

# Study on Aging of Clay–Rubber Masterbatch from Modified Clay

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**ABSTRACT:** Clay was modified by using a polymeric coating agent, a silicane coupling agent, and a titanate coupling agent together with the antioxidant for preparing the clay–rubber masterbatch. After the thermooxidative, photooxidative, and ozone aging, the properties of the masterbatch were also determined. The results indicate that, under the synergistic actions of the polymeric coating agent, antioxidant, and coupling agent, the thermooxidative and photooxidative aging resistances of the masterbatch were greatly improved. The properties of ozone aging resistance of the masterbatch can be increased by 50% under the combined action of a new kind of amine antioxidant with a titanate coupling agent. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 338–342, 2001

**Key words:** clay; modification; clay–rubber masterbatch; aging

## INTRODUCTION

Previous research work shows that red clay (clay for short), which has a significant reinforcing action on rubber, can replace or partly replace HAF, GPF, and SRF for manufacturing bicycle tires, soles, and hoses. The properties of the products conform to national standards.<sup>1</sup> However, further application of the masterbatch is restricted because of the masterbatch's poor aging resistance, which is greatly affected by the metal components in clay.<sup>2</sup> It is established that metal components with a variable-valence state such as cobalt, copper, iron, and manganese adversely affected the

aging resistance of the clay, although it is impossible to completely remove these metal components. To remove the bad effects of the trace metals in natural latex and ingredients, an ion-chelating agent and an antioxidant were used to treat the latex and ingredients.<sup>3</sup> However, there are no reports on how to eliminate the actions of the metal components in fillers. In this study the clay was modified by using a coating agent, a coupling agent, and an antioxidant, and the variations in the properties of the masterbatch from modified clay after aging were also studied.

## EXPERIMENTAL

### Materials

The clay was obtained from Nanhua state farm (Guangdong province, China). The natural rubber

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**Table I The Modified Clay Samples**

Sample	Components and Modifying Agents							
	Clay	Polymeric Coating Agent	Antioxidant DFC	Antioxidant MB	Coupling Agent KH550	Coupling Agent KH570	Coupling Agent NDZ201	Coupling Agent NDZ 401
I	+							
II	+	+	+					
III	+	+		+				
IV	+	+		+	+			
V	+	+				+		
VI	+	+					+	
VII	+						+	+
VIII	+	+	+					+

latex was obtained from Qianjin state farm (Guangdong province). The dispersion agent and coagulant were of AR or CP grade. The silicane coupling agent, the titanate coupling agent, and the antioxidant are commercial chemicals. The polymeric coating agent was prepared in our laboratory.

#### Preparation of Unmodified Clay Sample

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

#### Preparation of Modified Clay Sample

The modified clay samples were obtained through the treatments with chemicals stated in Table I.

#### Preparation and Determination of Properties of Masterbatch

The natural rubber latex was coprecipitated with unmodified clay sample and modified clay samples stated in Table I, then the coprecipitates were sheeted and dried to prepare the masterbatch samples (samples I–VIII) for the determination of the physical and aging properties of vulcanized masterbatches. The mechanical properties of the masterbatch were determined according to Chinese standard GB/T 528. The hardness of the samples was determined according to Chinese standards GB/T 531 and GB/T 2411.

The thermal aging of samples in air was carried out according to Chinese standard GB/T 3512-1983 (equiv. ISO 188-1982) and the thermooxidative aging condition for masterbatch was at 100°C hot air for 24 h.

The photooxidative aging of masterbatches was carried out in an Atlas UC-1 ultraviolet fluorescence aging oven according to Chinese standard GB/T 16585-1996 (equiv. ASTM G 53-88).

The ozone aging of masterbatches was carried out in a Suga OMS-IVCR ozone aging oven at 40°C according to Chinese standard GB/T 7762-1987 (equiv. ISO 1431/1), with an ozone concentration of 50 ppm; the static elongation was 20%.

The thermooxidation and photooxidation properties of masterbatches were expressed by the variation ratios of masterbatch properties before and after aging, which was expressed as

$$P = \frac{A - O}{O} \times 100$$

in which *A* and *O* stand for the properties of samples after and before aging, respectively.

The ozone aging properties of the masterbatch were expressed at the time when the first ozone crack appeared.

## RESULTS AND DISCUSSION

#### Thermooxidative Aging of Masterbatch from Modified Clay

Table II shows the properties of clay-rubber masterbatch before aging. Table III shows the thermooxidative aging properties of masterbatch from modified clays.

It can be seen that the masterbatch properties from unmodified clays obviously decrease after the thermooxidative aging, whereas the ther-

**Table II Properties of Clay–Rubber Masterbatch**

Properties	Masterbatch Sample							
	I	II	III	IV	V	VI	VII	VIII
Hardness (Shore A)	61	63	60	66	65	63	63	64
Tensile strength (MPa)	24.8	25.0	25.7	26.9	26.3	25.2	25.5	25.1
Elongation at break (%)	590	600	610	630	620	610	610	600
Tear strength (kN/m)	94	99	98	112	109	102	104	103

thermooxidative aging resistance of masterbatches from modified clays are improved in different degrees, among which samples II, III, and IV are especially prominent. During the thermooxidative aging of natural rubber, the rubber hydrocarbon, under the action of the oxygen, produced free radicals. The radicals were oxidized into hydroperoxide, which is decomposed further into oxide and new free radicals. As a result of the continuous scission of the molecular chain of the rubber hydrocarbon, the properties of the masterbatch deteriorate. The metal components with variable-valence state existing in the rubber cause electron transfer and accelerate the production of free radicals, thereby promoting the oxidation and cracking of rubber hydrocarbon.<sup>4</sup>

The results from this study show that the thermooxidative aging resistance of the masterbatch can be improved significantly after addition of the polymeric coating agent and the coupling agent. Hence, it can be concluded that the metal components in clay can accelerate the thermooxidative aging of the masterbatch. The coating agent and the coupling agent can cover the surface of the clay particles, thus isolating the metals from rubber hydrocarbon and preventing the adverse effect of the metal components in clay on rubber hydrocarbon. Because DFC is an amine antioxidant and MB is both a thiol antioxidant and a decomposing agent of the hydroperoxide, it can be

considered that during the thermooxidative aging of the masterbatch, the formation of hydroperoxide is an important step; the amine and thiol antioxidants have positive effects on the aging resistance of the masterbatch. Moreover, the antioxidants, when used together with the polymeric coating agent, show a synergistic action. Meanwhile, the coupling agent not only can produce coating action but also is a releasing agent of the active hydrogen, because it contains organic functional group R–NH<sub>2</sub>, which can terminate the formation of peroxide free radical from rubber hydrocarbon. Therefore the coupling agent shows a good thermooxidative aging resistance.

#### Photooxidative Aging Properties of Masterbatch from Modified Clay

The variations in the properties of the masterbatch in different ultraviolet fluorescence aging times are shown in Tables IV and V.

It can be seen that the deterioration of the properties of the masterbatch from unmodified clay is more obvious than that of the masterbatch from modified clay, whether the aging time is 20 or 30 h. The effects of ultraviolet fluorescence on rubber are mainly embodied in two aspects.<sup>3</sup> First, the rubber hydrocarbon is excited after absorbing the photo and free radicals are formed; at the same time, the hydroperoxide in rubber forms

**Table III Thermooxidative Aging Properties of Masterbatch**

Properties Variation (%)	Masterbatch Sample							
	I	II	III	IV	V	VI	VII	VIII
Variation ratio of hardness	1.6	4.5	9.1	10.2	4.5	6.0	1.5	1.6
Variation ratio of tensile strength	–88.1	–21.4	–13.2	–10.8	–48.0	–47.8	–53.3	–59.4
Variation ratio of elongation at break	–51.7	–4.2	–19.7	–34.6	–21.0	–15.1	–12.3	–18.3
Variation ratio of tear strength	–62.4	–5.9	–6.7	–1.1	–39.9	–41.0	–24.4	–43.0

**Table IV Properties of Masterbatch after Photooxidative Aging for 20 h**

Properties Variation (%)	Masterbatch Sample							
	I	II	III	IV	V	VI	VII	VIII
Variation ratio of hardness	3.3	1.6	1.7	3.4	4.8	3.2	0	0
Variation ratio of tensile strength	-5.5	-0.1	-1.1	-1.0	-4.3	-7.1	-5.3	-2.8
Variation ratio of elongation at break	-4.2	-11.5	-6.2	-2.9	-4.1	-0.5	-2.1	-3.2
Variation ratio of tear strength	-5.2	-1.2	-2.5	-1.4	-3.2	-4.2	-4.4	-3.0

the peroxide free radicals after adsorbing the photo. Second, the photo, in the presence of oxygen, can activate the oxygen molecule and accelerate the oxidation of rubber hydrocarbon and the formation of peroxide, which eventually results in the scission of rubber molecular chains, thus destroying the material. Salomon<sup>5</sup> proposed that the photooxidative aging and the thermooxidative aging of natural rubber are similar, with no substantial difference. Yano<sup>6</sup> and Morand<sup>7</sup> also confirmed this viewpoint. The results of our study also indicate that the photooxidative and thermooxidative aging of the masterbatch are similar; the only difference is in the degree of aging. The polymeric coating agent; coupling agent; and antioxidants DFC and MB, which have significantly protective action against the thermooxidative aging, can also protect the masterbatch from photooxidative aging. However, it should be noted that there is no corresponding relationship that exists in thermooxidative and photooxidative aging properties of the masterbatch from clays with different treatments.

#### Ozone Aging Properties of Masterbatch from Modified Clay

The variations in the ozone aging properties of masterbatches from modified clays and unmodified clay are shown in Table VI.

It can be seen that the ozone aging resistance of the samples from modified clay (except sample VIII) is reduced. It also can be seen that the mechanism of ozone aging of the masterbatch is different in nature from that of the thermooxidative aging. The metal components in clay have no positive effect on the ozone aging resistance of the masterbatch. Hence, the coating of the polymeric coating agent and silicane coupling agent on clay particles does not improve the ozone aging resistance of the masterbatch; on the contrary, it hinders and isolates the interaction between the clay particle and rubber hydrocarbon, which results in the deterioration of the ozone aging resistance of the masterbatch. This result is consistent with that of Dweik, who suggested that clay can improve the ozone aging resistance of rubber.<sup>8</sup> At the same time, we also discovered that the antioxidant MB has no positive effect on the ozone aging of the masterbatch. The reason is that the active hydrogen in MB will react with the added silicane coupling agent, titanate coupling agent, and polymeric coating agent, which will prohibit the diffusion of MB onto the surface of the rubber and lead to deterioration of the ozone aging resistance of the masterbatch.<sup>9</sup> It was also discovered that a new kind of amine antioxidant, DFC, has an obvious effect on the ozone aging resistance of the masterbatch. When DFC was used together with the titanate coupling agent and polymeric

**Table V Properties of Masterbatch after Photooxidative Aging for 30 h**

Properties Variation (%)	Masterbatch Sample							
	I	II	III	IV	V	VI	VII	VIII
Variation ratio of hardness	3.3	4.8	5.0	8.5	1.6	3.2	1.6	3.3
Variation ratio of tensile strength	-11.2	-2.2	-0.7	-4.6	-6.7	-3.8	-4.0	-2.3
Variation ratio of elongation at break	-11.7	-6.9	-11.2	-7.3	-0.9	-2.0	-1.4	-5.2
Variation ratio of tear strength	-10.3	-3.9	-4.4	-4.0	-4.7	-5.2	-6.2	-4.7

**Table VI Properties of Ozone Aging of Masterbatch**

Property	Masterbatch Sample							
	I	II	III	IV	V	VI	VII	VIII
Ozone cracking time (h)	16	9.5	5.5	5.0	7.5	12	4.5	18

coating agent, the ozone aging resistance of the masterbatch increased by 50%.

## CONCLUSIONS

1. Under the synergistic action of the polymeric coating agent, antioxidant, and coupling agent, the thermooxidative and photooxidative aging resistance of the masterbatch can be improved greatly.
2. The ozone aging resistance of the masterbatch can be increased by 50% under the combined action of a new kind of amine antioxidant with a titanate coupling agent.

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