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## Filler dispersion and associated tribological properties of rubber

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**Abstract:** A degree of filler dispersion is commonly used in industry as a criterion in evaluation of efficiency of mixing process and quality of rubber mixes. Paper presents new approach to phenomenon of filler dispersion and distribution in rubber. Conventional Philips' test, commonly used in rubber industry, has been found inadequate and fails in many cases. Analysis carried out in a sub-micron level can differentiate rubber samples according to material morphology and matches their exploitation characteristics. AFM pictures of filled rubber samples are presented and quantified applying a fractal analysis together with distribution of an average neighbouring distance between filler particles. Dynamic properties of rubber are more appropriate, in comparison to static ones, to exhibit differences in internal structure of agglomerates. In order to classify rubber samples according to their quality, simple friction tests have been suggested, and experimental parameters for the analysis proposed. Apart friction characteristics, very valuable seem to be their transformation into frequency domain. Energy spectra presented provide some information on wear of materials studied.

**Keywords:** Rubber and filler distribution, Dispersion, Friction and wear

### 1. INTRODUCTION

Vulcanized rubber mix is a multicomponent and multiphase system. Its morphology, determining exploitation properties of material, depends on several factors, both of material engineering and technological nature [1]:

1. type of a rubber matrix and its molecular and physico-chemical characteristics,
2. type of a filler, size distribution and surface activity of its particles,
3. overall mix composition
4. efficiency of mixing (deciding a degree of filler dispersion and uniformity of its distribution), and
5. parameters of vulcanization.

Many physico-chemical phenomena take place both between filler particles, as well as in a filler-matrix interphase on the following steps of rubber processing. Traditional approach to the problem of relationship between conditions of a rubber mix preparation and its morphology is oversimplified. It is generally assumed that distributive mixing should not

cause any problem on the present state of machine design. More attention has been paid to dispersive mixing, which efficiency is commonly assessed applying the so-called Philips' test. Size and number of agglomerates is controlled with a reflected light microscope under magnification of 100× and a number assigned according to ISO 11345 [2].

## 2. EXPERIMENTAL

### 2.1 Materials

Carbon black and silica mixes of isoprene (IR), styrene-butadiene (SBR) or ethylene-propylene-diene rubber (EPDM) were prepared with an internal laboratory mixer, under various technological regimes, in order to produce material of different morphology. Silica mixes contained 50 phr of both: silanized (Coupsil) or unsilanized (VN 3) filler. Carbon black of different activity (from N 234 to N 772) was added to the rubber in the amount from 30 to 50 phr. Specimens were vulcanized with sulphur under optimal conditions, determined rheometrically, according to ISO 3417.

### 2.2 Techniques

**Philips test (ISO 11345):** Cross-sectioned rubber samples were studied with a DisperGrader 1000 (Optronic S.A. USA) instrument under 100× magnification. Pictures of filler dispersion were compared to the reference “X” scale by computer software and value of a dispersion index (DI) assigned.

**Atomic Force Microscopy (AFM):** Surface morphology of rubber samples was studied with a Metrology Series 2000 (Molecular Imaging, USA) atomic force microscope. In the case of silica filled mixes images were collected applying the contact mode (LFC), making advantage of apparent difference between mechanical and tribological properties of the filler and the matrix. The commercial silicon cantilevers CSC 37 (MikroMasch, Estonia) were used. In the case of carbon black filled mixes the oscillating mode was applied, differing filler and a rubber matrix by their stiffness. The commercial silicon cantilevers NSC 16 or NSC 11 (MikroMasch, Estonia), operating with height and phase scale, were used at scan frequency of 1 Hz.

**Image Analysis – Fractal Approach (WSxM) [3]:** AFM and optical microscope images were analysed using the WSxM software, enabling fractal analysis and determination of an average distance between filler objects. Fractal dimensions of filler aggregates were calculated applying the so-called “slit island” approach. Prior to analysis pictures were binarized, assuming the filler cut-off level being adequate to the mix composition. The following equation was applied for calculations:

$$P = \mu A^{D/2}$$

where: P-perimeter of filler particles/agglomerates;  
A-area of filler particles/agglomerates;  
 $\mu$  - fractal factor;  
D-fractal dimension.

**Tribological properties:** Friction was determined with a block-on-ring T-05 tribometer (ITeE, Poland). The 35 mm of diameter rubber ring rotated against the flat block made of stainless steel with the rotational speed of  $n = 1.0$  rps (equivalent sliding speed calculated for the

contact surface was  $v = 12$  cm/s) and the normal load of 10 N. at ambient temperature ( $20^{+5}$  °C). The tribometer was equipped with a multi-channel electronic PC measurement unit – Spider 8 (HBM, Germany) for data acquisition. During experiment lasting 2 hrs the friction force was collected with frequency of 1200 Hz in 2000 scans, each containing 4096 experimental points. Example of a friction trace together with determined parameters are presented in Figure 1. The following parameters were calculated:  $T_0$  – starting value of a friction force;  $T_1$  – maximum value of a friction force;  $t_1$  – period of time before wear starts;  $T_2$  – friction force during “stable” wear;  $t_2$  – time for stabilisation of a friction force.

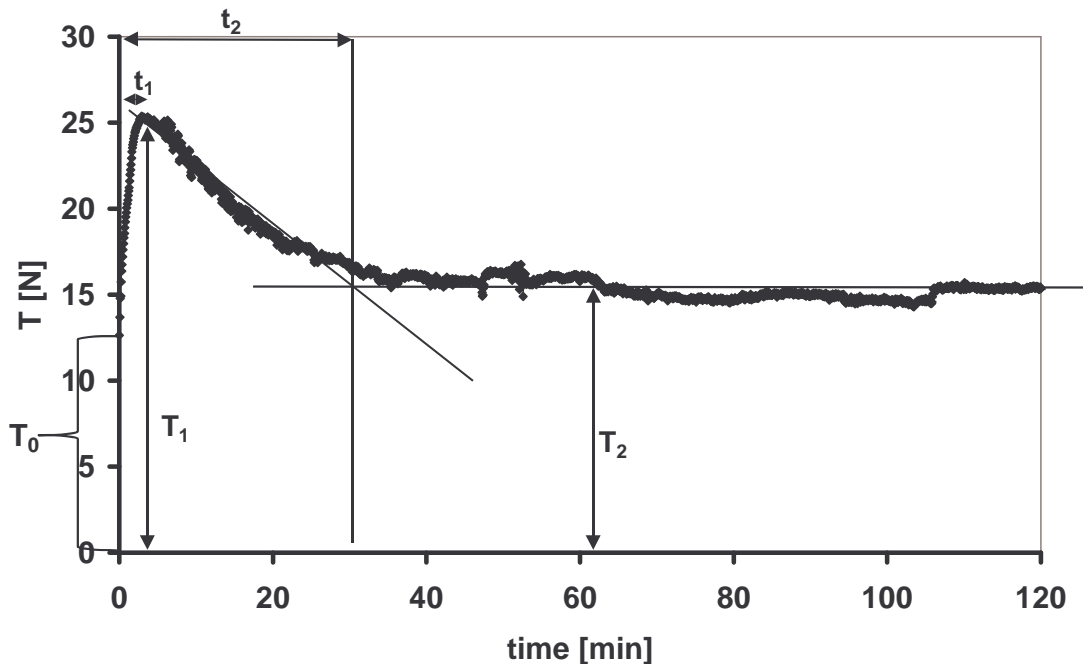


Figure 1. Example of a trace representing friction force versus time for rubber.

Friction characteristics were transformed into frequency domain applying the Fourier transformation to friction force fluctuations. Discrete levels of energy, dissipated by rubber samples during friction, were determined [4]. Example of an energy characteristics for rubber is given in Figure 2.

### 3. RESULTS & DISCUSSION

Magnification offered by a DisperGrader apparatus (Optronic, USA), operating according to ISO 11345 and commonly used in rubber industry, is not sufficient to reveal differences between a degree filler agglomeration in rubber mixes prepared with modern internal mixers. It requires application of more powerful analytical techniques, being able to look inside structure of filler agglomerates, e.g. atomic force microscopy (AFM), scanning electron (SEM) or transmission (TEM) microscopy. Internal morphology of agglomerates determines beginning of destruction processes taking place in a macro-scale and thus should reflect exploitation properties of rubber, especially under dynamic conditions [5]. Table 1 contains an example of micro-scale morphological analysis for series of carbon black mixes.

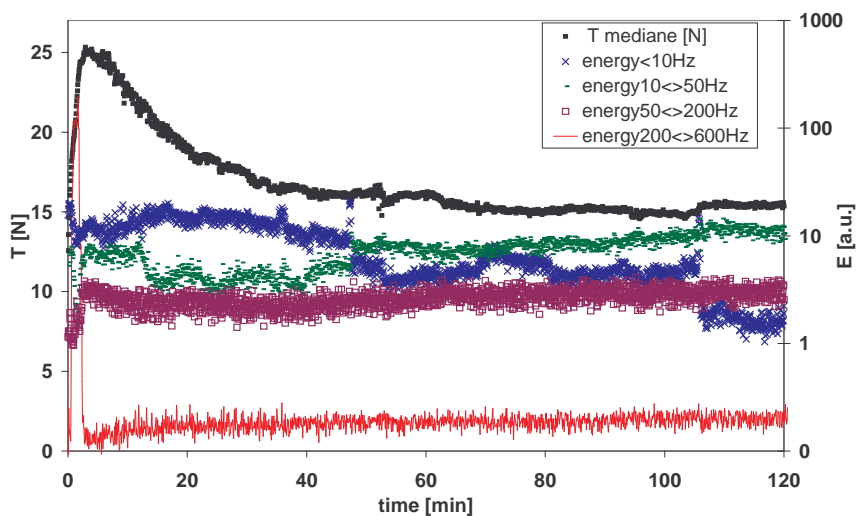
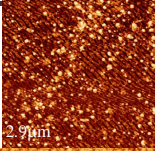
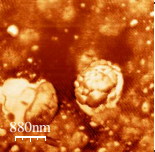
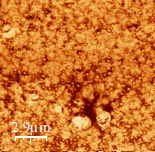
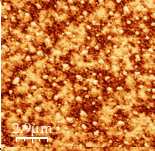
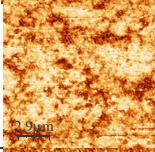
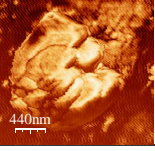
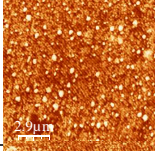
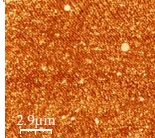


Figure 2. Example of an energy dissipation spectrum for rubber during a friction test.

Table 1.

An example of micro-scale morphological analysis for series of carbon black mixes (SBR/50phrN234).

Sample no.	Agglomerate structure / Filler distribution	Dispersion Index (DI)	Interparticle distance [ $\mu\text{m}$ ]		Fractal dimension (D)	
			average	median	average	median
1		2.4	866	871	1.89	1.87
2	 	5.8	866	876	1.87	1.87
3		2.5	956	962	1.94	1.93
4		1.9	1080	1080	1.83	1.83
5	 	6.1	773	767	1.88	1.89
6		6.1	847	837	1.90	1.91

Micro-morphological data, contrary to DI values, at least to some extent reflect tribological performance of the materials studied, what is demonstrated by tribological parameters given in Table 2.

Table 2.

An example of tribological analysis for series of carbon black mixes(SBR/50phrN234)

Sam ple no.	Friction characteristics					Dissipated energy [a.u.]					
	T <sub>0</sub> [N]	T <sub>1</sub> [N]	t <sub>1</sub> [min]	T <sub>2</sub> [N]	t <sub>2</sub> [min]	<t <sub>1</sub>	t <sub>2</sub> - t <sub>1</sub>	after t <sub>2</sub>	<t <sub>1</sub> h.freq	t <sub>2</sub> - t <sub>1</sub> h.freq	after t <sub>2</sub> h.freq
1	15,51	26,33	2,5	16,07	39,41	2188	9890	13497	1540	113	226
2	24,78	27,12	5,54	15,39	37,94	1040	1080	36670	254	30	264
3	19,22	28,74	3,05	18,14	36,66	3744	8452	13021	2949	79	167
4	17,35	26,76	10,70	20,44	42,25	3632	8542	17805	1076	134	288
5	16,62	23,34	2,38	13,53	40,61	5413	5461	9345	5003	101	220
6	19,83	28,08	7,99	18,90	43,11	4874	5410	13640	4105	125	250

#### 4. CONCLUSIONS

1. New approach to evaluation of fillers distribution and dispersion has been proposed.
2. Differences in morphology of filled rubbers are reflected by their tribological characteristics.

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