

9 Reinforcing Fillers and Liquid Additives

9.1 Reinforcing fillers

9.1.1 Introduction

In this chapter, reinforcing fillers, carbon black and precipitated silica, will be discussed. Because a reference book on carbon black [1] and a review article on silica [2] are available, the discussion will be limited to the aspects that are pertinent to mixing.

Major properties characterising these fillers are surface area (particle size) and structure (bulkiness). The commercial grades of carbon black and their characteristics are given in Table 9.1 [3]. When discussing mixing one more property must be considered, the mixing ease, which will be part of the discussion that follows.

9.1.2 Mixing ease of fillers

The ease of mixing has two aspects, one is ease of incorporation and the other is dispersion. How can the ease of mixing be quantified and how can it be related to the appropriate properties of a filler? These questions concern characterisation of fillers and may be called the property-processability relationship. Whereas the effect of fillers on the performance of vulcanisates has been quite extensively researched and the reinforcing mechanisms have been examined, the ease of mixing has not been investigated as much. This chapter is also limited to primarily qualitative discussions. Scientific investigation is very much in order.

Consider first the phenomenon, which is called rejection of a filler by rubber. When a silica filler is charged onto premasticated natural rubber, fine particles of the filler are blown out from the charge hole of the internal mixer like smoke. It is interpreted as a repulsion by the electric charge built in the rubber during mastication. When silica is premixed with carbon black or fine powdered metal carbonates, the repulsion is significantly reduced [9].

The second aspect is the affinity between filler and rubber which, affects incorporation. The stronger this affinity the easier that incorporation appears. Concerning the filler-

Table 9.1 Properties of Rubber-Grade Carbon Blacks

ASTM ^a designation	Former industry designation	I ₂ absorption number (D1510) [4], g/kg	DBPA ^b , (D2414) [5], cm ³ /100 g	DBPA ^{b,d} (compressed sample) (D3493), cm ³ /100 g	CTAB ^{c,e} surface area (D3765), m ² /g	Nitrogen surface area ^f (D3037), m ² /g	Tinting strength (D3265) [7],	Pour density (D1613) [6], kg/m ³
N110	SAF	145	112	98	126	143	124	335
N121	SAF-HS	121	132	112	121	132	121	320
N220	ISAF	121	114	100	111	119	115	345
N231	ISAF-LM	121	92	86	108	117	117	390
N234	ISAF-HS	120	125	100	119	126	124	320
N299	ISAF-HS	108	124	105	104	108	113	335
N326	HAF-LS	82	72	69	83	84	112	465
N330	HAF	82	102	88	83	83	103	375
N339	HAF-HS	90	120	101	95	96	110	345
N347	HAF-HS	90	124	100	88	90	103	335
N351	HAF-HS	68	120	97	74	73	100	345
N358	HAF-HS	84	150	112	88	87	99	290
N375	HAF-HS	90	114	97	98	100	115	345
N539	FEF	43	111	84	41	41	0	385

Table 9.1 Properties of Rubber-Grade Carbon Blacks (continued)

ASTM ^a designation	Former industry designation	I ₂ absorption number (D1510) [4], g/kg	DBPA ^b , (D2414) [5], cm ³ /100 g	DBPA ^{b,d} (compressed sample) (D3493), cm ³ /100 g	CTAB ^{c,e} surface area (D3765), m ² /g	Nitrogen surface area ^f (D3037), m ² /g	Tinting strength (D3265) [7],	Pour density (D1613) [6], kg/m ³
N550	FEF	43	121	88	42	42	0	360
N650	GPF-HS	36	122	87	38	38	0	370
N660	GPF	36	90	75	35	35	0	425
N683	GPF-HS	35	133	0	39	37	0	335
N762	SRF	27	65	57	29	28	0	505
N765	SRF-HS	31	115	86	33	31	0	375
N774	SRF	29	72	62	29	29	0	495
N990	MT	0	43	40	9	9	0	0

a: ASTM D1765-99a [8]
 b: Dibutyl Phthalate (84-74-2) absorption
 c: Cetyl trimethylammonium bromide (57-09-0)
 d: ASTM D3493-99
 Standard Test Method for Carbon Black-*n*-Dibutyl Phthalate Absorption Number of Compressed Sample
 e: ASTM D3765-99
 Standard Test Method for Carbon-Black-CTAB (Cetyltrimethylammonium Bromide) Surface Area
 f: ASTM D3037
 Test Methods for Carbon-Black-Surface Area by Nitrogen Adsorption (Discontinued 1999)

rubber affinity, for quantifying the filler-rubber interaction, the conventional method has been to measure the bound-rubber content [10]. More recently, NMR has been used for characterising the interaction [11]. Because the present interest is in the processing behaviour of the material, mechanical methods are also needed. In Chapter 7, a method of evaluating the strain-amplification was developed [12]. The method was designed to treat dynamic conditions rather than quasi-equilibrium conditions of Mullins and Tobin [13]. Using dynamic conditions, the new method yields the strain amplification as a function of strain and strain rate. Subsequently, the strain-rate amplification had also been evaluated [14]. In this work, three NBRs, two SBRs and two ACMs were examined together with several grades of carbon black having different particle size and different structure.

However, the method requires elongational measurements of gum rubber and its unvulcanised compound. The experiments as well as the calculation are somewhat involved. If only a relative measure of the filler-rubber interaction is needed, dynamic mechanical measurements and subsequent comparison of modulus of the compound against that of the gum rubber are much simpler. Such comparisons with N550 carbon black were made with the samples listed in Table 9.2 and the moduli data of Figures 9.1 and 9.2 [12]. The modulus ratio is found to be independent of the frequency of the dynamic measurements but varies considerably among different gum rubbers.

Table 9.2 Samples							
Type	Trade Mark	Code for gum ^g	Code for compound ^g	Mooney index of gum ^b	% gel of gum	Carbon black phr	Modulus ratio ^f
NBR	Hycar ^a 1052	A	1	35	0 ^c	40	1.94
NBR	Hycar ^a 1042x82	C	3	81	48.6	40	1.21
NBR	Hycar ^a 1002	D	4	85	74.3	40	3.30
SBR	Ameripol ^a 1502	H	5	52	1.8 ^d	40	1.49
SBR	Ameripol ^a 1712	I	7	55	4.4	40 ^e	1.21
a: Registered trademark of the BFGoodrich Company b: ASTM D1646 [15] c: ASTM D3616 [16] d: A method similar to that of <i>c</i> , but toluene was used instead of MEK e: Parts per hundred of gum rubber plus extending oil f: Modulus ratio is the absolute value of shear complex modulus of compound, $ G^* _{cp}$, over that of gum rubber, $ G^* _g$ g: Sample codes for the experiment							

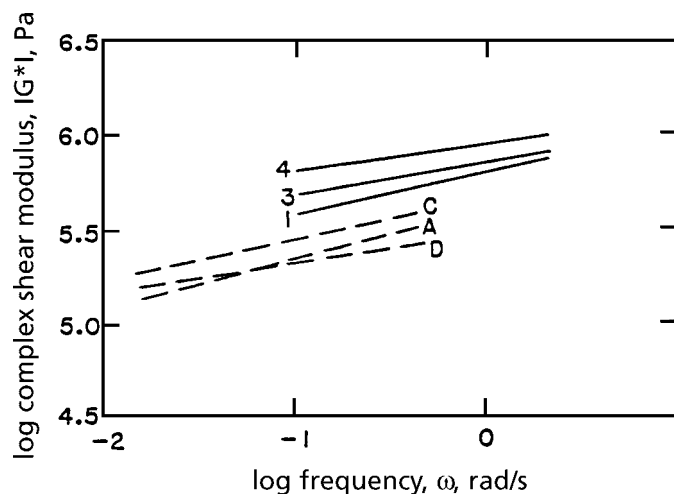


Figure 9.1 Complex shear modulus as a function of frequency for filled and unfilled NBRs.

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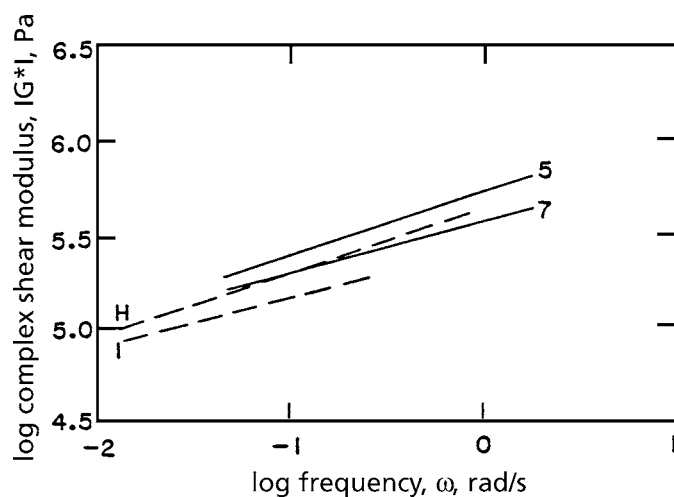


Figure 9.2 Complex shear modulus as a function of frequency for filled and unfilled SBRs.

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The strain amplification, is expressed as a ratio of the absolute value of the complex shear modulus $|G^*|_{cp}/|G^*|_g$. The value of compound 4 is very high compared to the others. The gum rubber D has long branches and a large amount (75%) of macrogel (see also sections 4.1 and 6.5). The long branches are known to have a higher affinity to carbon black but the reason why is not clear. However, if the branches of one gel-molecule tie up a number of carbon black particles, the modulus may become higher than those containing unbranched rubber. The gel in the compound 3 is a microgel. Since the microgel is a particle of crosslinked network, it may be ineffective in tying up the carbon black particles; and therefore the amplification is rather low.

In comparing compounds 5 and 7, the oil-extended rubber, SBR 1712, shows a lower amplification. A smaller amount of rubber against the amount of carbon black may be the reason.

Whether or not there is a difference between NBR-A and SBR-H in the affinity towards carbon black is not certain with this data alone, because the Mooney indices are different. If the difference is significant, NBR has somewhat higher affinity than SBR toward carbon black.

Rather unexpectedly a build-up of bound-rubber of the polyisoprene was observed on the surface of silica in the absence of the coupling agent. Polyisoprene is usually considered to be unreactive with silica. The compound was kept at 120 °C for up to 18 hours and the development of the bound rubber was examined with NMR [17].

Nakajima preheated silica in an oven set at 200 °C to remove water. When the hot silica was added directly from the oven to the premasticated NR, it dispersed without use of a coupling agent. When the silica was removed from the oven and cooled to room temperature, mixing the heated silica was just as difficult as mixing silica without heat-treatment. Evidently the hot silica helped mixing. Examples in literature about interaction with silica are mostly with polar rubbers [2]. The above examples illustrate that even nonpolar rubber like NR interacts with silica [18].

Neither silica nor carbon black fillers are pure material. Their surfaces have chemically reactive groups. Their physical-chemical interaction and chemical reaction with rubber have been extensively investigated as a part of the reinforcing mechanisms [19]. How these chemical groups contribute to the mixing mechanism is an obvious interest. Wang, Wolff and Donnet investigated the surface energies of fillers and their interaction with model compounds using an inverse gas chromatography. The model compounds were selected to simulate various rubbers including polar rubbers. Both carbon black and silica were studied [20, 21, 22, 23], to characterise the rubber-filled interaction.

The next subject is the ease of dispersion. Generally, when the incorporation of rubber is difficult the problem is carried over into the dispersion of the rubber. The filler-rubber interaction also plays an important role here. In addition, there are cases where the ease of dispersion is significantly different among the same grade of silica for a reason that is not exactly clear [24].

The sample used was Hycar 4051EP (ACM), a product of the BFGoodrich Company. The Hycar homopolymer, has a glass-transition temperature of $-14\text{ }^{\circ}\text{C}$ and a Mooney index (ML-(1 + 4) at $100\text{ }^{\circ}\text{C}$), in the range of 35-50.

The silica fillers used are given in Table 9.3. All the compounds contained 50 phr of a filler by weight. The compounds were prepared with a Haake Buchler Rheocord 750 laboratory mixer at 50 rpm and a machine temperature of $100\text{ }^{\circ}\text{C}$. The fresh rubber was charged and masticated for one minute. After that silica was added over a period of about 2.5 minutes. An additional 6.5 minutes was required to complete the mixing. No coupling agent was required.

Table 9.3 Silica Fillers used with Hycar 4051EP			
Compound Code	Filler	Identification Surface Area, m^2/g	Manufacturer
1	Precipitated silica	170	Manufacturer A, spray-dried commercial product
2	Precipitated silica	200	Manufacturer B, rotary-dried commercial product
3	Precipitated silica	150	Manufacturer B, rotary-dried commercial product
4	Precipitated silica	200	Manufacturer B, spray-dried experimental product

All compounds were compression moulded at $100\text{ }^{\circ}\text{C}$ for 30 minutes. The spray-dried silicas were found to be much easier to disperse than the rotary-dried ones. This was readily seen in the mixed compounds, for which a good dispersion resulted in a transparent material, whereas the poor dispersion gave an opaque white material, Figure 9.3.

When the opaque compounds were remilled many times through a roll-mill with a tight gap (no clearance), they became transparent. This fact is a further confirmation that the opaqueness comes from poor dispersion.

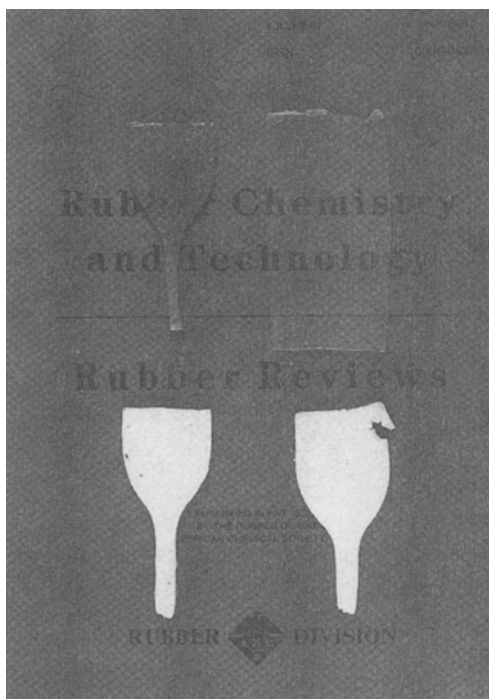


Figure 9.3 Silica compound specimens: transparent specimens with spray-dried silica and white specimens with rotary-dried silica.

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The rotary-dried silica presumably contained more water. This is thought to be the reason why the silica agglomerates are not easily broken down to the aggregates. In addition, the spray-drying might have given a more uniform and milder heat history, so that the agglomerates are more friable. The difference in friability of the agglomerates causes the difference in the dispersibility.

However, the above interpretation must be confirmed. The presence of some additive is also suspected.

Just how friable the filler agglomerates should be, is an important question. For the ease of dispersion, a more friable filler is desirable. But, this brings a material-handling difficulty at any time before the filler is added to a rubber [25]. Incorporation is facilitated if the agglomerates retain their integrity. This means that a delicate control of the cohesive strength among aggregates is necessary for providing sufficient resistance to break before

incorporation is completed. Then, they must break up easily as soon as dispersion starts. Such a contradicting requirement is common in industrial practice and this is one of the best examples.

9.1.3 Structure of aggregate and agglomerate

A question of the friability of agglomerates leads to an inquiry into structure of both agglomerate and aggregate. The structure of aggregate has been a subject of intensive study. A review of this subject is given by Medalia [26], who produced the electron microscope images in Figure 9.4.

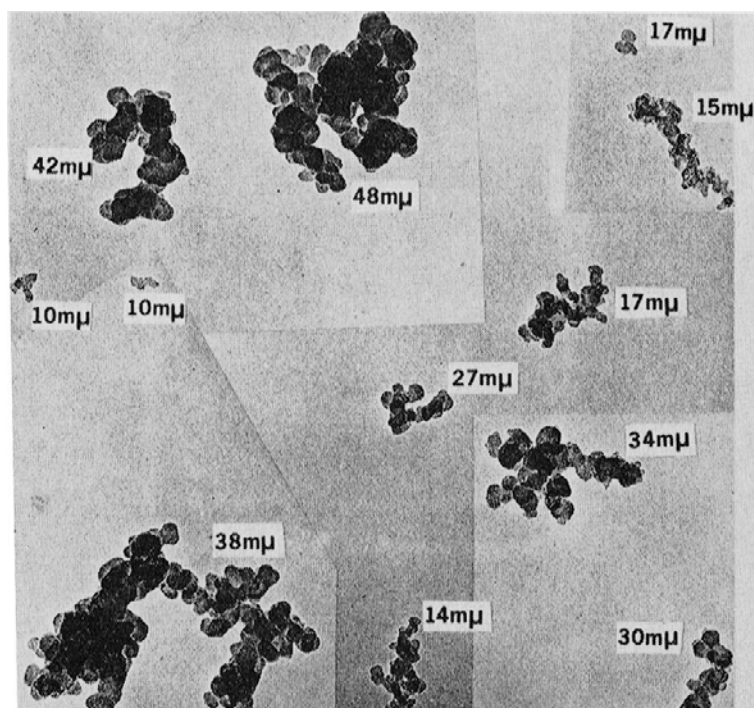


Figure 9.4 Montage of aggregates in a single field of N220 carbon black. Numbers beside each aggregate indicate average particle size.

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The aggregates are in the size range of approximately 10 to 100 nm in diameter. They consist of strings of smaller spheres fused together. The size of the sphere determines the total surface area, and the manner by which the spheres are strung together determines structure. More recent studies are directed toward converting the electron microscopic images to three-dimensional morphology [27].

The application of fractal analysis enabled the characterisation of the aggregates, which by nature consisted of wide varieties of size and shape.

One method is called the perimeter-area (P - A) relationship, $P \sim A^{D_p/2}$, where the perimeter fractal, D_p , relates to the degree of irregularity or ruggedness of the perimeter of the two-dimensional profile. Gerspacher and O'Farrell [28] applied the method to 15 commercial grades of carbon black. The values of D_p were from 1.14 to 1.34 and tended to be higher for more reinforcing, smaller particle size grades.

Herd, McDonald and Hess [29] applied both the perimeter-area relationship and the mass-size (M - R) relationship, $M \sim R^{D_m}$ to 19 grades of commercial carbon blacks. On-line transmission-electron-microscopy/automated-image-analysis was used for rapid sampling of 1,000 aggregates per grade. Values of D_p and D_m were 1.05 – 1.23 and 2.47 – 2.85, respectively, and they were related to the structure and size characteristics observed with the conventional methods. Further, they classified a variety of shapes into four categories, spheroidal, ellipsoidal, linear and branched. For each category fractal analysis was applied to determine D_p and D_m . From the mass fraction of each category and their D_p and D_m values, the composite fractal indices, D_p^* and D_m^* , were calculated for each grade. The composite fractal indices are more sensitive than D_p and D_m for distinguishing between different grades of carbon black.

For very practical reasons simple tests are needed to determine the surface area and structure of fillers. However, defining the test condition is not without problems. The surface area based on a monolayer adsorption of a small molecule depends upon the size of the adsorbent molecule, because the filler surface is made up of irregular topology.

A practical definition of surface area must be related to the adsorption of rubber molecules. Upon consideration the current choice of adsorbent is cetyltrimethylammonium bromide (CTAB). However, nitrogen adsorption (BET) is also in common use.

The structure determination utilises absorption of liquid into pores of agglomerate. Therefore, it depends not only upon the structure of the aggregate but also how tightly aggregates are packed in an agglomerate. The usual procedure is to compress the sample under a very high pressure prior to the absorption of DBP [30]. More detailed discussion on the surface area and structure are given by Donnet and Voet [1]. In addition to the

surface area and structure, another parameter called ‘occluded volume’ is frequently used [26]. This parameter has multi-meanings or multi-purposes, which require some clarification. The first meaning is the assigning of a volume of an equivalent sphere for the complexed shape of the aggregates. The second is a volume of an aggregate plus the volume of the immobilised rubber trapped by the aggregate. The third is an assumed existence of the rubber, which has penetrated and filled voids of the agglomerate. In practice all three definitions are interpreted to give the same quantity. The concept has been used to explain the mixing mechanisms and rheology. These are discussed later in this chapter.

The structure of the agglomerates has escaped the attention of researchers. Figure 9.5 is an imaginary structure of agglomerate, showing a small section, 100 x 100 nm, out of the overall diameter of 10-100 μm [31]. It is based on the crushed DBP value of 95 $\text{cm}^3/100\text{ g}$ for N339 carbon black, the data reported by Cotten [32]. Using the density of 1.86 g/cm^3 for the carbon [33], the volume fraction occupied by carbon in the agglomerate is calculated to be 0.36. The area it corresponds to is about 50% occupied and 50% void. In the lower left corner the 20 nm square shows 50% of the area occupied by carbon. In the rest of the area, a model of stacking of aggregates is illustrated; one in the lower left is drawn to fit in the 20 nm square; others are made to fit either a 40 nm square or 20 x 40 nm area. The shapes of the aggregates are made to resemble to those in Figure 9.4, except that the particles are represented with squares instead of circles. This is to make the estimate easier for 50% area occupancy. Also, it is drawn to make the aggregates touch their neighbour at some point. This model assumes that the void is more or less uniformly distributed within the agglomerate.

A similar structure was observed by Misono for N330 carbon black. Much denser packing is shown for the low structure, N880, Figure 9.6 [30].

A variation in the strength of the pellet has been recognised and a test method is defined in ASTM D1937-62T [35]. The fact indicates that the packing of the aggregates is variable.

Then, the packing within an agglomerate may be non-uniform.

According to Donnet and Voet [36] in *Carbon Black: Physics, Chemistry and Elastomer Reinforcement* (Reproduced by permission of Marcel Dekker, Inc.): ‘the pelletisation is not merely a physical densification, since many properties of the black appear to undergo irreversible changes, incompatible with a mechanical or physical view of pelletisation. The change in free radical content upon pelletisation supports the argument that chemical bonding is involved’.

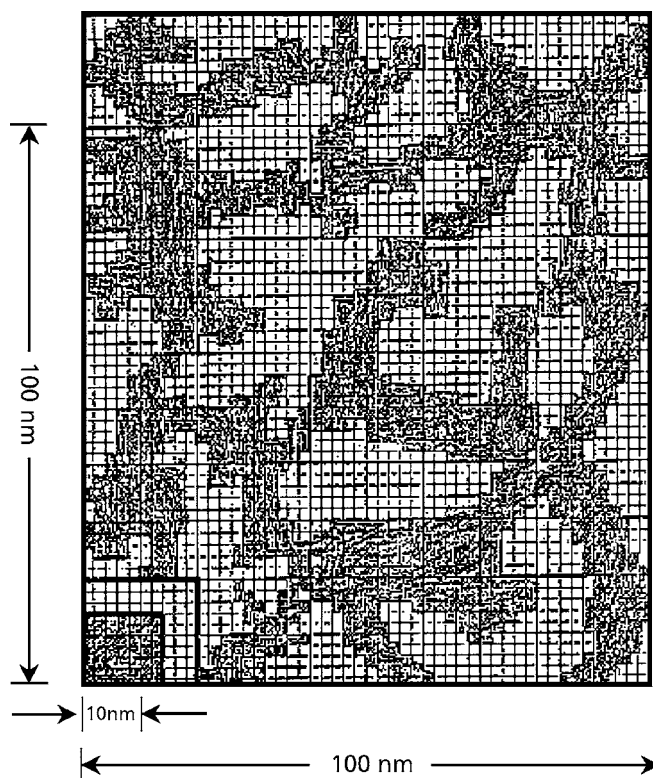


Figure 9.5 Imaginary structure of carbon black agglomerate.

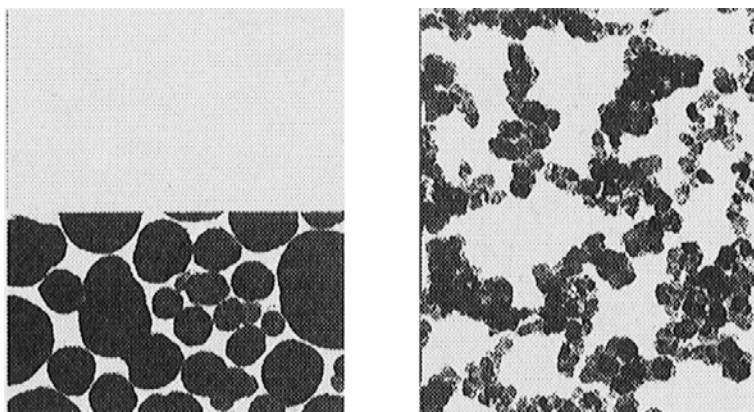


Figure 9.6 Carbon blacks having different agglomerate structure.

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They state further that ‘generally, to promote the formation of firm, yet easily dispersible pellets and to minimise the presence of undesirable fines, additives are used in the water of pelletisation for rubber grade of blacks’ [37]. Molasses and lignosulphonic acids are mentioned as examples of additives. ‘These additives function as binders only upon carbonisation in the dryer. It seems likely that the free radicals formed during carbonisation tend to create carbon-to-carbon bonds, thereby promoting the formation of firmer pellets, which are still dispersible in elastomers’.

Previous examples of silicas show that there is a difference of friability, i.e., dispersibility among the same grade of fillers. As discussed before, a control of the friability plays an important role in dispersing fillers. Cotten [32] examined the dispersion rate in mixing of oil-extended *cis*-1,4-BR with thirteen grades of carbon black varying the surface area and structure. The decreasing torque after the second peak in mixing with a miniature mixer was used as the indication of the dispersion rate. The curve was fitted to an empirical equation of a form:

$$\ln[(P_t - P_\infty)/(P_0 - P_\infty)] = -kt \quad (9.1)$$

where P_0 and P_∞ are limiting torques at the assumed initial and final condition and P_t is the torque at time, t . Therefore, k is the rate constant of the progress of dispersion. The value of k was related to the surface area (CTAB) and structure (DBPA) with a correlation coefficient of 0.98. Because the surface area and the structure are assigned as the properties of the aggregate, this result indicates that the friability of the agglomerate is controlled solely by the properties of the aggregate. Because the previous discussion points towards variation in the friability of agglomerate for the same aggregate properties, the samples chosen by Cotten may have been manufactured to give the same degree of friability. Another possibility is that because DBPA was measured with the agglomerates, it might have represented a variation in the agglomerate structure as well as the aggregate structure.

Donnet and Voet [38] state that the DBP number is somewhat dependent upon the mechanical treatment of the carbon black during pelletisation. An increase in work done leads to an increase in pellet density and a reduction in DBP number. The variation in DBP number is partially related to a variation in the agglomerate morphology.

Jansen and Kraus [25] evaluated the dispersibility of two commercial N220 carbon blacks. The rubber used was SBR and the amount of oil was varied at 0, 15, 30, 45 or 60 phr. The mixing was done with a miniature mixer. The same mixing condition was used for two carbon blacks. The dispersion rating with a photomicrographic technique gave an identical rating within experimental error if no oil was present. However, at all concentrations of added oil, there were differences of the rating between two carbon blacks.

Jansen and Kraus state that two oil levels (30 and 60 phr) are adequate to define relative dispersibility of carbon blacks. Evidently, there is a subtle difference in the friability of the

agglomerate even if the aggregate properties are the same. The reason why the difference is magnified in the presence of oil is that the oil makes dispersion more difficult. In the same article Jansen and Kraus present two more examples of the differences in dispersibility within a given grade. One example was with N339 carbon black. A significant difference in dispersibility was observed in mixing with S-SBR and SBR as well as in dispersion in chloroform by ultrasonic device.

An even more dramatic example was obtained with N326, a low structure carbon black, known to be difficult to disperse. The results are reproduced in Figure 9.7. More discussion on the subject of friability in relation to mixing mechanisms is given in Chapter 11.

Shiga and Furuta [39] investigated the breakdown mechanisms of agglomerates of N330 and N550 carbon black in mixing with six grades of EPDM. An optical-micrograph was used with samples taken during both the incorporation and dispersion stage. The breakdown was found to proceed in two steps: first is the breakdown of large agglomerates into smaller agglomerates (see Figure 9.8), and second is the disintegration of the surface layer of the agglomerate in a way which has been compared to the way an onion peels, see Figures 9.9 and 9.10. The explanation given is from the point of view of the mechanical action of rubber onto the agglomerate.

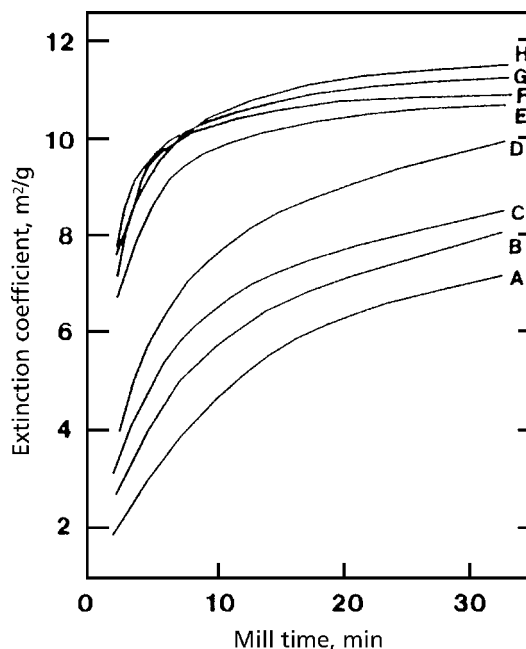


Figure 9.7 Dispersion of N326 blacks in polybutadiene.

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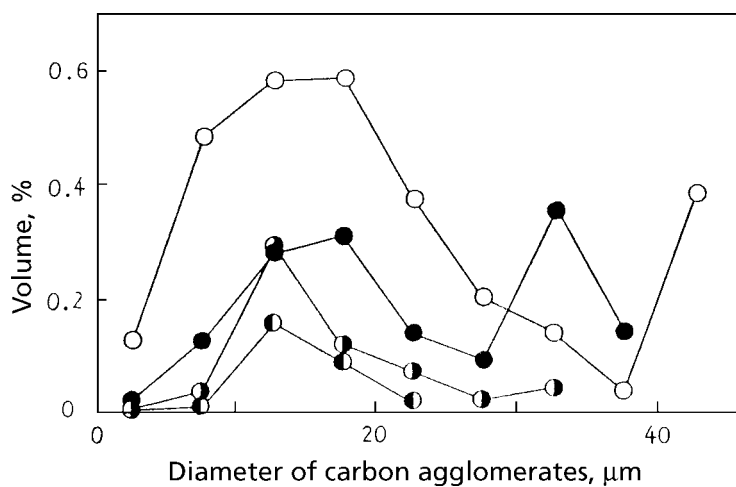


Figure 9.8 Distribution of diameter of carbon agglomerates at each mixing time. Recipe: EPDM, 100; N330, 10; oil, 10; zinc oxide, 5; stearic acid, 1. ○, 30 seconds mixing; ●, 2 minutes mixing; ◐, 4 minutes mixing; ●, 6 minutes mixing.

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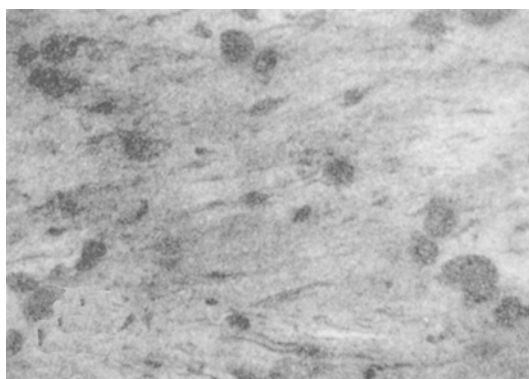


Figure 9.9 Photomicrograph of EPDM compound after 2 minutes mixing. EPDM, 100; N330, 10; oil, 10; zinc oxide, 5; stearic acid, 1.

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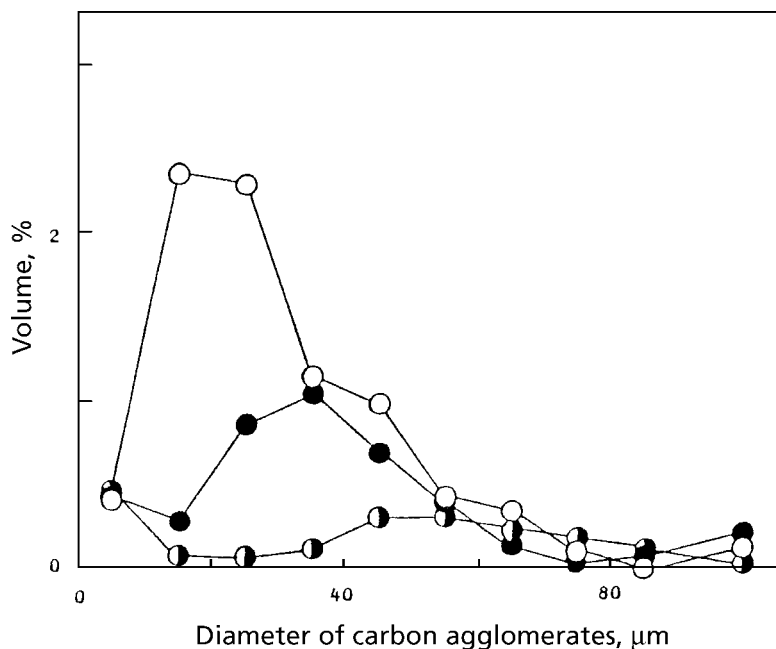


Figure 9.10 Distribution of diameter of carbon agglomerates for Sample E at each mixing time (PI recipe). O, 2 minutes mixing; ●, 5 minutes mixing; ◐, 10 minutes mixing.

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These two steps of the breakdown may also be related to the morphology of the agglomerate. The first step appears to be the generation of a large number of smaller agglomerates, the size of which is centred around 25 μm diameter. This suggests that the larger agglomerates and pellets are made up of units of smaller agglomerates. The scanning electron micrographs, Figures 9.11 and 9.12 are suggestive of this point of view.

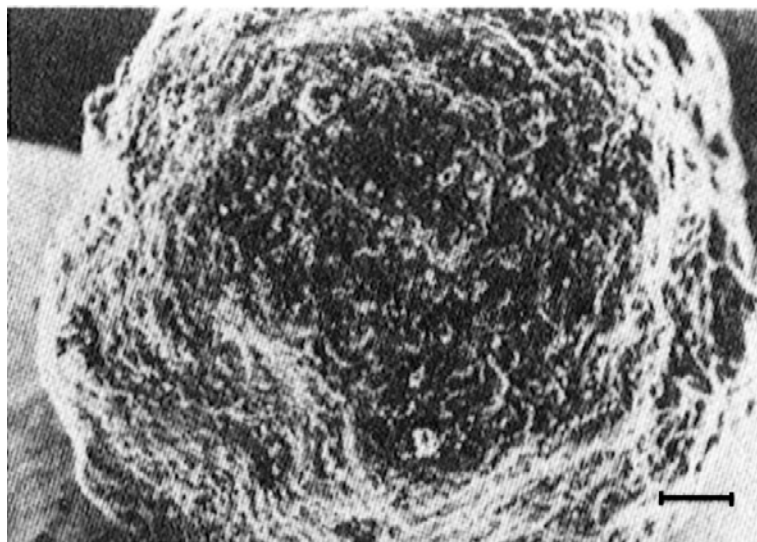


Figure 9.11 Scanning electron micrograph of N330 pellet. Scale bar 100 μm .

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Figure 9.12 Scanning electron micrograph of N330 carbon black after mixing or crushing for one minute. Scale bar 100 μm .

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The second stage (peeling of an onion), may be related to the presence of a shell-over-shell structure with a fault between the shells. Such a structure is conceivable from rolling actions involved in the process of pelletisation.

Even identical molecules in the process of crystallisation generate defects and dislocations. The aggregates having a wide variation in size and shape are not likely to pack uniformly like the one depicted in Figure 9.5. Recognising that even equal sized spheres may pack into varying degree of tightness, it is conceivable that both larger and smaller agglomerates consist of non-uniformly packed aggregates. The loosely packed location may be the inter-particle boundary between the smaller agglomerates and inter-shell faults in the smaller agglomerates.

The morphological causes of the agglomerate break down may be examined by proper sampling during carbon black manufacture. The nascent carbon particles, i.e., aggregates, go through several steps before ending up as a pellet. The carbon particles coming out of the furnace are cooled with water and carried through an electrostatic precipitator of the Cottrel type at 60,000 V DC [40]. What do the precipitated carbons look like? After precipitation they are collected in a number of cyclones and bag filters. Then, they are pulverised in a micropulveriser. They are described as ‘the fluffy black’. What does it look like? According to Donnet and Voet [36] in *Carbon Black: Physics, Chemistry and Elastomer Reinforcement* (Reproduced by permission of Marcel Dekker, Inc.): ‘The ‘fluffy black’ is charged into a pin type mixer and agitated with an approximately equal quantity of water. Firm, spherical pellets are formed within minutes and the quantity of water used is critical. Fully automatic proportioning systems are used to control water addition simultaneously with the charging of the carbon black into the pelletiser with an accuracy of at least $\pm 0.5\%$ ’ [41]. Evidently, water plays a critical role in the manner of packing of particles.

Recent advances in the characterisation of carbon blacks have been reviewed by Gerspacher *et al* [42]. Among the new methods scanning tunnelling microscopy and atomic force microscopy have revealed fine details of the surface topology.

The question is whether or not the surface topology may be modified to our benefit. A recent development by Cabot [43] on doping carbon black with silica achieved this objective. The carbon-silica dual phase fillers (CSDP) consist of two phases, a carbon phase and finely divided silica phase dispersed in it. A higher filler-rubber interaction is demonstrated by the higher amount of bound rubber at less than 10% silica and mostly at the few percent level. The scanning tunnelling microscopy revealed the surface topology, where the area of well-organised structure (quasi-graphitic) is smaller and more surface defects are present.

The ease of mixing of CSDP was demonstrated by a lower mixing torque and a shorter incorporation time, compared to the counterpart grade of carbon black or silica-coupling agent. The resulting CSDP compound showed better dispersion.

9.2 Liquid additives

Liquid additives such as extending oil often play a unique and decisive role in mixing of rubber. Hess *et al* [44] conducted an extensive mixing study involving a variety of rubbers, carbon blacks and oils. The rubbers were SBR1712, SBR1500 and EPDM1070. Seven grades of carbon black were selected to statistically represent particle size and structure of commercially available carbon blacks. Variable amounts of aromatic and paraffinic oil were used. The degree of dispersion was evaluated after mixing under controlled conditions. Capillary rheometry was used to characterise viscosity and die-swell of the compounds. Properties of the vulcanisate were also measured, to establish the relationship amongst the variables.

There are three kinds of liquid additives: plasticiser, extending oil and tackifier. Plasticisers usually have a T_g lower than those of gum rubbers, extending oils have similar T_g , tackifiers have higher T_g , although exceptions are found in the literature [45]. Most tackifiers are solid at room temperature and require heating during mixing. Once mixed a tackifier remains as a liquid and forms a rubber solution. Therefore, it is classified here as one of the liquid additives. Some tackifiers are only partially soluble so that a broadening of the glass transition peak is observed in the dynamic mechanical studies [46]. Plasticisers and extending oils are absorbed quickly and almost instantaneously by gum rubbers. They are completely soluble with gum rubbers, unless the solubility is mismatched. The purpose of using a plasticiser is to lower the T_g of the composition, and it also facilitates the mixing of rubber with fillers. Plasticisers are polar liquids and are usually used with polar rubbers such as NBR and ACM, which have relatively high T_g .

The reasons for using an extending oil are not necessarily economic. Extending oil facilitates the mixing of difficult-mixing rubbers which provides the desired properties in the finished products. In this book the plasticiser and extending oil will be discussed primarily. The order of addition is very important; if the liquid is added first to the rubber followed by the other additives, it is similar to using an oil-masterbatch, because the oil mixes quickly with rubber. If the liquid and filler are added together to the rubber, it becomes mixing of rubber with an oil-filler mixture. In the former case the viscoelastic characterisation method is applicable to the mixture of the liquid-rubber composition in just the same way as the oil-extended gum rubbers. From the characterisation results processability may be assessed as explained in Chapter 6.

The latter case is more complicated. A part of the liquid is absorbed in the filler. Eventually the liquid migrates into rubber and at the same time the rubber becomes adsorbed onto the filler. More discussion is given on this subject in Chapter 11.

The interaction between a liquid additive and a rubber is an obvious interest not only from the solubility point of view but also from the resulting mechanical properties. Scientific studies of this subject belong to current and future activities [47, 48, 49].

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