Statistical Characterisation of TEM Images of Silica-filled Rubber

A. Tscheschel*, D. Stoyan
Institut für Stochastik, TU Bergakademie Freiberg, Germany

J. Lacayo
Continental AG, Hannover, Germany

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Summary

Transmission electron microscopy (TEM) is used to study the micro-dispersion of silica fillers within the polymer matrix of rubber. The resulting grey-value images are interpreted as realisations of random fields and characterised by means of variograms. To serve this purpose, the so-called Cauchy class is a suitable model. Statistical analysis shows that different filler dispersion properties are reflected in different variogram parameters. As a form of case study, the random field approach is demonstrated for four exemplary rubber compounds.

*Correspondence to: A. Tscheschel. Fax: +49 3731 39 3598; e-mail: A.Tscheschel@gmx.net
Introduction

Elastomers are cross-linked polymers with a low modulus and the capability to reverse large deformations at their service temperatures. The process of creating cross-links in a polymer matrix is known as vulcanisation in rubber technology. Thus, polymers in vulcanised rubber are elastomers. The low modulus of elastomers combined with their high reversibility of deformation allows a wide range of industrial applications. Developing rubber products includes dedicated efforts of materials engineering with the aim to improve the properties of a specific rubber compound for a certain application. Such optimised compounds are commonly composed of special polymer blends, fillers, chemical vulcanisation aids, and other chemical additives to improve processing and ageing behaviour. For instance, a conventional tire for passenger cars contains more than ten different rubber compounds developed for a specific purpose at a precise position within the tire.

In most cases, the role of the fillers is to increase the strength of the vulcanised rubber, as reinforcing active fillers. Inactive fillers do not primarily influence the mechanical properties of the rubber, but include other effects like colour, volume, absorption of radiation or sound. There are only a few applications for unfilled elastomers. Rubber materials as widely used in industrial products, like tires, are filled elastomers.

The reinforcement of rubber materials by active fillers signifies an increase of the modulus of elasticity and an improvement of the ultimate properties like tear and tensile strength as well as abrasion resistance. The effect of the reinforcement by
active fillers is also crucial for the dynamic-mechanical properties of the elastomers, and thus, for the behaviour of the rubber product under dynamic conditions. In the case of tires, dynamic mechanical properties of materials directly influence product characteristics like rolling resistance and ABS-wet braking.

Active fillers are able to interact with the surrounding elastomer matrix forming physical or chemical links to the polymer chains. The most important reinforcing active fillers in rubber technology are carbon black and silica. Overview articles about the filler reinforcement of elastomers were published, for example, by Medalia & Kraus (1994), Donnet & Voet (1976) and Donnet (1998).

The reinforcement mechanism is based on the Payne effect. Mechanical property enhancement in filled elastomers is the result of combining the properties of the elastomers, the hydrodynamic effect, the elastomer-filler interaction, and the filler-filler interaction. Built on the filler-filler interaction, active fillers form a three-dimensional network that is responsible for the reinforcement and the hysteretic effects, see Donnet (1998), Gerspacher et al. (1994) and Heinrich & Vilgis (1993). Because of the strength of the filler-filler interaction, active fillers cannot be observed as isolated elementary particles (10 - 30 nm). They always tend to create aggregates (100 - 300 nm) as primary sub-units, and those aggregates will generate self-identical agglomerates (in the sense of the theory of fractals) covering several degrees of magnitude in size during the agglomeration process. Since filler-filler and filler-polymer interaction are decisive for the mechanism of elastomer reinforcement, it is plausible that there is a connection between the properties of the reinforced rubber
after vulcanisation and the morphology of primary aggregates and their distribution in the elastomer matrix.

Apart from its importance for understanding the reinforcement mechanism, filler distribution is also an indicator of the quality of rubber processing. Fillers with different grades of surface area (elementary particle size) and structure (aggregate shape, branching) will differ in processability as indicated by the degree of their incorporation into the matrix, the breakdown of their agglomerates into aggregates, and the random distribution of those aggregates. Diverse steps of rubber processing influence filler dispersion in different ways. The measurement of filler dispersion is indicative of the quality in rubber processing. Filler dispersion is measured at two levels: macro-dispersion, which characterises the incorporation of fillers into the matrix, and micro-dispersion, which describes the random distribution of aggregates in the matrix. The latter can be investigated directly by methods like TEM and Atomic Force Microscopy, or indirectly by dynamic-mechanical tests. Thus, the measurement of the undispersed part, which is the remaining amount of agglomerates not incorporated into the matrix (Medalia & Kraus, 1994), is the common way to differentiate the dispersion of fillers in elastomers avoiding the methods mentioned above. A brief overview of methods used to characterise macro-dispersion was presented by Kelbch et al. (2003). However, the topic of the distribution of the incorporated fillers is only accessible by the measurement of micro-dispersion. Based on Transmission Electron Microscopy and Automated Image Analysis (TEM/AIA), several methods of characterisation for the aggregate morphology of fillers have been
developed (Maas & Gronski, 1999; Gruber & Herd 1997; Herd & Gruber, 1998). Aggregate characterisation is commonly performed on both raw materials of the filler and filled elastomers at low loading.

TEM images are considered as powerful tools to qualitatively characterise micro-dispersion, but they are difficult to be quantified at the high levels of filler loading typically used in tire technology because of the three-dimensional superposition of the aggregates inside agglomerates. The aim of this paper is to develop an adequate statistical approach to investigate the variability of the micro-distribution of fillers within a polymer matrix. Statistical analysis is concentrated on the grey-value distribution of the TEM images, as shown in Fig. 1. They are considered as realisations of random fields, and analysed by means of geostatistical methods.

Materials and experimental setup

Both elastomers and active fillers used in tire technology are amorphous materials. Thus, rubber compounds are observed in TEM in the so-called scattering contrast. In the bright field mode of TEM, the diaphragm in the focal plane of the objective stops all electrons scattered through angles greater than the objective aperture after passing through the object. The transmitted intensity $I$ of the electron beam for a given objective aperture depends on the primary intensity $I_0$, the mass-thickness $\varrho \cdot t$ ($\varrho$: density, $t$: thickness) and the scattering conditions, the latter being given by the scattering constant $S$, which depends on electron energy and material composition. In most cases, elastomers are used as blends in rubber products. It is not possible to
separately visualise their phase morphology by means of TEM, since their densities are very similar (about 1 g/cm$^3$). TEM imaging of elastomer phase morphology requires experimental techniques of staining. Therefore, TEM images of unstained rubber compounds filled with carbon black or silica can be regarded as images of two-phase materials, in which one phase corresponds to filler particles and the other one to the elastomers. In these images, filler particles appear as dark objects, because of their higher density (about 2 g/cm$^3$). Since they are projections of thin sections of a certain thickness, several filler particles may overlap. The more filler particles overlap the darker is the TEM image at the specific position. Although the methods described in the present work were developed and tested using real rubber compounds typical for tire applications, also experimental compounds were prepared in order to systematically illustrate the statistical analysis approach. The compound recipes are shown in Tab. 1 and expressed in the mass unit phr (per hundred rubber), which is a non-SI unit used in rubber technology that relates the mass of ingredients to the mass of the main component: rubber.

The experimental compounds consist of styrene-butadiene-rubber (SBR) filled with 85 phr silica and two different contents of silane without any changes or adaptation of the mixing process. Silane is the coupling agent for filler reinforcement. The mechanism of the coupling agent comprises two phases: first, the silanisation reaction with the silica surface during mixing, and second, the formation of cross-links between the modified silica surface and the polymer during vulcanisation. The silanisation reaction leads to hydrophobic behaviour of the modified silica surface in-
fluencing the dispersion properties. Expectations justifying the experimental set-up are the following. Compound A is the reference compound with the optimal mixing process. Compound B is based on the same recipe of compound A but with an excess of silane. It is known that excessive silane content, meaning without adaptation of the mixing procedure, leads to slippery mixing goods affecting the dispersion of the fillers. Compound C is the result of mixing A and B, now yielding 7 phr silane on average. As the mixing time of compound C is considerably increased, it should lead to a higher dispersion grade in comparison to both A or B. Finally, compound D is a mixture of compound A and 10% unfilled SBR rubber. Thus, D is expected to have a lower dispersion grade than A, showing more inhomogeneities. It is reasonable to assume that the process of vulcanisation does not influence filler dispersion properties. In the present study, all four compounds were vulcanised in the same way (160 °C, 14 min).

Specimens for TEM were prepared by means of ultra-cryomicrotomy. Thin cuts of 100 nm thickness were obtained from frozen samples of each compound. Since the particle size of elementary silica particles forming aggregates is nearly constant 20 nm, a maximum of 5 particles may overlap within the 100 nm foils. Elementary particles can be considered as being not divisible. Hence small caps to the outside occur when particles exceed the border of the thin section or small empty caps when particles are removed. The exceeding and empty caps at the border are less than half particle size and this effect is neglected in the following.

The specimens were investigated with a conventional transmission electron mi-
croscope at only 80 kV accelerating voltage in order to increase the scattering con-
trast. The transmission electron microscope was equipped with an in-column digital
camera to acquire 12 bit grey-value images whose grey levels correspond to the in-
tensity of the electron beam in the image plane. Ten images of each compound at
different positions were taken at a nominal magnification of 50000-times, yielding
images of size 1280 pixels × 1024 pixels corresponding to an area of 1.94 µm × 1.56 µm.
The selection of the specific magnification represents an optimum: The statistical
error increases at higher magnifications because of the smaller area investigated;
at lower magnifications, image details get lost in consequence of the lower pixel
resolution. Fig. 1 shows typical TEM-images for each compound.

Methods and results

Image calibration

The grey-value $grey(x)$ at location $x$ of a TEM image corresponds to the intensity
$I(x)$ of the electron beam on the image plane after passing through the object at
location $x$. It is assumed that $grey(x)$ is proportional to $I(x)$.

The intensity $I_0$ of the electron beam before passing through an object is called
primary intensity. It depends on the nominal parameters of the transmission electron
microscope and is consequently image-dependent. Inhomogeneity properties of $I_0$
are reduced using an adapted background filter, as described below.

After passing through the object, the intensity $I$ of the electron beam is given
by

\[ I = I_0 \exp\{-t \varrho S\}, \]

(1)

where \( t \) and \( \varrho \) are the thickness and specific density of the object and \( S \) the scattering constant.

In the case of unstained specimens, the images show the distribution of two phases: the polymer and the filler. The local filler loading \( \lambda(x) \) denotes the relative fraction of the filler at location \( x \). The absolute thickness of the filler phase at location \( x \) is given by \( \lambda(x) \cdot t \), where \( t \) again denotes the thickness of the object. For all images to be considered, the same thickness \( t \) should be used. The absolute thickness of the polymer phase at location \( x \) is given by \([1 - \lambda(x)] \cdot t\).

The beam intensity \( I(x) \) after passing through a filled compound can be calculated by subsequent application of Eq. (1) on the filler phase and the polymer phase, i.e.

\[
I(x) = I_0 \cdot \exp\{-\lambda(x) \cdot t \cdot \varrho(\text{filler}) \cdot S(U, \text{filler})\}
\]

\[
\cdot \exp\{-[1 - \lambda(x)] \cdot t \cdot \varrho(\text{polymer}) \cdot S(U, \text{polymer})\}
\]

\[ = I_0 \cdot \exp\{-t \cdot \varrho(\text{polymer}) \cdot S(U, \text{polymer})\}
\]

\[
\cdot \exp\{-\lambda(x) \cdot t \cdot [\varrho(\text{filler}) \cdot S(U, \text{filler}) - \varrho(\text{polymer}) \cdot S(U, \text{polymer})]\}.
\]

Taking logarithms leads to

\[
\ln(I(x)) = c_1 - c_2 \lambda(x)
\]
with

\[ c_1 = \ln(I_0) - t \cdot \rho(\text{polymer}) \cdot S(U, \text{polymer}), \]
\[ c_2 = t \cdot [\rho(\text{filler}) \cdot S(U, \text{filler}) - \rho(\text{polymer}) \cdot S(U, \text{polymer})]. \]

While \( c_1 \) is an image-dependent constant, \( c_2 \) is image-independent, provided the specific densities of filler and polymer remain the same. The proportionality between \( \text{grey}(x) \) and \( I(x) \) leads to

\[ \ln(\text{grey}(x)) = \ln(c_3 \cdot I(x)) = c'_1 - c_2 \lambda(x) \] (2)

with \( c'_1 = \ln(c_3) + c_1 \). Here, \( c_3 \) is the proportionality factor between \( \text{grey}(x) \) and \( I(x) \).

Because the subject of investigation is the distribution of filler loading \( \lambda(x) \) and not the distribution of beam intensity \( I(x) \), relation (2) gives a plausible reason to use \( \ln(\text{grey}(x)) \) instead of \( \text{grey}(x) \).

As aforementioned, the TEM images are preprocessed by means of background filtering. All subsequent computations use floating point arithmetics, omitting unnecessary rounding operations. In the first step, double iteration of an averaging filter with an \( N \times N \) matrix is applied to the original image with \( N = 197 \) pixel (300 nm). The resulting image is a first approximation of the background intensity image, its grey-values are denoted by \( b_1(x) \). This first background image is highly affected by image objects (filler particles). A ‘reduced’ image is given by its grey-values \( b_2(x) \) as

\[ b_2(x) = \max(\text{grey}(x), b_1(x)). \] (3)
In this image, the very dark grey-values corresponding to image objects are replaced by the lighter local background intensity. Double iteration of the averaging filter is applied to the ‘reduced’ image yielding a new background intensity image with grey-values \( b_1(x) \). \( b_2(x) \) is updated accordingly to Eq. (3). After applying the averaging filter to the ‘reduced’ image, the resulting background image characterises the distribution of primary intensity \( I_0 \). Consequently, the original image is pixel-wisely divided by the background image, a procedure which yields very homogeneous images. This filtering procedure reduces effects resulting from inhomogeneously distributed image illumination, as given by primary intensity \( I_0 \), and is only little affected by image objects.

The size of the averaging filter \((N = 197 \text{ pixel})\) was carefully chosen: If \( N \) is too large, then no background filtering takes place; if \( N \) is too small, then there is a heavy influence of image objects on the background intensity image. Edge effects play some role: The averaging filter is for pixels near the image border smaller than for pixels in the image centre. That means that image objects influence the border of the background intensity image. Hence it is useful to exclude the border of the filtered image in the further analysis.

**Grey-value images and random fields**

Grey-value images, as shown in Fig. 1, are given as arrays \((x, \text{grey}(x))\), in which a grey-value \( \text{grey}(x) \) belongs to every pixel \( x \). Taking logarithms leads to arrays \((x, Z(x))\) with \( Z(x) = \ln(\text{grey}(x)) \). In the modelling approach of this paper, pixels \( x \)
are points in the Euclidean plane \( \mathbb{R}^2 \). \( Z(\mathbf{x}) \) is a random variable, and consequently, family \( \{Z(\mathbf{x})\} \) is a random field. The theory of random fields and their statistics is described in books on geostatistics, for example Chilés & Delfiner (1999), Cressie (1993) and Matheron (1971). An other example for the analysis of TEM images by means of geostatistical methods is Pinnamaneni et al. (1991).

Investigation of Fig. 1 and similar images of filled elastomers suggests that filler distribution is statistically stationary (homogeneous) and isotropic. The distribution of the random field is invariant with respect to translations and rotations. This does not mean that all properties of filled elastomers are homogeneous, which is unlikely the case for the polymer network after vulcanisation (Vilgis & Heinrich, 1994).

The first order characteristic of a stationary random field is its mean \( m \),

\[
E Z(\mathbf{x}) = \langle Z(\mathbf{x}) \rangle = m,
\]

where \( E \) denotes the expectation operator. Because of stationarity, mean \( m \) does not depend on \( \mathbf{x} \). For the investigation of TEM images however, mean \( m \) is non-informative because \( m \) depends directly on the image-dependent constant \( c_1 \) in Eq. (2).

The usual second order characteristic of random fields is the (semi-)variogram \( \gamma(\mathbf{h}) \), which is defined as the half mean squared difference of the field values at \( \mathbf{x} \) and \( \mathbf{x} + \mathbf{h} \),

\[
\gamma(\mathbf{h}) = \frac{1}{2} E (Z(\mathbf{x}) - Z(\mathbf{x} + \mathbf{h}))^2,
\]

where \( \mathbf{h} \) is a difference vector. Because of the stationarity assumption, \( \gamma(\mathbf{h}) \) does
not depend on $x$; because of the isotropy assumption, $\gamma(h)$ depends only on the length $h$ of $h$ or the distance $h$ between $x$ and $x + h$. Therefore, in the following the symbol $\gamma(h)$ is used.

A variogram $\gamma(h)$ has the properties

$$\gamma(0) = 0$$

and

$$\gamma(\infty) = \sigma^2,$$  \hspace{1cm} (4)

where $\sigma^2$ is the field variance ('sill'), i.e. the variance of $Z(x)$.

Because the variogram only characterises differences between random variables, it depends neither directly on mean $m$ nor the image-dependent constant $c'_1$ from (2). Thus, the variogram characterises the variability of the local filler loading $\lambda(x)$.

The speed of convergence of $\gamma(h)$ towards $\sigma^2$ for $h \to \infty$ characterises the range of correlation. If there is a finite $h_0$ with $\gamma(h) = \sigma^2$, for $h \geq h_0$, then $h_0$ is called range of correlation. Otherwise the smallest value $h_p$ with $\gamma(h_p) = (1-p)\sigma^2$ is used for some $p$. The specific value $h_{0.05}$ is often called practical range. In this paper, $h_{0.5}$ is used in order to obtain a statistically robust parameter and is called median range. Obviously, the median range $h_{0.5}$ is smaller than the practical range $h_{0.05}$.

It is possible that

$$\lim_{h \to 0} \gamma(h) = \kappa^2 > 0.$$  

If this is the case, there is a nugget effect and $\kappa^2$ is called nugget variance. The nugget effect indicates short-range irregularities caused by very small structures or measurement errors.
Estimating variograms from the observed arrays \((x, Z(x))\) yields so-called sample variograms or empirical variograms \(\hat{\gamma}(r)\). The usual geostatistical variogram estimator, see e.g. Chilès & Delfiner (1999), is given by

\[
\hat{\gamma}(h) = \frac{1}{2N_h} \sum_{|x_\beta - x_\alpha| = h} (Z(x_\beta) - Z(x_\alpha))^2,
\]

(5)

where the sum is extended to the \(N_h\) pairs \((x_\beta, x_\alpha)\) of image pixels of distance \(h\).

**Characterisation of compounds by random field characteristics**

For each compound there is an ideal random field \(\{Z_0(x)\}\) with mean \(m = 0\). The observed random fields \(\{Z_i(x)\}\) are realisations of the ideal random field plus image-dependent means \(m_i\), i.e.

\[
Z_i(x) = Z_0(x) + m_i.
\]

(6)

This approach is motivated by Eq. (2).

The empirical variograms estimated from a number of TEM images can be interpreted as estimates of the variogram of the ideal random field \(\{Z_0(x)\}\). Thus, the variogram of each TEM image characterises the variability of filler distribution of its corresponding compound. Because of statistical fluctuations, the empirical variograms of the TEM images of the same compound may differ slightly.

The two most important variogram characteristics for our analysis are field variance \(\sigma^2\) and median range \(h_{0.5}\). They can be interpreted in the context of filler distribution as follows: A high field variance \(\sigma^2\) indicates high fluctuations in local
filler loadings and consequently indicates the existence of big clusters of filler particles and/or unfilled areas. In contrast, a small field variance $\sigma^2$ is the result of nearly constant local filler loadings. Thus, $\sigma^2$ is a measure of the grade of micro-dispersion of filler particles. Smaller values of $\sigma^2$ indicate a higher grade of dispersion. The median range $h_{0.5}$ is related to the size of ‘objects’, which are either clusters of filler particles or unfilled areas. In particular, small values of $h_{0.5}$ indicate smaller objects and consequently a higher grade of dispersion.

The field variance can be estimated either from the empirical variogram using relation (4) or using

$$\hat{\sigma}^2 = \frac{1}{n-1} \sum_{x} (Z(x) - \bar{z})^2,$$

where $n$ is the number of pixels and $\bar{z}$ is the mean grey-value given by

$$\bar{z} = \frac{1}{n} \sum_{x} Z(x).$$

The median range $h_{0.5}$ can be estimated from the empirical variogram.

**Exemplary case study**

For each compound A, B, C and D, 10 TEM images were investigated. This led to 40 estimates for the field variance $\sigma^2$ and the median range $h_{0.5}$. The results are shown in Fig. 2. The four point clouds corresponding to compounds A, B, C and D are relatively compact and well separated. In particular, Fig. 2 clearly shows that both the variances $\sigma^2$ and the median range $h_{0.5}$ of the images corresponding to compound A are smaller than those of compound B. This indicates that A has
got better dispersion properties than B and, consequently, that the silane content is probably too high in the compound recipe of B.

The median range of compound C is similar to the median range of A but it has a slightly smaller variance. Thus, C has the best dispersion properties, which is plausible because of the long mixing time it has experienced. Finally, the values for compound D are located between those of A and B, which confirms the assumption that D has a lower dispersion grade than A.

Fig. 2 clearly shows a plausible positive correlation between $\sigma^2$ and $h_{0.5}$: A low dispersion grade caused by large clusters of filler particles induces high values of both $\sigma^2$ and $h_{0.5}$. The joint observation of both characteristics allows to discriminate different compounds.

**Variogram models and simulations**

Geostatisticians have developed several theoretical variogram models. These models help to interpret the spatial variability, and they introduce further useful variogram parameters.

As a suitable and flexible approach, this paper applies variograms from the so-called Cauchy class having the form

$$
\gamma(h) = \sigma^2 \cdot \left\{ 1 - \left[ 1 + \left( \frac{h}{a} \right)^{\alpha} \right]^{-\frac{\beta}{\alpha}} \right\}.
$$

Any combination of the parameters $\sigma^2 > 0$, $a > 0$, $\alpha \in (0, 2]$ and $\beta > 0$ is permitted. $\sigma^2$ is the field variance as above. $a$ is a scale parameter. This means that the
variogram graph is stretched by the factor $a$ (see Fig. 3). $\alpha$ is the first shape parameter. For small $h$, $\gamma(h)$ behaves asymptotically like $h^{\alpha}$. The smaller $\alpha$ the greater is the short-range irregularity of the random field. $\beta$ is the second shape parameter, which has influence on the speed of convergence of $\gamma(h)$ towards $\sigma^2$: $\sigma^2 - \gamma(h)$ behaves asymptotically like $h^{-\beta}$ for large $h$. The smaller $\beta$ the greater are the long-range correlations. According to Gneiting & Schlather (2004), the shape parameters $\alpha$ and $\beta$ are related to the concepts of fractal dimension and Hurst coefficient characterising fractal processes. However, the grey-value structures are not considered here from a fractal point of view. Nevertheless, $\alpha$ and $\beta$ may serve as valuable model parameters.

Variograms of the Cauchy class do not have a finite range of interaction. Therefore, range parameters $h_{0.05}$ or $h_{0.50}$ are used. Cauchy class variograms do not have a nugget effect. Investigation of the empirical variograms for small $h$ supports the assumption that there is no or only a negligible nugget effect. However, the application of high pass filters on the TEM images increases the short-range irregularity and, consequently, the nugget effect.

The parameters of the Cauchy class model are estimated using the least square error method. The variogram is determined by the best fit of the empirical variogram. In this method, a robust estimation of $\beta$ is not possible with the experimental data. Thus for the present analysis, the parameter $\beta$ is set constant to 4 yielding good fits for all variograms investigated. Fig. 4 shows the empirical variograms of the four images shown in Fig. 1 and their corresponding best fits of the Cauchy class
model. The agreement between the empirical variograms and the theoretical ones is good, i.e. the sum of squared errors is small compared to other standard variogram models. In particular, the characteristic shape in the range of 50–200 nm is matched very well; even the deviation for D-2 can be explained by statistical fluctuations. So we conclude that the Cauchy model may serve as reasonable approximation.

The estimated parameters for the images shown in Fig. 1 are given in Tab. 2. For illustration, Fig. 5 shows two simulated realisations of Gaussian random fields with Cauchy variograms using the estimated parameters of the images A-6 and B-4. Gaussian random fields are random fields where \( Z(\mathbf{x}) \) and random vectors \( (Z(\mathbf{x}_1), \ldots, Z(\mathbf{x}_n)) \) have multivariate Gauss distributions. The similarity between the simulations and the original images is obvious, showing that a large amount of information from the associated random field is contained in the second order characteristics. However, a Gaussian random field is a realistic model only in the (most important) case of filled elastomers having a high volume content of fillers, if applied to \( \{\ln(\text{grey}(\mathbf{x}))\} \). The simulations have been performed using the Random-Fields package (Schlather, 2001) in the statistical computing environment R.

**Conclusions**

The random field method is a suitable approach to characterise the micro-dispersion of fillers in rubber visualised by TEM. The grey-values of TEM images are interpreted as local filler loadings. Uniformly distributed local filler loadings mean adequate micro-dispersion. In contrast, strong fluctuations indicate inadequate micro-
dispersion, caused by big clusters of filler particles and unfilled areas.

The random field method has got two advantages over methods which analyse binarised images: fluctuations in the grey-values are exploited without using a threshold grey-value, which is often difficult to adjust. Binarisation becomes dubious when the unfilled area is rather small, as this is the case for highly filled rubber.

The present paper applies two random field parameters: variance $\sigma^2$ and median range $h_{0.5}$. Variance $\sigma^2$ describes the level of fluctuations of the local filler loadings, while median range $h_{0.5}$ is a measure of the size of objects such as clusters of filler particles or unfilled areas. Thus, both characteristics describe aspects of the grade of dispersion. Obviously, $\sigma^2$ and $h_{0.5}$ together are successful in the description of the dispersion grade of different compounds.

In the presented case study, $\sigma^2$ and $h_{0.5}$ were successfully used to discriminate the dispersion grade of four experimental compounds.

Finally, variograms from the Cauchy class fit the empirical variograms very well. Simulations of Gaussian random fields with suitable Cauchy variograms show that indeed valuable information is contained in the second order characteristics of random fields.

The random field approach is not only of interest for characterising TEM images of filled rubber, but also for images containing valuable information in the grey-value distribution without any affordable possibility of three-dimensional reconstructions.
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<td>SBR</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Oil</td>
<td>37.5</td>
<td>37.5</td>
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<td>1.8</td>
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<tr>
<td>Compound C</td>
<td>50% Compound A + 50% Compound B</td>
<td></td>
</tr>
<tr>
<td>Compound D</td>
<td>90% Compound A + 10% SBR</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Estimates of random field characteristics for the images shown in Fig. 1: median range $h_{0.5}$, variance $\sigma^2$ and Cauchy class parameters $a$ and $\alpha$.

<table>
<thead>
<tr>
<th></th>
<th>A-6</th>
<th>B-4</th>
<th>C-6</th>
<th>D-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{0.5}$ (nm)</td>
<td>26.0</td>
<td>39.4</td>
<td>23.0</td>
<td>36.4</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>0.031</td>
<td>0.045</td>
<td>0.025</td>
<td>0.038</td>
</tr>
<tr>
<td>$a$ (nm)</td>
<td>59.7</td>
<td>90.3</td>
<td>62.7</td>
<td>74.2</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.44</td>
<td>1.48</td>
<td>1.35</td>
<td>1.55</td>
</tr>
</tbody>
</table>