

## ***Effect of an Antioxidant System on the Structure and Properties of Natural Rubber-Clay Composite***

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*The clays were modified by using an antioxidant, metal passivating agent and polymeric coating agent, and the corresponding clay-rubber masterbatch was prepared from the modified clay. The properties and structure of the masterbatch after thermo-oxidative aging were studied. The results indicated that the actions of the antioxidant, polymeric coating agent and metal passivating agent, the thermo-oxidative ageing resistance of the masterbatch was significantly improved. Properties such as tensile strength, elongation at break and tear strength of the masterbatch could be increased from -61.4%, -40.9% and -57% to -11.1%, -9.7% and -8.9%, respectively. The SEM ultrastructure of the cross section of the modified clay-rubber masterbatch after aging showed that the boundary surface between layers of section was smooth, which meant that the structure of the rubber was preserved satisfactorily.*

**Key words:** clay; antioxidant system; modified clay-rubber; masterbatch; thermo-oxidative aging; SEM; structure; physical properties

The red clay (referred to as clay for short) is an inexpensive and abundant mineral which is widely dispersed over the rubber planting areas in South China and South-East Asia. Its reinforcing action on rubber is greater than that of SRF black and is similar to that of HAF black, the clay can therefore be used to replace or partly replace SRF, GPF and HAF blacks in the manufacture of bicycle tyres, shoe soles and hoses<sup>1-3</sup>. Previous research has shown that metal components with variable valencies as cobalt, copper, iron and manganese are present in the clay, which can greatly accelerate the aging of rubber<sup>4,5</sup>, especially the

thermo-oxidative aging of rubber-clay masterbatch<sup>6</sup>. In this paper, clays were modified by using antioxidant, metal passivating agent and polymer coating agent, and the variations in the ultra-microstructure and the physical properties of the masterbatch from modified clay after thermo-oxidative aging were studied.

### MATERIALS AND METHOD

The clay was obtained from Jiaolin state farm in Hainan province, P. R. China. The natural

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rubber latex was obtained from Tuanjie state farm in Guangdong province, P. R. China. The dispersion agent and coagulant are of AR or CP grade. The antioxidants are commercial chemicals. The polymeric coating agent prepared by our laboratory from the reaction of long-chain fatty acid with polyol is a polymer with hydrophilic and rubber-phile structure.

**Preparation of Unmodified Clay Sample**

The unmodified clay sample, which is a 20% dispersion of clay in water, was obtained from raw clay by dispersing, filtrating and settling.

**Preparation of Modified Clay Sample**

The modified clay samples were obtained through the treatments with chemicals shown in Table 1.

**Preparation and Determination of Properties of Masterbatch**

The natural rubber latex was co-precipitated with an unmodified clay sample and the modified ones stated as in Table 1. The co-precipitates were sheeted and dried to prepare the masterbatch samples (*Sample A–H*) for determination of the physical and aging properties of vulcanised masterbatches according to *Chinese Standards GB/T 528* and *GB/T 531*. The ratio of NR and clay used was 55/45. The thermo-oxidative aging conditions of samples in air were at 100°C for 36 h. The thermo-oxidation properties of the masterbatch were expressed by the variation ratios of the physical properties before and after aging, which was expressed as:

$$P = \frac{A - B}{B} \times 100 \qquad \dots 1$$

TABLE 1. THE MODIFIED CLAY SAMPLES

Sample	Components and modifying agents					
	Clay	Antioxidant DFC®	Antioxidant 300®	Antioxidant MB®	Metal passivating agent GI-09-367®	Polymeric coating agent
A	+					
B	+	+	+			
C	+		+	+		
D	+		+		+	
E	+	+	+			+
F	+	+		+	+	
G	+			+	+	+
H	+	+		+	+	+

Note: The amounts of antioxidant DFC®, antioxidant 300® and antioxidant MB® used are 2/100 NR each, and the amounts of passivating agent GI-09-367® and polymeric coating agent used are 2/100 clay each.

Antioxidant DFC® = styrenated diphenylamine;  
Antioxidant 300® = 4, 4'- thio bis ( 6-tert-butyl-m-cresol);  
Antioxidant MB® = 2-mercaptobenzimidazole;  
Metal passivating agent GI-09-367® = N, N-diacetyl adipic acid dihydrazide.

in which *A* and *B* stand for the properties of samples after and before aging, respectively. The aging coefficient of the masterbatch was expressed in the ratio of products of tensile strength and elongation at break, after and before aging. The analyses of the ultra-microstructure of masterbatch were performed on Philips XL-30 SEM.

## RESULTS AND DISCUSSION

### Thermo-oxidative Aging of Masterbatch from Modified Clay

The physical properties of masterbatches from modified and unmodified clays before aging are shown in *Table 2*. The variations of

the relevant properties after thermo-oxidative aging are shown in *Table 3*.

It can be seen from the tables stated above that the properties of *Masterbatch A* from the unmodified clay decrease significantly after the thermo-oxidative aging, whereas the thermo-oxidative aging resistance of masterbatches from the modified clays improved in different degrees, among which *Samples E, G* and *H* are particularly good. During the thermo-oxidative aging of natural rubber, the rubber hydrocarbon, under the action of heat and oxygen, produce free radicals. The radicals are oxidised into hydroperoxides which decompose further into oxide and new free radicals. Owing to the continuous scission of the molecular chain of the rubber hydrocarbon, the

TABLE 2. PROPERTIES OF CLAY-RUBBER MASTERBATCH

Properties	Masterbatch samples							
	A	B	C	D	E	F	G	H
Hardness (Shore A)	63	64	65	63	65	64	67	64
Tensile strength (MPa)	23.6	24.1	26.7	26.7	25.0	26.2	25.2	25.3
Elongation at break (%)	585	589	594	591	605	599	596	600
Tear strength (kN/m)	68.9	75.6	71.2	71.5	70.4	72.5	77.3	72.7

TABLE 3. THERMO-OXIDATIVE AGING PROPERTIES OF MASTERBATCH

Variation in properties	Masterbatch samples							
	A	B	C	D	E	F	G	H
Ratio of hardness (%)	4.7	3.1	0	6.3	7.6	4.7	6.9	6.3
Ratio of tensile strength (%)	-61.4	-31.5	-32.2	-19.9	-12.0	-25.5	-14.3	-11.1
Ratio of elongation at break (%)	-40.9	-24.6	-16.5	-18.6	-11.2	-18.2	-10.7	-9.7
Ratio of tear strength (%)	-57.4	-16.8	-21.8	-13.1	-10.2	-15.2	-10.1	-8.9
Ageing coefficient	0.228	0.516	0.566	0.652	0.781	0.601	0.765	0.803

Ageing condition in hot air = 100°C × 36 h

properties of the masterbatch deteriorate. Large amounts of metal components with variable valencies such as copper, cobalt, iron and manganese exist freely in the clay. According to the previous research, these metal components have various oxidation-reduction potential. By decreasing the reaction activation energy, such metal components can accelerate the initiation of oxidation and shorten the induction period of oxidation, causing the thermo-oxidative aging resistance of rubber to deteriorate. On the other hand, these metal components can catalyze the decomposition of hydroperoxide into free radicals which promote the rapid deterioration of rubber properties<sup>7</sup>. It can be concluded that the masterbatch from unmodified clay is affected by heat and oxygen, at the same time large amounts of metal components in clay become strongly active under heat and air, which accelerates the oxidation of natural rubber and thermal degradation of rubber hydrocarbon<sup>8,9</sup>. Therefore, the physical properties of the masterbatches after thermo-oxidative aging deteriorate significantly.

In this study, thermo-oxidative aging resistance of the masterbatch is improved in different degrees with the additions of antioxidant, metal passivating agent and polymeric coating agent. Hence, it can be presumed that in the masterbatch from modified clay, the activity of metal components are decreased owing to chelation of metal ions by the metal passivating agent. In addition, the physical and chemical actions between the polar groups of polymeric coating agent and the polar groups on clay particle surfaces as well as the actions between the non-polar groups of polymeric coating agent and the rubber hydrocarbon, can cover the surfaces of clay particles and isolate the metal components from rubber hydrocarbon. Besides, as DFC is an amine antioxidant, 300 is a phenol antioxidant and MB is a thiol antioxidant as

well as a decomposing agent of the hydroperoxide, it can be considered that they will have a positive effect on the aging resistance of the masterbatches. These antioxidants, when used together with the metal passivating agent and polymeric coating agent, significantly improve the thermo-oxidative aging resistance of masterbatches.

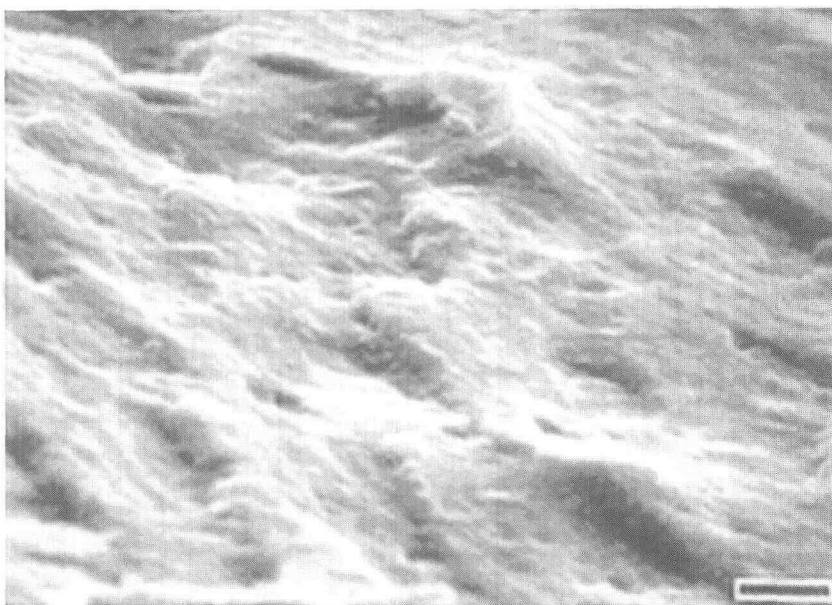
### SEM Ultra-microstructure of Clay Masterbatches

Figures 1,2,3 and 4 are SEM ultra-micrographs of the cross sections of masterbatches before and after thermo-oxidative aging. The sections of masterbatch samples were obtained by using freeze-peeling treatment with liquid nitrogen.

Figure 1 is the sectional view of masterbatch *Sample A* (see Table I) from unmodified clay before aging. From Figure 1, it can be seen that the section assumes a slight wave-like shape, its boundaries are not clear but rather even, indicating that the bond between clay and natural rubber is good; the masterbatch still retain the properties of natural rubber.

Figure 2 is the sectional view of the masterbatch *Sample A* from unmodified clay after aging; the section is like a weathered rock full of lumps and cavities. The boundaries between layers and between layer and cavity are clear, which indicate that the metal components in clay accelerate the thermo-oxidative degradation of natural rubber, causing the macromolecules of natural rubber to turn into small molecules.

Figures 3 and 4 are sectional views of the masterbatch from modified clay after aging. Figure 3 is the section of the masterbatch *Sample F* with no polymeric coating agent



*Figure 1. SEM ultra-micrograph of masterbatch from unmodified clay before aging. (Bar = 5  $\mu\text{m}$ .)*



*Figure 2. SEM ultra-micrograph of masterbatch from unmodified clay after aging. (Bar = 10  $\mu\text{m}$ .)*



*Figure 3. SEM ultra-micrograph of aged Masterbatch F. (Bar = 5  $\mu\text{m}$ .)*



*Figure 4. SEM ultra-micrograph of aged Masterbatch H. (Bar = 3  $\mu\text{m}$ .)*

added. *Figure 4* is the section of the masterbatch *Sample H* with polymeric coating agent added. From *Figure 3*, it can be seen that the part of the section between layers is not quite even and there exists some cavities. The boundaries between the layers and between the layer and cavity are rather clean. *Figure 4* shows that the section was rather even and the boundary between layers is smooth. Although there is a few small cavities, the boundary between the layer and cavity is very clean. It can be presumed that under the action of heat and oxygen, the antioxidant and metal passivating agent can increase the thermo-oxidative aging resistance of the masterbatch, which has certain protective action to the structure of masterbatch. The addition of polymeric passivating agent makes the surface of clay particles to be coated by this agent; besides, the polar group and non-polar group of the polymeric passivating agent can promote the interaction between clay and natural rubber, therefore the structure of the masterbatch is preserved after thermo-oxidative aging.

### CONCLUSIONS

The physical properties of masterbatch from unmodified clay deteriorated significantly on aging. Under various conditions, rubber was degraded by heat and oxygen; there was thermo-oxidative degradation, promoted by the metal components in the clay, as shown in the SEM ultra-micrograph, that the cross sections of the aged masterbatch were full of lumps and cavities; the boundaries, however, were clear.

The thermo-oxidative aging resistance of masterbatch could be improved greatly by applying antioxidant, polymeric coating agent and metal passivating agents together. The cross section of the aged masterbatch, as

shown by the SEM ultra-micrograph, indicated that the boundaries between layers were rather smooth, the structure of rubber was satisfactorily preserved.

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