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The Use of Fly Ash Fillers in Rubber

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ABSTRACT

The effect of using fly ash on the compounding, processing and physical properties of cured rubber is demonstrated. The results compared to those obtained with conventional fillers are highlighted. Advantages as well as limitations of using alumina silicate spheres recovered from fly ash are discussed.

INTRODUCTION

With annual global sales of 6,5 million tons natural rubber can be considered an integral part of industry as there is scarcely a technological sector that does not use rubber products in some form or another.

Since its discovery rubber has been subjected to numerous developments and has progressed from a “black art” to a science as the influence of processing technology and the role of additives and fillers became fully appreciated.

While carbon black still remains the most widely utilised reinforcing filler, the use of other mineral fillers such as silica, kaolin, carbonates, barytes, and whiting have become commonplace in the rubber industry. The reinforcing properties of silica and silicates have, for example, been used to achieve hardness, stiffness and improve abrasion resistance[1]. While carbon black provides greater reinforcement than precipitated silica it cannot be used in light-coloured products or where non-marking is required

Spherical fillers have, by virtue of their morphology, many advantages over their irregularly shaped counterparts. As a result, artificially manufactured microspheres are finding increasing application in the polymer industry. In this regard particular interest has been shown in the use of alumina silicate spheres recovered from fly ash. Research has shown that an appropriately beneficiated and treated fraction of the fly ash can be advantageously utilised in a wide variety of polymer matrices[2-4].

In this paper the characteristics of a fly ash filler are discussed. Its properties and application in rubber compounding and curing is described. Comparative data with conventional fillers is presented to illustrate the unique advantages that can be achieved when such fillers are replaced by processed fly ash.

THE CHARACTERISTICS OF THE FILLER

There are many properties of fly ash to consider when it is used as a filler in the polymer industry. These include particle size distribution, morphology, surface characteristics and most importantly, colour.

For this study two grades of microspheres recovered from fly ash by aerodynamic classification were utilised. In **Table 1** the typical chemical composition, particle size and other physical data of the two grades are given. From this it can be seen that the major difference between the products is particle size. Structurally, both products are glass ceramic spheres encapsulating a skeletal of mullite, magnetite, quartz and other minor crystalline phases. Both products are commercially available under the trade name ***Plasfill***.

Table 1: Typical composition and sizing of Plasfill

Chemical			Physical		
Mass %	**Plasfill 5**	**Plasfill 15**	**Parameter**	**Plasfill 5**	**Plasfill 15**
SiO_2	52.5	53.5	D_{50} µm	3.8	11.50
Al_2O_3	35.1	34.3	D_{99} µm	19.5	110
CaO	4.6	4.4	D_{90} µm	8.5	52
Fe_2O_3	3.4	3.6			
MgO	1.3	1.2	Relative Density g/cm^3	2.15	2.25
TiO_2	1.9	1.9	% Oil Absorption	18	17

The spherecity of fly ash particles provides a low surface area to volume ratio which in turn results in a relatively low oil absorption value **(Table 1).** Comparative figures for carbonates and other fillers are, dependent on particle size distribution, generally in the 20-35% range. Most other conventionally used fillers have a higher relative density so that replacing them with an equal mass of Plasfill results in a higher volume loading. This can lead to significant savings of polymer which is substantially more expensive.

From their spherical morphology it was suggested that, when used as fillers, ceramic spheres would in all probability be non-reinforcing. This research was thus confined to a comparison with other relatively cheap non-reinforcing fillers such as whiting, carbonates and kaolin along with fly ash. The effect of these fillers on the processing, cure and final vulcanisate were examined.

COMPARATIVE TESTS ON RUBBER COMPOUNDING AND PROCESSING

Compounding

A 20 kg rubber masterbatch was prepared on a water-cooled, two-roll mill using frictional speed. The composition of this product is given in **Table 2.**

Table 2: Composition of rubber master batch

Component	Concentration (pphr)
SMRS Natural Rubber	100
Zinc Oxide (Activator)	5
Stearic Acid (Activator)	1
NBTS Accelerator (Primary)	1
TMTD Accelerator (Secondary)	0.1
Sulphur (Vulcanising agent)	2.5
Anti-oxidant	1

From this masterbatch 12 filled rubbers were prepared using fly ash (Plasfill 5 and 15), calcium carbonate (Kulu 5 and 15), clay (Kaolin) and whiting at 50, 100 and 150 parts per hundred (pphr). All rubber compounding was conducted under identical conditions with a water-cooled two-roll mill.

As can be seen from the data in **Table 3** where the time taken to reach homogeneity is listed, the Plasfill incorporated far more rapidly than any of the other fillers used.

Table 3: Incorporation time for various fillers compounded into natural rubber at different levels

Filler		Compounding Time	
Type	Level pphr	Minutes	Seconds
Plasfill 15	50	5	20
	100	8	17
	100	12	31
Kulu 15	50	7	03
	100	11	14
	150	16	48
Kulu 5	50	9	04
	100	13	12
	150	18	34
Kaolin	50	8	50
	100	12	12
	150	16	42

The ease with which the fly ash spheres are incorporated when compared to other fillers is illustrated in **Table 4** where the difference in time taken to prepare a homogeneous compound with Plasfill is compared to that of the other fillers. These figures should be regarded as indicative rather than absolute since the actual time taken to reach homogeneity will depend upon the characteristics of the mill and the properties of the natural rubber. These figures are, however, comparable as all mixes were prepared by the same operator on the same mill under identical conditions.

Table 4: Additional time taken to incorporate fillers into natural rubber when compared to Plasfill 15

Filler	**Level of addition (pphr)**		
	50	**100**	**150**
Kulu 15	1.43 (32)	2.57 (36)	4.17 (33)
Kulu 5	3.44 (70)	4.55 (59)	6.03 (48)
Kaolin	3.30 (66)	3.55 (47)	4.11 (33)

Absolute time given in min.sec. The values in brackets represent the % additional time.

It is interesting to note than in the case of Kulu 15 about 33% extra time is required irrespective of filler loading whereas for the other fillers the relative amount of extra time required decreases with filler loading (**Table 4**).

For further testing rubber sheeting approximately 5 mm thick was prepared by individually passing the respective rubber formulations through a tight nip roller. Each sample was passed through the rollers three times, reversing the grain between each pass.

Inspection of the various sheets showed little or no difference in colour. From this it was concluded that none of the fillers had any pronounced pigmenting effect.

Processing

In order to compare the flow behaviour of the filled rubber compounds with natural rubber, a Wallace rapid plasticity test was carried out at 100 °C. The results given in **Table 5** indicate that large quantities of Plasfill can be incorporated without having any negative influence on the flow properties of the compound. In fact, the filled product shows flow properties superior to those of the unfilled natural rubber. This feature has been linked to lubricating effect of the ultra fine spheres that act as slip planes between the polymer chains.

Table 5: The Wallace plasticity of various natural rubber formulations compounded with different fillers

Filler			Wallace Plasticity
Type	Relative density	Level pphr	
Plasfill 15	2.25 g/cm^3	50 100 150	17 18 16
Kulu 15	2,75 g/cm^3	50 100 150	20 17 23
Kulu 5	2.75 g/cm^3	50 100 150	22 17 22
Kaolin	2.60 g/cm^3	50 100 150	21 18 30
Natural Rubber	0.92 g/cm^3	0	20

These results are even more significant when one considers that due to differences in the density of the fillers, 150 pphr Kulu equates on an equal volume basis to 180 pphr Plasfill.

Many rubber formulations use organo-metallic complexes (peptisers) to catalytically assist in the scission of molecular chains, thereby reducing viscosity. The incorporation of Plasfill may require a reduction in the level of peptiser used.

Curing

The curing characteristics of a rubber compound can be considered as one of its most important features as it determines behaviour during processing and therefore indirectly the physical properties.

Curing or vulcanisation is the process whereby cross-linking of the polymer chains hardens the pliable rubber into a solid product that is able to exhibit elasticity. The process is initiated by the application of heat. Activations or catalysts are used along with sulphur donating compounds to control the cross-linking or bridging of the rubber molecules by sulphur which acts as the curing agent. Once vulcanised, the structure of rubber has been altered from one of molecular entanglement to a bound lattice orientation which provides the physical strength and elasticity.

An oscillating disc rheometer (Monsanto) was used to determine the curing characteristics of the various rubber compounds. The essential features of the respective torque vs time curves are summarised in **Table 6**.

Table 6 **Salient features of the rheometer curve for the various natural rubber formulations with different fillers cured at 150 °C**

Filler		Minimum Torque (inch pounds)	Maximum Torque (inch pounds)	Curing Time (mins)	Induction Time (mins)
Type	**Level pphr**				
Plasfill 15	50	5	46	5.0	2.2
	100	5	46	5.0	2.5
	150	3	62	4.9	2.2
Kulu 15	50	7	48	4.6	2.3
	100	5	56	3.5	1.4
	150	7	67	3.2	1.2
Kulu 5	50	8	49	3.9	1.7
	100	8	59	3.2	1.2
	150	12	69	2.6	1.0
Kaolin	50	6	43	6.3	3.2
	100	5	41	5.8	2.8
	150	6	44	6.4	2.1
Natural Rubber	0	10.5	39	5.1	2.1

The minimum torque value may be regarded as representative of the plasticity of the compound at 150 °C and thus also indicative of its processability. As can be seen from these results the incorporation of Plasfill aids processing to a greater degree than any of the other fillers.

The accelerating effect of calcium carbonate (Kulu) on the curing can be seen by the reduction in curing time along with filler loading for both the fine (5) and coarser (15) grades. Plasfill had no effect on the curing process. When compared to natural unfilled rubber Kaolin retarded the cure but this did not appear to be dependant upon filler loading.

As indicated by the increase in maximum torque, hardness of the cured rubber increased with the addition and loading of the carbonates. No significant effect was found with kaolin and a harder rubber product only ensues at high (150 pphr) loadings of Plasfill.

The effect of the filler on the early stages of the curing process can be gauged by changes in the induction time. Similar times were found for natural rubber and those filled with Plasfill. This once again indicates the neutral role Plasfill plays in the curing process. When carbonate fillers are utilised, the induction time is reduced concomitantly with an increase in the level of filler loading. At low levels of incorporation kaolin increases the induction time substantially but at higher levels (150 pphr) it is reduced to 2.1 minutes the same as for unfilled natural rubber. Given these results it can be concluded that the introduction of fly ash as a filler for rubber eases processing but does not alter the curing regime. This can be a major advantage as it removes a variable from the already complex process of manufacturing rubber with specific physicial properties.

COMPARATIVE EVALUATION OF PHYSICAL PROPERTIES OF FILLED CURED RUBBER

At this stage of the investigation it was decided to introduce two additional fillers for comparative testing on the cured rubber compound. These were whiting and a finer grade of the spherical alumina silicate viz Plasfill 5. This would allow more meaningful comparison of the performance of the fillers based on their equivalency in particle size.

The physical properties of the various cured rubber compounds are depicted in **Figures 1 - 5.**

Tensile Strength

As expected all fillers reduce the tensile strength of natural rubber. At higher loadings the same tensile strengths were achieved with kaolin and the finer Plasfill. In fact, at 150 pphr the tensile strength of the rubber filled with Plasfill 5 was 50% higher than its counterpart filled with the coarser grade (15).

Tear Strength

Fillers reduce the tear strength of natural rubber although at higher loadings the introduction of kaolin goes a long way to restoring the tear strength. Both Plasfill and Kulu have a similar effect and the tear strength is not dramatically effected either by the level of filler used or its particle size.

Hardness

All fillers increase the Shore hardness of natural rubber compound. The higher the filler loading the greater the increase in hardness above that of natural rubber.

Elongation at Break

The effect of Plasfill on the resilience i.e. the ability of rubber to stretch before breaking appears to be less than that for the other fillers. Once again especially at higher loadings (150 pphr) the benefit of a spherical filler is noticed. Natural rubber breaks at about 750% whereas the 150 pphr Plasfill product it is 575% but for the carbonate filled compound this value is further reduced to 475%.

Modulus of Elasticity

All fillers and particularly kaolin and to some degree whiting increases the modulus of elasticity.

Density

As indicated earlier, the introduction of a filler with a lower relative density has widespread implications. At equivalent mass loading the volume of the rubber vulcanisate will increase. In the work carried out the relative density of the carbonate filled rubber (150 pphr) was 1.55 g cm^{-3}. In the case of whiting it was 1.54, for kaolin 1.52 and for Plasfill 1.41 g cm^{-3}. In essence this means that when Plasfill is used to replace calcium carbonate the volume if the rubber compound is increased. More significantly the unit cost of the product is reduced since more items can be manufactured from a particular mass of compound.

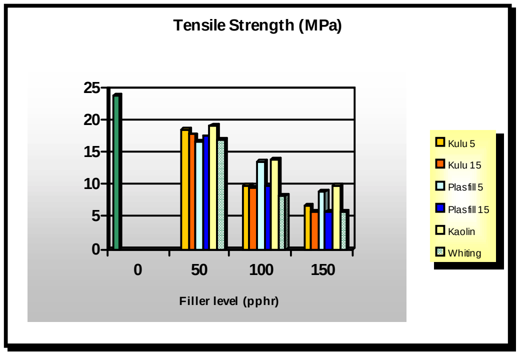

Figure 1. The effect of filler loading on the tensile strength of natural rubber

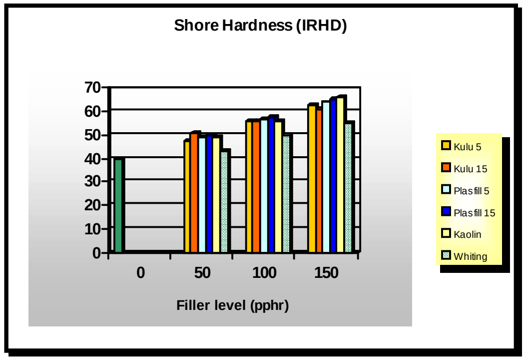

Figure 3. The effect of filler loading on the hardness of natural rubber

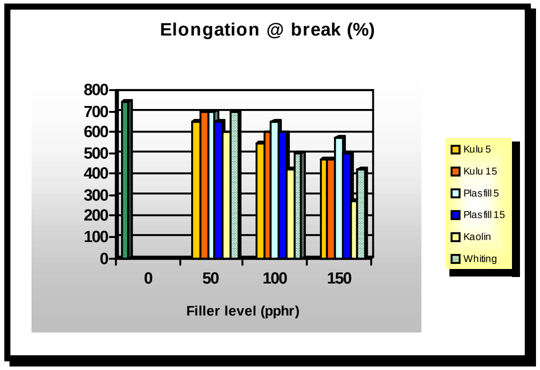

Figure 4. The effect of filler loading on elongation at break

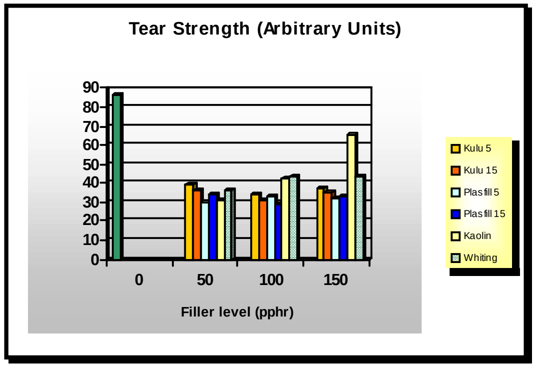

Figure 2. The effect of filler loading on the tear strength of natural rubber

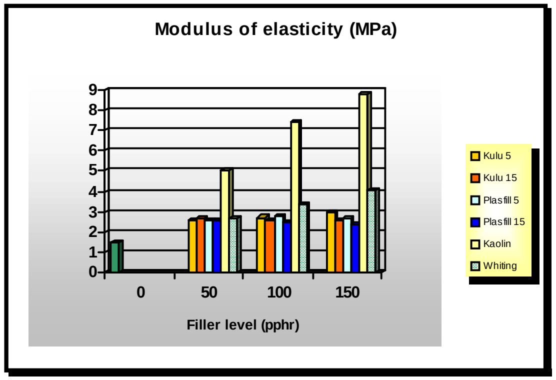

Figure 5. The effect of filler loading on the modulus of elasticity

SUMMARY AND CONCLUSION

The use of microfine alumina silicate spheres as a filler for natural rubber lowers the viscosity and therefore aids processing and reduces the time required to compound products. In contrast to many of the other fillers tested Plasfill does not affect the curing cycle. This can be advantageous since it eases the task of formulation by eliminating a source of variance. The use of Plasfill influences the physical properties of the cured compound to about the same degree as most of the other fillers with the exception of kaolin.

Given the enhancement of physical properties, especially tear strength and modulus of elasticity achieved with the introduction of kaolin and the improvement in the elongation at break by the introduction of Plasfill it would be very interesting to use these two fillers together. In this case one could use the Plasfill to promote compounding efficiency and the kaolin to engineer specific physical properties. This is currently being investigated.

The results of this work indicate that spherical fillers recovered from fly ash can be successfully used in the manufacture of rubber products. The technology is still in its infancy and many new and exciting developments can be expected.

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