Numerical model of randomly distributed particles generated from the material structure as a quantitative analysis of structure/rheology relationship

BERENIKA HAUSNEROVA[1], JAN ZIDEK[2]

[1]Centre of Polymer Systems
Polymer Centre
Tomas Bata University in Zlín
nám. T.G.Masaryka 5555, 760 01 Zlín
CZECH REPUBLIC
hausnerova@ft.utb.cz http://web.utb.cz/
[2]Institute of Materials Chemistry
Brno University of Technology
Purkynova 118, 612 00 Brno
CZECH REPUBLIC
zidek@fch.vutbr.cz

Abstract: A numerical model is used to relate particle filler characteristics to flow properties of 50 vol. % polymer based composites. The model allows transformation of material structure to a virtual one, and thus compares structural and rheological behaviour in a quantitative way. The reliability of the method is demonstrated by a close proximity of simulated and experimental (SEM micrographs) structures. The obtained structural functions in terms of the statistical distribution of interparticle distances and the histograms of particle clusters are ordered in the following way: BC10U ≈ BC17S < BC37S < BC55S < BC75H corresponding precisely to the powder particle size distributions as well as flow properties of tested materials.

Key-Words: numerical model, particle size distribution, highly filled polymer melts, interparticle distance, viscosity

1 Introduction

The relation between characteristics of a particle filler and flow properties in a composite is complicated by the high number of material (particle size and its distribution, particle shape, matrix composition) and process variables (mainly packing conditions), and also affected by interparticle interactions resulting in redistribution and reorientation of a composite structure. The structure control in terms of tailoring powder characteristics brings the necessity to correlate physical properties e.g. viscosity to the material structure of the studied systems in the quantitative way.

Structural properties are usually determined by electron microscopy or X-ray and related qualitatively to macroscopic properties by means that e.g. SEM micrographs of two or more materials are compared and given to the relation to the physical properties.

The numerical model presenting the structure of material transformed to the virtual structure serves as an extension of such methods as introduced by Torquato [1] or Tovmasyan et al [2]. The transformation to the model has an advantage of a quantitative 3D insight in comparison to the direct analysis of real structure performed with 3D Raman spectrometry, X-ray tomography, or 3D transition electron microscopy, which can draw the domains of different phases, but still is limited to the qualitative insight only. Important advantage of the numerical model is also the possibility to analyze material, which has not been prepared yet.

The model proposed in this paper can predict formation of particle clusters, interparticle distances, or space cells in the matrix between particles and clusters (agglomerates). If some property is related to the material structure, it is supposed to be related also to the virtual (model) structure in the same way.

2 Problem Formulation

The set-up of the model is similar to the work with the real material as schematically shown in Table 1.

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The input variables are only powder particle size distribution and its volume fraction. The model outputs are model properties analogous to real material - for example SEM image, and those, which are only the model outputs - a histogram of interparticle distances or particle clusters. The task is to relate such functions to macroscopic properties as viscosity and provide a quantitative analysis of structure/flow property relationship.

Table 1 Parameters of real and model structures.

	Real	Model
Intput	particle size distribution	distribution of spheres diameters
	volume fraction of filler	volume fraction of spheres
Output	SEM image	simulated image
	flow properties	quantified structure

3 Problem Solution

3.1 Experimental

Particle filler based on tungsten carbide was admixed into polyolefin based matrix in a laboratory kneader (Brabender Plasticorder PL-2000-6, mixer type W 50E) at 150 °C and 80 rpm. Five types of compounds were tested (BC10U, BC17S, BC37S, BC55S, and BC75H) differing in their particle size distributions as shown in Figure 1.

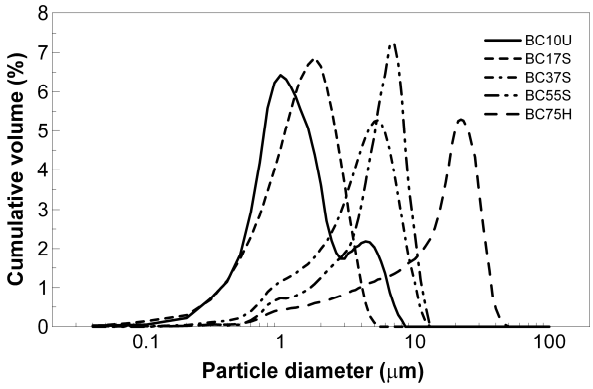

Figure 1 Particle size distributions of powders used as composites filler.

Flow properties in terms of complex viscosity were measured with plate-plate rotational rheometer (ARES, Rheometrics, USA) equipped with RSI orchestrator software package. Plate diameter was 25 mm, angular frequency ranged from 0.1 to 100 rad/s at 140, 150 and 160 °C.

3.2 Results and Discussion

The model was generated by AGLOMER software [1] using the cumulative distribution function of particle size and the volume fraction of employed powders. The generation method has implemented a function of controlled macroscopic homogeneity; 95% of all generated systems have the difference from desired concentration ≤ 1%. The software created a set of coordinates and radii of individual particles as shown in Figure 2.

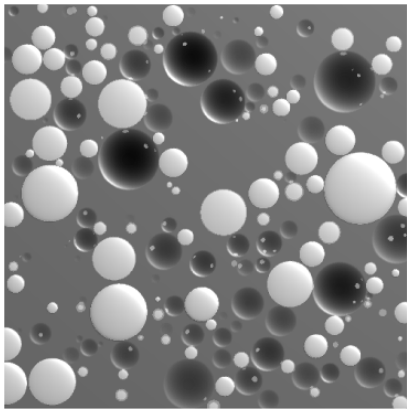

Figure 2 Material structure obtained from the model (example for composite based on BC 37S powder).

The plane was projected in the model. The intersection of particles and plane generated several types of visible objects; three types of particles can be distinguished. First object is a particle which is visible in the matrix. The second object is the particle above the plane of fracture represented by a hole which appears after the extracted particle. The third type of particle is a particle which does not intersect with plane, but it shines through the matrix as it is not deeply under the surface. In the real SEM, there also exist particles, which are not at the surface, but they are registered by an electron beam.

In the following phase, the radii of points were forgotten. The shadows of particles were reduced to the central points. They were processed by Delaunay triangulation (DT), which represents an optimal division to triangle mesh. The vertices of triangles are the central points of particles shadows. They can be covered back by the shadow of particle with appropriate radius as shown in Figure 3. The lines, which stood visible, thus represented the width of channel of matrix in the interparticle space. They can be analyzed statistically.

The cluster (agglomerate) analysis was performed in the following way: the core of cluster is composed of two particles, whose distance is lower

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than some critical distance. In Figure 4 such pair is shown as grey dashed line connecting two particles. Then, all non-classified particles were investigated. If some particle was closer to some particle in a cluster, it was added to cluster. The particles were cumulated in the cluster until there existed the particles which can be added to the cluster.

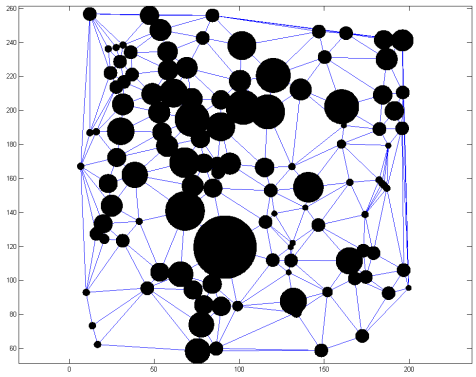

Figure 3 Delaunay triangulation of particle centres and covered by particles shadows.

The single parameter of this analysis is the critical distance. It is a distance when the particles are in the same cluster. It must have optimal value. If it will be too large, the particles will be in the percolated state. Above reaching percolation threshold, the cluster analysis is not valid.

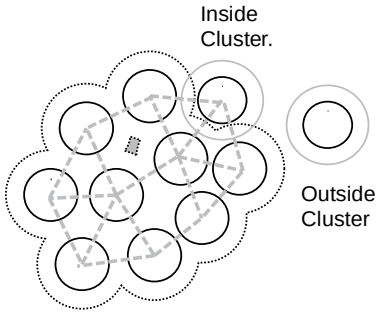

Figure 4 Analysis of a cluster: particle lying inside and outside the cluster; *solid circles* – particles, *dashed* lines detecting close contact, *dotted* lines representing boundary of a cluster.

The volume of cluster was calculated as a sum of volume of all particles in the cluster. The volume of a cluster in a model can be schematically approximated as surface of grouped squares in the sketch. Thus, the smaller were the volumes of clusters, the higher viscosity was expected. The cluster (agglomerated) sets were described by histograms, Figure 5.

As can be seen from the similarity of BC10U and BC17S powders as well as BC 37S and BC55S in terms of their particle size dsitributions (see Figure 1), the model precisely reflects characteristics of powders.

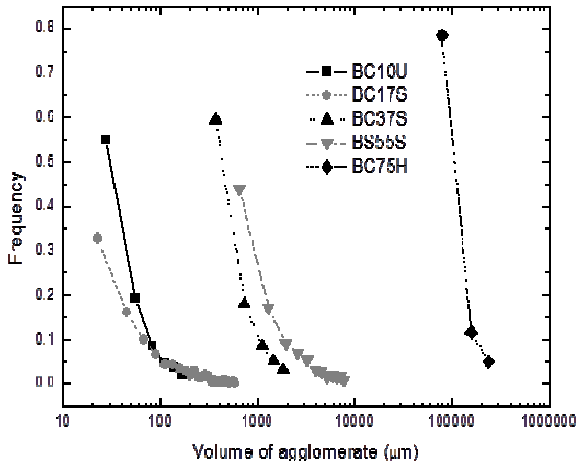

Figure 5 Histograms of effective volumes of clusters (agglomerates) of close particles; data calculated from the model.

The results presented with histogram reflect the flow properties represented by complex viscosity of composites, which is ordered in the following way: BC10U ≈ BC17S > BC37S > BC55S > BC75H as shown in Figure 6.

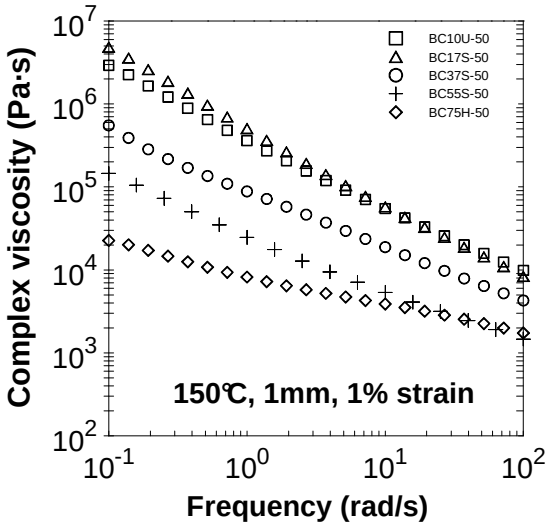

Figure 6 Flow properties of 50 vol. % composites.

Finally, the reliability of the model was tested via comparison of simulated images with scanning electron microscope (SEM) ones acquired from a plane of crack as demonstrated with Figure 8. The particles were first recognized by the procedure of

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automatic (pattern) recognition of spots. It was failed due to a weak contrast. Therefore, the spots belonging to the particles were detected in a graphic editor based on vector graphics.

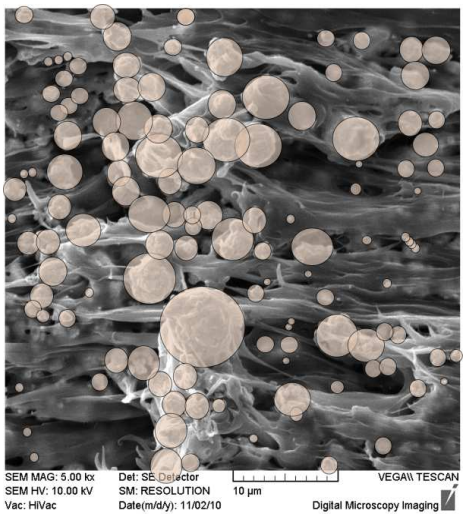

Figure 7 Material structure obtained from SEM analysed in a graphic editor based on vector graphics (example for composite based on BC 37S powder).

The vector graphics is a coding of graphic files, which does not loose information about graphical objects. The spots corresponding to particles were covered by object of circles. The circle is a shadow of particle in a vector graphic file. The properties of shadows coordinates and radii were exported, and the Delaunay triangulation analysis was applied as described for simulated (model) structure.

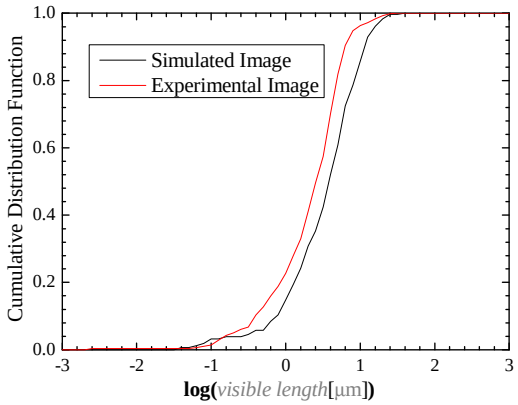

Figure 8 Distribution of visible lengths by the triangulation method for material based on BC37S powder - comparison of real and model structures.

As demonstrated on analysis of interparticle distances (visible lines) in Figure 8, the results obtained for real and model structure shows rather good agreement.

4 Conclusion

The obtained results imply that the numerical modelling might serve as the reliable and sensitive approach to analyze the influence of the particle size distribution of powder on the processability of the highly filled particle composites. The analysis of the simulated structure and the image derived from the real material serves as the confirmation of the model reliability.

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