

## 3D FINITE ELEMENT MODELLING OF FILLER REINFORCED ELASTOMERS

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### Abstract

*Filled polymer is a material of great practical importance due to its unique properties. Non reinforced polymer matrices generally do not exhibit properties suitable for practical purposes. On the contrary, polymers filled with carbon black have a shear modulus much (up to 100 times) higher than that of pure polymer matrix. The presence of carbon black in polymer matrix introduces certain non-linear effects like Payne and Mullins effect. The aim of this work is to develop a micro-mechanical finite element model of filler reinforced polymers which serve to better understand and quantitatively analyze their complex behavior.*

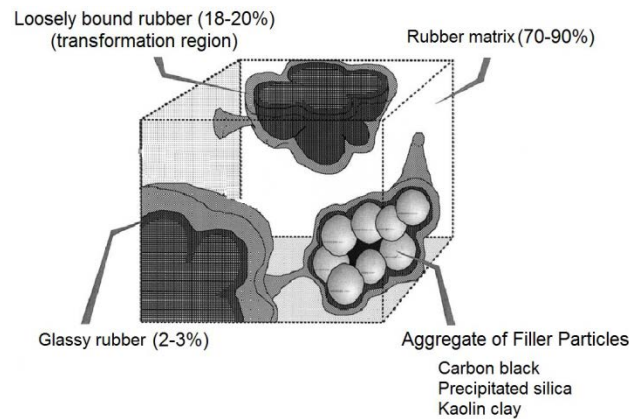
### 1 Introduction

Stronger, stiffer polymeric materials are attractive to numerous industries due to their light weight, easy manufacturing, low cost and recyclability. Reinforcement of polymer matrices with inorganic nanoparticles produces composite materials that exhibit enhanced mechanical and thermo-mechanical properties without significant increase in the weight of the material. Excellent stiffness and strength are achieved while utilizing far less high-density inorganic material than is utilized in conventional composites. Independent of whether the nano filler is spherical (carbon black), cylindrical (carbon nanotubes) or a platelet (clay) the efficiency of the inorganic nano-reinforcement depends on three parameters: filler mechanical properties, filler aspect ratio and adhesion between the matrix and filler [1].

The main goal of the present work is to develop a micro-mechanically motivated finite element model of filler-reinforced polymers which serves to better understand and quantitatively analyze their complex physical behavior. Some effects like strain amplification, inter-penetration of clusters and pore-space filling can only be modeled in a reliable way if the three-dimensional sophisticated geometry of the clusters is represented as realistically as possible. For this reason, the finite element method has been used as it permits to construct complex geometries and include sophisticated mathematical descriptions of the thermo-mechanical polymer and filler behavior.

### 2 System of filled elastomer

The system of filled elastomer can be described as a dispersion of solid particles in polymeric network. The system can be divided into four main domains as shown in Figure 1, namely aggregate of filler particles, glassy rubber, loosely bound rubber and pure rubber matrix.



**Figure 1.** Pictorial representation of carbon black filled rubber compound [2].

### 2.1 Filler particle

Most of the rubber fillers used today offer some functional benefit that contributes to the process ability or applicability of the rubber product. Of the many fillers used to modify the properties of rubber products, carbon black, calcium carbonate, kaolin clay and precipitated silica are the most common. In this work we keep our focus on carbon black filler particles.

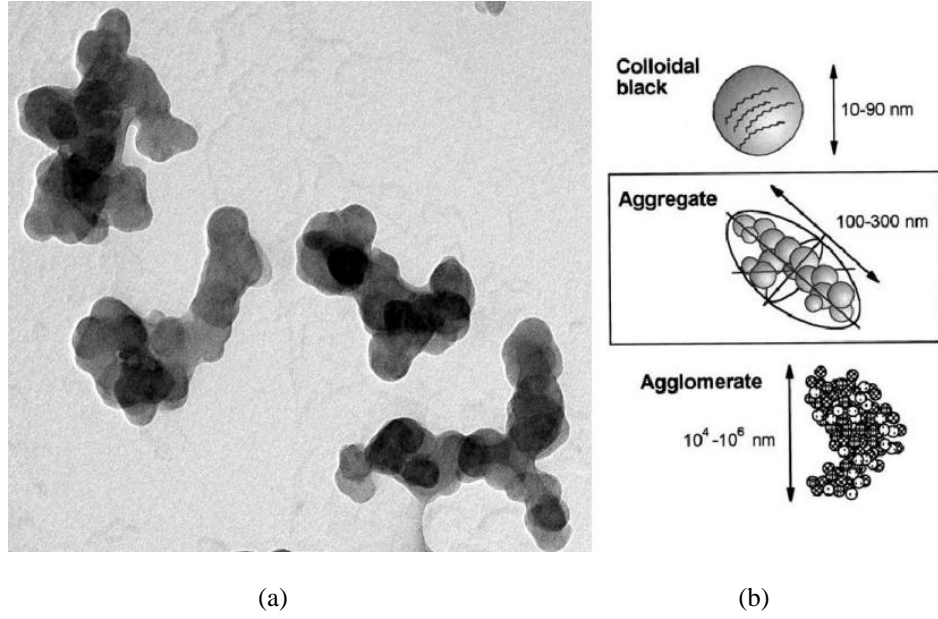
Carbon black is considered to be linear elastic in nature. Carbon black (c.b) plays an important role in the improvement of the mechanical, thermal and electrical properties of rubber materials. Carbon black is a form of amorphous carbon that has a high surface area-to-volume ratio. The reinforcing potential is mainly attributed to two effects: (i) the formation of a physically bonded flexible filler network and (ii) strong polymer filler couplings. Filler particles exist as an aggregate in the rubber matrix. So as the size of the particle decreases the overall surface area of the aggregate increases providing more area for a strong polymer filler coupling [4].

So far, the formation and structure of the c.b network and the mechanical response is not fully understood. For a deeper understanding of the mechanical and thermal properties of c.b filled rubbers, it is necessary to consider the morphology of the c.b particles (primary aggregates) more closely.

### 2.2 Primary Aggregate

Carbon black is produced by incomplete combustion of heavy petroleum products. C.b generally exists as an aggregate which is considered to be a fractal object of sintered c.b particles. Each of such aggregates is referred to as primary aggregate. Figure 2(a) is a transmission electron microscope (TEM) image of a primary aggregate. The collection of many such primary aggregates is known as agglomerate. Figure 2(b) shows the relevant dimensions of carbon black filler particles and its aggregates.

The morphology of c.b is closely related to the conditions of surface and primary aggregate growth during c.b processing. To be able to represent the aggregates and agglomerates more realistically using finite elements, it is important to generate such aggregates computationally considering the fractal parameters. There are at least three well-studied particle-particle aggregation models (ballistic, diffusion-limited, and reaction-limited) [7].



**Figure 2.** (a)TEM image of a primary aggregate; (b) relevant dimensions of filler and its aggregates [2]

In this work a more recent approach proposed by Morozov et al. [4] for particle-particle aggregation has been used due to its simplicity. The aggregation algorithm in which the particles are randomly placed in a layer-by-layer fashion around the first particle is based on the following equations;

$$n \approx C \left( \frac{R}{r_p} \right)^D \quad (1)$$

$$\Delta n_M \approx C \left( \frac{R}{r_p} \right)^D - n_{M-1} \quad (2)$$

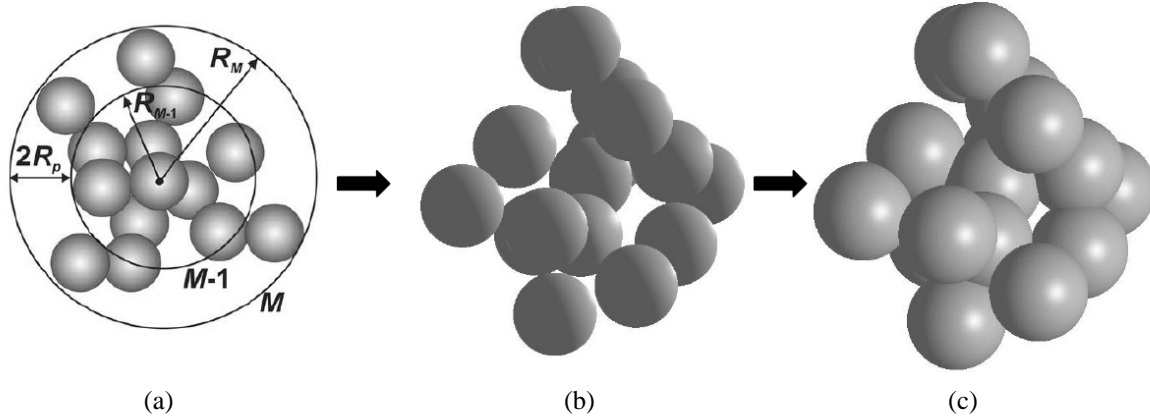
$$R_M = (2M + 1)r_p \quad (3)$$

where  $n$  is the number of particles located at distance  $R$  from the aggregate center,  $r_p$  is the particle radius and  $D$  is the mass fractal dimension. The number of particles with centers in the  $M$ -th layer is given by  $\Delta n_M$  Figure 3(a). It is assumed that the particles increase in size during furnace annealing. To take into account this process, one half of the originally defined value of the particle radius is considered. When aggregate of desired size is constructed, the radius of aggregate particles is increased to its real value. As a result, the spheres representing the aggregate particles overlap each other Figure 3(c). The constant  $C$  in (1) is chosen in a way that the specific areas of particles, correspond to the specific areas obtained experimentally [4].

### 2.3 Polymer matrix

The micro structure of polymer consists of long, randomly oriented molecular chains which are linked together. In this way an arbitrary three-dimensional network is formed. In addition there exist intermolecular interactions between the particular atoms which have an important influence on the dilatational response of rubber-like materials.

Eg. elastomers can be described by a network model of Böl and Reese [6], which is based on the concept of Langevin statistics. The Böl and Reese [6] approach is based on the idea of representing the polymer network by means of an assembly of non-linear truss elements. Each truss element models the force–stretch behavior of a certain group of chains. The truss elements are configured in such a way that six of them form a cell of tetrahedral shape. These tetrahedral elements serve to model the hydrostatic pressure built up in the network. Using a random assembling procedure one can model arbitrary geometries.



**Figure 3.** Algorithm for generation of filler aggregates [5]

One fundamental material property of rubber-like material is its high elasticity which permits stretching of several hundred percent. The reason for this behavior is the particular micro structure of rubber. It is characterized by a huge number of chain-like macromolecules which form a three-dimensional network. The material exhibits so-called statistical behavior, i.e. the network configuration actually taken on by the material is the most probable one under the given circumstances. Describing the entropy of a single chain with the help of Langevin function and assuming the internal energy of the chain to be negligible, the Helmholtz free energy function has been described as

$$W_{chain} = kn\theta \left( \beta\gamma \frac{\lambda_{chain}}{\sqrt{n}} + \ln \frac{\beta}{\sinh\beta} \right) \quad (4)$$

where  $k$  is Boltzmann's constant,  $\theta$  the absolute temperature, and  $\lambda$  is the stretch of the chain.  $\beta$  can be expressed as series expansion of inverse Langevin function[8] which depends on the number of approximations  $n$  and  $\gamma$  which is a function of rotation angle and bond angle of an idealized chain.

The statistical properties of a single chain depend on geometrical parameters. However, intermolecular interactions, in particular the effect of the well-known van der Waals forces, cannot be completely neglected because they are mainly responsible for the fact that rubber is almost incompressible. To give the structure additional volumetric stiffness, the space between the chains is filled with artificial material using a tetrahedral element. This is modeled by means of the Helmholtz free energy function per reference volume:

$$W_{tetr} = K/4(J^2 - 1 - 2\ln J) \quad (5)$$

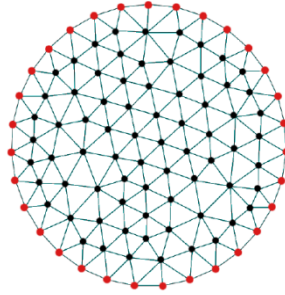
### 3 Finite element modeling

#### 3.1 Filler element

Filler particles are modeled using the so called super element. A super element is a group of finite elements that, upon assembly, may be regarded as an individual element for computational purposes. The motivation to use the concept of super elements is to take advantage of repetition and reduce the computational effort. In the given system filler particle is a repeating unit i.e. tens and hundreds of filler particles combine to form an aggregate and hundreds of aggregates combine to form agglomerate.

Degrees of freedom (d.o.f) of a super element are classified into two groups: *Internal d.o.f*: Those that are not connected to the freedoms of another element. Nodes whose d.o.f are internal are called internal nodes. *Boundary d.o.f*: these are connected to at least one other external element. They usually reside at boundary nodes placed on the periphery of the super element. See Figure 4. The objective is to get rid of all internal d.o.f. This elimination process is called static condensation, or simply condensation. This help to reduce the d.o.f of the entire system by reducing the computational time [9].

To carry out the condensation process, the assembled stiffness equations of the super element are partitioned as follows:



**Figure 4.** 2D representation of a filler element; red dots: boundary nodes, black dots: internal nodes

$$\begin{bmatrix} \mathbf{K}_{bb} & \mathbf{K}_{bi} \\ \mathbf{K}_{ib} & \mathbf{K}_{ii} \end{bmatrix} \begin{bmatrix} \mathbf{u}_b \\ \mathbf{u}_i \end{bmatrix} = \begin{bmatrix} \mathbf{f}_b \\ \mathbf{f}_i \end{bmatrix} \quad (6)$$

where sub vectors  $\mathbf{u}_b$  and  $\mathbf{u}_i$  collect boundary and interior d.o.f, respectively. Take the second matrix equation:

$$\mathbf{K}_{ib}\mathbf{u}_b + \mathbf{K}_{ii}\mathbf{u}_i = \mathbf{f}_i \quad (7)$$

If  $\mathbf{K}_{ii}$  is nonsingular we can solve for the interior unknowns:

$$\mathbf{u}_i = \mathbf{K}_{ii}^{-1}(\mathbf{f}_i - \mathbf{K}_{ib}\mathbf{u}_b) \quad (8)$$

Inserting into the first matrix equation of (6) yields the condensed stiffness equation

$$\tilde{\mathbf{K}}_{bb}\mathbf{u}_b = \tilde{\mathbf{f}}_b \quad (9)$$

In this equation,

$$\tilde{\mathbf{K}}_{bb} = \mathbf{K}_{bb} - \mathbf{K}_{bi}\mathbf{K}_{ii}^{-1}\mathbf{K}_{ib} \quad \tilde{\mathbf{f}}_b = \mathbf{f}_b - \mathbf{K}_{bi}\mathbf{K}_{ii}^{-1}\mathbf{f}_i \quad (10)$$

are called the condensed stiffness matrix and force vector of the super element, respectively.

From this point onward, the condensed super element may be viewed as an individual element whose element stiffness matrix and nodal force vector are  $\tilde{\mathbf{K}}_{bb}$  and  $\tilde{\mathbf{f}}_b$ , respectively. This super element will now be referred to as filler element which is repeated several times in order to represent aggregates. Using this technique filler particle of any shape can be modeled easily. Please note, that as the filler particle is considered to be linear elastic, inversion of the stiffness matrix  $\mathbf{K}_{ii}$  has to be carried out only once for the filler element in each time step.

### 3.2 Polymer element

According to the remarks in section 2.3 a finite element unit cell that consists of one tetrahedral element and six truss elements lying on each edge of the tetrahedron has been established, Figure 5. The Helmholtz free energy of one unit cell then includes one contribution coming from the tetrahedral element ( $W_{tetr}$ ) and another one coming from the truss elements ( $W_{truss_j}$ ,  $j = 1, \dots, 6$ )

$$W = W_{tetr} + \sum_{j=1}^6 W_{truss_j} \quad (11)$$

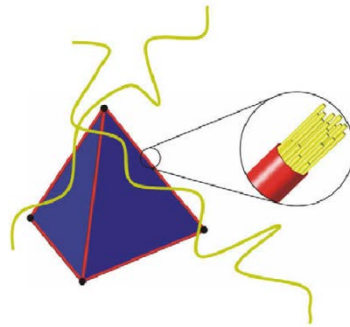
In reality, the number of chains per volume is huge. As it is not possible to describe each chain by a single truss element, one truss element is used to represent several polymer chains, i.e. a bundle of chains (see the enlargement of Figure 5. The Helmholtz free energy function of the truss element  $j$  ( $j = 1, 6$ ) then has the form

$$W_{truss_j} = \frac{1}{A_{0j}L_{0j}} f_{chain} W_{chain_j} \quad (13)$$

with

$$W_{chain_j} = kn_j \theta \left( \beta_j \gamma_j \frac{\lambda_{chain_j}}{\sqrt{n_j}} + \ln \frac{\beta_j}{\sinh \beta_j} \right)$$

where  $A_{0j}$  is the cross-section and  $L_{0j}$  the length of the truss element in its underformed state.

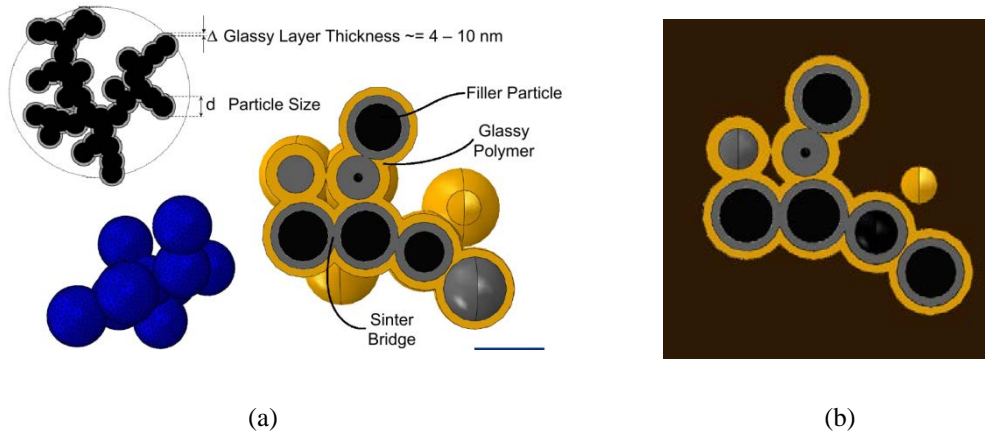


**Figure 5.** Tetrahedral unit cell. Blue: tetrahedral element, red: truss elements and yellow: polymer chain bundles [6].

Exploiting (11) one can further derive the constitutive material matrix for implementation in a finite element code [6]. The advantage of this approach is that it is conveniently applied to a finite element mesh for complicated realistic geometries using tetrahedral elements superimposed with truss elements.

### 3.3 Complete System

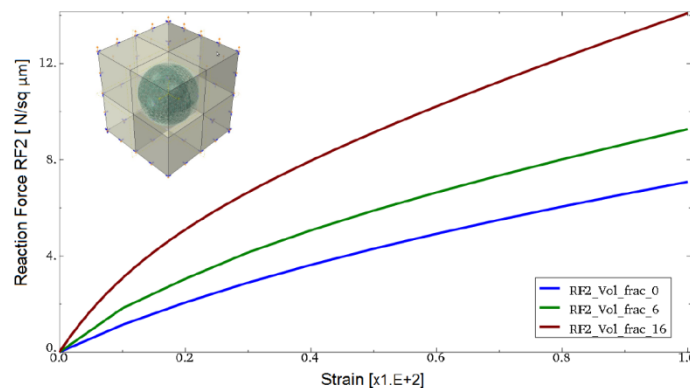
Figure 6(a) shows the modeling of primary aggregate. Filler particles are surrounded by a layer of elements representing the sinter bridges bounding different filler particles into a primary aggregate. This is then surrounded by a layer of elements representing bounded polymer. The bounded polymer layer is described as the polymer in its glassy state which is several times stiffer than the polymer in its rubbery state. This system is then embedded into the polymer matrix as shown in Figure 6(b). Polymer elements, introduced in section 3.2 have been used to model the glassy layer and the polymer matrix.



**Figure 6.** (a) Model for the primary aggregate, (b) model for the system of filled rubber

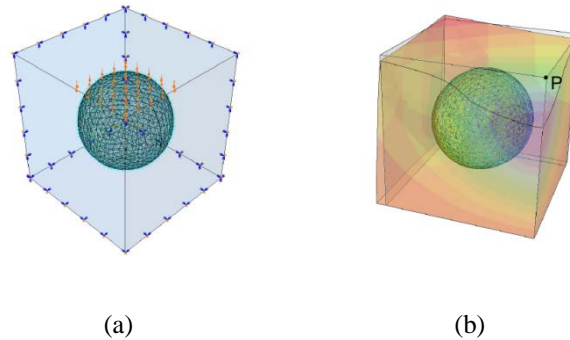
## 4 Numerical Examples

Simple uniaxial tension and compression tests are carried out to understand the behavior of a filled elastomer system. Simulations have been carried out for filled elastomer system with different volume fractions of filler aggregates (volume fraction  $\phi$  is the ratio of filler aggregate volume to the volume of the entire system). For the case of uniaxial tension we observe that the reaction forces in the system increase with increase in volume fraction (Figure 7) and for the compression test we observe that the displacement of point P reduces as the volume fraction increases (Figure 8 and Table 1).



**Figure 7.** Reaction forces vs. strain for uniaxial tension test; (inset-boundary conditions)

We can conclude that the stiffness of the filled elastomer system increases with volume fraction of the filler aggregate.



**Figure 8.** (a) Boundary conditions for compression tests, (b) displacement of point P

Volume Fraction	Displacement at P
No filler volume	-24.86 $\mu\text{m}$
6 %	-22.25 $\mu\text{m}$
16 %	-20.63 $\mu\text{m}$

**Table 1.** Displacement for different volume fraction

## 5 Conclusions and Outlook

The system of filled elastomer was successfully modeled at a microscopic level using the finite element method for which: (1) a filler element was developed to represent filler particles and (2) different phases of polymer was modeled using the polymer element developed by Böl and Reese [6]. There is a need to further include the temperature dependence of the polymer to simulate the effect of glass transition temperature in the vicinity of filler particles. Also, the model will be enhanced to simulate the non-linear Mullins effects due to breakage of bonds between filler particles and polymer chain at the interface under dynamic loading conditions.

## References

- [1] S.M.Liff, *Thermomechanics of Nano-Filled Elastomers*, Dissertation, MIT, USA, (2008).
- [2] J.L.Leblanc, *Rubber filler interactions and rheological properties in filled compounds*, Prog. Polym. Sci. 27, 627-687,(2002).
- [3] S.Merabia et al., *A Microscopic Model for the Reinforcement and the Nonlinear Behavior of Filled Elastomers and Thermoplastic Elastomers (Payne and Mullins Effects)*, Macromolecules 41, 8252-8266, (2008).
- [4] M.Klüppel et al., *Chapter 31* in “Physical Properties of Polymers Handbook”, Springer New York, 359-550, (2007).
- [5] I.Morozov et.al, *A new structural model of carbon black framework in rubbers*, Computational material Science 47, 817-825,(2010).
- [6] M.Böl and S.Reese, *Finite element modelling of rubber-like polymers based on chain statistics*, International Journal of Solids and Structures 43, 2–26, (2006).
- [7] P.Meaking, *A Historical Introduction to Computer Models for Fractal Aggregates*, Journal of Sol-Gel Science and Technology 15, 97-117, (1999).
- [8] W.Kuhn and F.Grün, *Beziehung zwischen elastischen Konstanten und Dehnungs doppelberechnung hochelastischer Stoffe*, Kolloid-Zeitschrift 101, 248-271, (1942).
- [9] *Chapter 10* in “Introduction to Finite Element Methods”, Department of Aerospace Engineering Sciences, University of Colorado at Boulder, (2011).