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CHARACTERIZATION OF DISPERSION MECHANISMS OF AGGLOMERATED FILLERS IN AN ELASTOMER MATRIX UNDER SHEAR BY IN-SITU OBSERVATIONS.

9th Fall Rubber Colloquium

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The mixing of carbon black or silica fillers and a polymer matrix in an internal mixer implies two processes: dispersion and distribution. To disperse implies to reduce the filler initial size (a hundred microns) down to the aggregate size (a few tens of nanometers). This size is necessary to ensure the reinforcement of the matrix. Although the mixing of a filler and a matrix is an usual operation, elementary mechanisms and key parameters responsible for the size reduction of the filler are not fully understood. The rheo-optical technique (counter-rotating shear cell coupled with an optical microscope) is an efficient technique to observe in-situ during shear the filler dispersion mechanisms. Kinetics and criteria of dispersion mechanisms such as erosion or rupture can be determined.

The present work compares the shear-induced dispersion mechanisms and criteria of different grades of carbon black and silica in a common polymer matrix (styrene-butadiene rubber). The objective was to determine the role of the intrinsic parameters of the filler (specific area) on dispersion. This study shows differences in the dispersion mechanisms of silica and carbon black. The data will be discussed in terms of internal organisation of the fillers.

Introduction

Carbon black and silica are widely used as reinforcing fillers for rubber compounds in the tire industry. Understanding how the filler size is reduced due to the hydrodynamic stress during the mixing operation is a key step in the tire manufacturing process. In the case of carbon black, two dispersion mechanisms are well known: rupture and erosion. Rupture is a sudden mechanism occurring at high hydrodynamic stresses and leading to the formation of a small number of relatively large fragments while erosion is a slow and gradual mechanism occurring at lower stresses and producing a large number of small aggregates [1-3].

In this paper, we focus on the direct observation and the characterization of dispersion mechanisms of carbon black and amorphous precipitated silica agglomerates suspended in a styrene-butadiene rubber matrix under shear. A particular attention is paid to the effect of the intrinsic parameters of the filler (specific area, structure) on the filler dispersion behaviour.

Experimental part

Materials: Filler types

The dispersion behaviour of three different carbon black grades from Cabot and two highly dispersible amorphous precipitated silica grades from Rhodia is investigated. Their respective characteristics are indicated in Tables 1 and 2 respectively.

Table 1

	Specific area (m ² /g)		Structure (ml/100g)	
	BET	CTAB	DBP	CDBP
N234	126	119	125	100
N326	82	81	70	65
N347	90	91	122	103

Carbon black characteristics

Table 2

	Specific area (m ² /g)	
	BET	CTAB
Zeosil 1115MP	103	97
Zeosil 1165MP	170	156

Amorphous precipitated silica characteristics

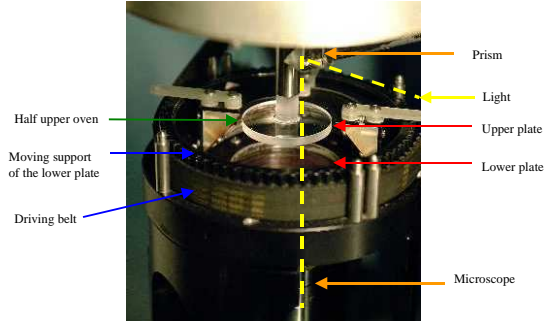
Materials: Matrix

The polymer matrix used is a styrene-butadiene copolymer rubber: SBR 25E from Michelin. The SBR is this study uncured.

Methods: Transparent counter-rotating shear cell

Dispersion experiments were carried out using a transparent counter-rotating shear cell [3]. This apparatus is shown in Figure 1 and the principle is represented in Figure 2.

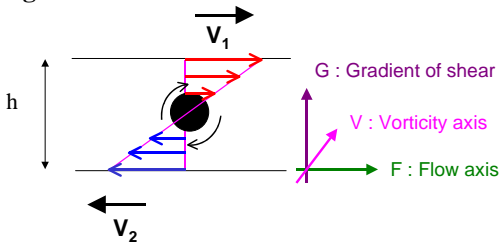
Figure 1



Picture of the counter-rotating device

The counter-rotating shear cell consists of two glass plates rotating in opposite directions. Each plate is driven by an independent motor. The advantage of this geometry is that the relative velocities of the two plates can be adjusted so that the velocity of a given particle can be set to zero in the reference framework of the laboratory. This allows to observe the behaviour of a particle suspended in a matrix under shear either for a certain period of time at a given shear or while increasing the shear rate and thus the applied shear stress.

Figure 2



Principle of the counter-rotating shear cell

Observations are made via an optical microscope and recorded via CCD camera. The apparatus is equipped with transducers and a computer where shear parameters are recorded. The macroscopic shear rate applied to the matrix around the particle observed is calculated as follow:

$$\dot{\gamma} = \frac{(\omega_{upper} + \omega_{lower})R}{H} \quad (1)$$

where ω_{lower} and ω_{upper} are respectively the rotational speed of the lower and upper plates, R is the radial position of the particle observed and H the gap between the two plates.

Samples were composed of several agglomerates inserted in between two polymer films. Experiments were carried out between 110 and 140°C.

In order to have reproducible results, attention was paid to the agglomerate radius relatively to the gap

dimension. We recently showed by numerical simulation that if the $R/h < 0.2$ (where R is the radius of the agglomerate and h is the distance between the center of the particle and the closest glass plate), the agglomerate is only subjected to the applied macroscopic shear stress and not to additional stresses due to the vicinity of the shear cell walls [4].

Methods: Rheometry

The rheological characteristics of the three elastomers were measured by oscillatory experiments using a RMS800 Rheometrics rheometer (25 mm diameter) in the temperature range 110-140°C. We used a 1% strain, which is in the linear viscoelastic regime, and a frequency range of 0.1-100 rad/s. The application of the Cox-Merz rule ($|\eta^*(\omega)| = \eta(\dot{\gamma})$, with ω in rad/s and $\dot{\gamma}$ in s^{-1}) was validated and was used in order to estimate the rheological behaviour of the elastomer under a constant shear rate (conditions applied in rheo-optical experiments).

Results and Discussion

Dispersion mechanisms of carbon black:

Carbon black can be dispersed either by erosion or rupture. Rupture is a sudden mechanism characterized by the sudden breakup of the agglomerate into a few large fragments and dust (Figure 3). Rupture is observed by increasing progressively the shear rate up to a critical shear rate value. Erosion is characterized by the continuous detachment of small fragments from the outside of the parent agglomerate (Figure 4). Erosion is observed at a constant shear rate as a function of time. By defining proper shear conditions, the rheo-optical device allows us to study separately rupture and erosion mechanisms which is not possible in an internal mixer.

Figure 3

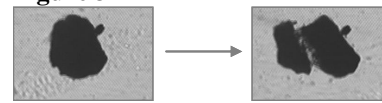


Illustration of the rupture mechanism for the N234 carbon black grade ($R_0 = 70 \mu m$) in SBR under shear ($3 s^{-1}$).

Figure 4



Illustration of the erosion mechanism for the N234 carbon grade ($R_0 = 22 \mu m$) in SBR under shear ($6 s^{-1}$).

The rupture mechanism is found to occur above a critical shear stress (defined as the critical shear rate multiplied by the matrix viscosity). Measurements performed on different initial agglomerate sizes show that the critical shear stress for rupture depends on the initial pellet size. The critical shear stress for rupture of a large agglomerate is lower than the one for small agglomerate. The rupture of larger agglomerates is easier. The critical shear stress for rupture appears to be inversely proportional to the initial agglomerate

size. Measurements performed on different carbon black grades (different via their specific area or structure) depicted the same behaviour. Rupture is observed in all cases and the critical shear stresses for rupture for identical agglomerate initial sizes but from different grades are the same. The criterion for rupture of carbon black depends on the agglomerate initial size but does not depend on the carbon black intrinsic characteristics.

Erosion kinetics were measured by following the size reduction with time under the application of a constant shear rate. Erosion was found to occur above a critical shear stress for erosion and to proceed via the detachment of a constant volume per strain unit and to be governed by the applied shear stress. Measurements performed on different carbon grades showed that the erosion process depends on carbon black intrinsic characteristics. Erosion is faster for a carbon black grade characterized by a lower specific area or a larger structure. This tendency is in agreement with studies performed in an internal mixer [5]. However this study points out that faster dispersions observed for low specific area or large structure carbon black grades in an internal mixer were only due to the erosion mechanism.

Dispersion mechanisms of precipitated amorphous silicas:

The increase of the shear rate leads in the case of Z1165MP silica grade to the rupture of the agglomerate into a few large fragments. This rupture occurs above a critical shear rate (and thus critical shear stress). As for the rupture mechanism observed with the carbon black, a much larger shear stress is necessary to breakup fragments resulting from the first rupture. The critical shear stress for rupture also depends on the agglomerate size. Rupture is easier for larger agglomerates. However the dependence of the critical shear stress for rupture with the agglomerate size is different than the one found for carbon black filler.

The same shear procedure applied to the Z1115MP grade also leads to the dispersion of the agglomerate above a critical shear stress but the mechanism is different from rupture. The agglomerate is suddenly fully desintegrated into micron size fragments (Figure 5).

Figure 5



Illustration of the disintegration mechanism for the Z1115MP silica grade ($R_0 = 37 \mu\text{m}$) in SBR under shear (56 s^{-1}).

This mechanism is very efficient in terms of dispersion. Agglomerates with an initial size above $100 \mu\text{m}$ radius do not disintegrate in one step as it is the case for smaller size but via the successive disintegration of large parts of the agglomerate.

The Z1115MP silica grade with the lower specific area is easier to disperse than the Z1165MP grade. For similar agglomerate sizes, the Z1115MP grade is dispersed at a lower critical shear stress than the other grade.

The measurement of the critical shear stress for the disintegration mechanisms versus the initial agglomerate size shows a similar tendency as the rupture mechanism for the Z1165MP grade but at a lower level of shear stress.

Conclusions

The dispersion mechanisms of different grades of carbon black and amorphous precipitated silicas were investigated by rheo-optics in a common SBR matrix. Fillers were characterized by different specific areas and structures.

The use of the rheo-optical technique allowed us to investigate separately the erosion and rupture mechanisms and to show that the effect of the carbon black intrinsic parameters is different for the two mechanisms. The rupture criterion is identical whatever the carbon black grade. On the contrary, the erosion mechanism does depend on the carbon characteristics. Erosion is more efficient in the case of a carbon black grade characterized by a low specific area or a large structure.

The study of the two amorphous precipitated silica grades shows different results. Although the two silica grades differ in their specific areas, the two grades do not have the same dispersion behaviours. The silica with the higher specific area disperse via a rupture mechanism, whereas the one with the lower specific area disperse via a different mechanism called disintegration. This mechanism is also observed above a critical shear stress but the mechanism results in the sudden fragmentation of the agglomerate into small fragments with an average size in the micron range.

Hypotheses for the different behaviours of carbon and amorphous precipitated silica fillers will be discussed.

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