the prediction of the final shape and surface area/volume occupied by a particle after deformation will help application experts to unravel the mechanisms of particle adhesion and will allow polymer reaction experts to improve the design new particles.

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