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EFFECT OF NON-BLACK FILLERS AND PIGMENTS ON THE PHYSICAL PROPERTIES AND DEGRADATION RESISTANCE OF NATURAL RUBBER LATEX THREAD EXPOSED TO UV-RADIATION

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The effect of titanium dioxide and its combinations with fillers such as china clay, precipitated calcium carbonate and barium sulphate at a low dosage on the physical properties and degradation resistance of latex thread prepared using conventional and efficient vulcanization systems were investigated. Though titanium dioxide had little effect, its combination with fillers attributed better modulus and tensile strength to the thread samples. Addition of titanium dioxide did not improve the degradation resistance of thread to heat and UV light. The combination of titanium dioxide with precipitated calcium carbonate showed better performance under photo oxidative ageing.

Key words : Degradation, Latex thread, Non-black fillers, Pigment, Rubber, Ultraviolet radiation.

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INTRODUCTION

Among the physical properties of latex thread, the most important parameters are the modulus and tensile strength. The effects of vulcanization systems and accelerator combinations on the above properties have been reported (Weiss, 1979; Collins and Gorton, 1984; 1985). Due to its large surface area, the thread is vulnerable to degradation by detergents, heat, light and oxygen. UV-light causes both degradation and discolouration (Morton, 1959; Robert, 1978). Studies have also been conducted on the effects of various antioxidants in retarding degradation (Gorton *et al.*, 1989). Generally certain non-black fillers are added at low dosages (below 10 phr) along with titanium dioxide to latex thread compounds for getting better modulus and colour respectively. But no systematic study on the effects of common non-black fillers and pigments on the physical properties of latex threads have been reported.

In dry rubber compounding, fillers generally act as reinforcing agents, but in latex they weaken the rubber film rather than improve its strength, due to the poor rubber-filler interactions (Blackley, 1997; Peethambaran and Kuriakose, 1989). But it has also been reported that china clay at low dosages can improve the physical properties of latex vulcanizates (Van Rossem and Plaizier, 1938).

The present work reports on the effect of titanium dioxide (pigment) and fillers like china clay, precipitated calcium carbonate and barium sulphate (barytes) along with titanium dioxide on the physical properties of latex thread, with special reference to its degradation under UV-radiation.

EXPERIMENTAL

Centrifuged high ammonia natural rubber latex conforming to BIS 5430-1981 was used in this study. Latex thread compounds were prepared as per the

Table 1a. **Formulations for latex compounds (CV system)**

Ingredients	Formulation				
	A	B	C	D	E
60% Centrifuged HA latex	167	167	167	167	167
10% Potassiumhydroxide solution	2	2	2	2	2
50% Sulphur dispersion	3.6	3.6	3.6	3.6	3.6
50% ZDEC* dispersion	2	2	2	2	2
50% ZMBT* dispersion	1	1	1	1	1
50% Zinc oxide dispersion	1	1	1	1	1
33% Titanium dioxide dispersion	-	22.5	7.5	7.5	7.5
50% China clay dispersion	-	-	10	-	-
50% Precipitated $CaCO_3$ dispersion	-	-	-	10	-
50% Barytes dispersion	-	-	-	-	10

* ZDEC – Zinc diethyl dithiocarbamate
ZMBT – Zinc 2-mercaptobenzothiazole

formulations given in Tables 1a and 1b. The compounding ingredients were added as fine dispersions/solutions. The compounds were matured at 30°C for 96 h and sieved through a 100 mesh sieve cloth. Each compound was then run on a pilot plant for thread manufacture through a glass capillary of 0.75 mm diameter using 20 per cent formic acid as the coagulant. The threads were then dried at 70°C for 1 h and vulcanized in boiling water. The threads with conventional cure system were vulcanized for 60 min and those with efficient vulcanization system, for 90 min. Cast latex film using each latex compound was also prepared and vulcanized to the same extent as that of the thread sample.

A portion of thread sample was tested for its tensile properties as per ASTM D412 using Instron D4411 universal testing machine. Another portion of thread sample and the film sample were then exposed to UV-radiation from a UV-source (Philips-TLD 30W, Holland) for 24, 48 and 96 h. The tensile properties of the thread samples after the exposure were also determined. The thread samples were also subjected to heat ageing at 100°C for 22 h in a multicellular ageing oven and their tensile properties determined.

Table 1b. **Formulations for latex compounds (EV system)**

Ingredients	Formulation				
	F	G	H	I	J
60% Centrifuged HA latex	167	167	167	167	167
10% Potassium hydroxide solution	2	2	2	2	2
50% Sulphur dispersion	0.5	0.5	0.5	0.5	0.5
50% ZDEC dispersion	1	1	1	1	1
50% TMTD* dispersion	4	4	4	4	4
50% Zinc oxide dispersion	1	1	1	1	1
20% Thiourea solution	3.5	3.5	3.5	3.5	3.5
33% Titanium dioxide dispersion	-	22.5	7.5	7.5	7.5
50% China clay dispersion	-	-	10	-	-
50% Precipitated $CaCO_3$ dispersion	-	-	-	10	-
50% Barytes dispersion	-	-	-	-	10

* TMTD - Tetramethyl thiuram disulphide

To assess the extent of rubber-filler attachment in the filled vulcanizates, rubber-filler bonds were cleaved chemically by swelling the vulcanizate samples for 48 h in flat dishes containing benzene in ammonia atmosphere (Polmanteer and Lentz, 1975). After swelling, the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature and tested for V_r by swelling in benzene.

RESULTS AND DISCUSSION

The tensile properties of latex thread samples containing fillers and titanium dioxide pigment having conventional and efficient vulcanization systems, before and after exposure to UV-light are given in Table 2.

Table 2. **Tensile properties of the latex thread under UV irradiation**

Formulation	Unexposed	Modulus 300% (MPa) UV-exposure time (h)			Unexposed	Tensile strength (MPa) UV-exposure time (h)		
		24	48	96		24	48	96
CV system								
A	1.26	1.4	1.4	1.2	21	15	13	9
B	1.3	1.1	1.1	1.0	23	14	9	4
C	1.5	1.5	1.5	1.1	26	20	14	4
D	1.6	1.7	1.6	1.6	26	22	20	11
E	1.5	1.8	1.4	1.4	26	22	14	4
EV system								
F	1.2	1.0	0.85	0.80	18	12	10	8
G	1.25	1.1	0.86	0.75	22	14	9	7
H	1.5	1.43	1.10	0.95	25	19	14	8
I	1.4	1.2	1.12	0.84	24	17	13	8
J	1.4	1.4	0.86	0.81	24	18	14	8

It can be seen that the latex compounds with titanium dioxide alone gave no marked improvement in the modulus and tensile strength. But all the thread samples with a combination of the filler and the pigment showed better modulus and tensile strength.

This may be due to the effect of better rubber-filler interaction (Mukhopadhyay and De, 1979; Dogadkin *et al.*, 1958). The difference in chemical crosslink density (measured as V_r values) as obtained by swelling studies in benzene of the original vulcanizates and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond.

Table 3. **Changes in V_r values after ammonia modified swelling and UV irradiation**

Formulation	V_r values			
	Original(V_ro)	Ammonia modified (V_ra)	Difference (V_ro - V_ra)	After 96 h UV irradiation
A	0.186	0.1823	0.0037	0.1768
B	0.1873	0.1794	0.0079	0.1712
C	0.1911	0.1757	0.0154	0.1693
D	0.1919	0.1722	0.0197	0.1800
E	0.1894	0.1722	0.0172	0.1709
F	0.1626	0.1617	0.0009	0.1544
G	0.1723	0.1591	0.0132	0.1582
H	0.1879	0.1652	0.0227	0.1716
I	0.1811	0.1685	0.0126	0.1668
J	0.1791	0.1687	0.0104	0.1641

The V_r values given in Table 3 for the samples with filler-pigment combination indicate the better rubber filler interaction. For the samples C, D and E, the V_r values reduced more after ammonia modified swelling. When the samples were exposed to UV light the tensile properties decreased in all cases. In the conventional vulcanization system thread sample containing precipitated calcium carbonate filler and titanium dioxide pigment gave better resistance to UV light whereas in efficient vulcanization system all the fillers behaved almost similarly. This can be attributed to the high sulphur content in the CV system which can contribute to more crosslink formation.

During the photo-oxidative ageing of natural rubber, the rubber hydrocarbon produces free radicals, by absorbing energy from UV-radiation of 290-350 nm (Carlsson *et al.*, 1979).

Water, which is capable of hydrolysis and the acidic nature of some fillers also cause the breakage of rubber hydrocarbon chain network under UV-light and heat. The alkaline nature of the precipitated calcium carbonate may have imparted high resistance to UV for the sample in which this filler was used. The white pigment TiO_2, which has good reflectance properties (Hepburn, 1982) against light when used alone or with other fillers, was not able to give satisfactory protection to NR latex thread. The chain breakage of NR hydrocarbon during photo-oxidative ageing resulted in poor properties of the exposed thread samples. The filled thread samples subjected to efficient vulcanization also showed a decreasing trend in properties after exposure to UV-light for 96 h. The changes in V_r values (Table 3) of the cast latex film samples which degraded after photo-oxidative ageing, support this.

The properties of the unfilled and filled thread samples before and after heat ageing at 100°C for 22 h are given in Tables 4. The properties, mainly the tensile strength values, decreased to a higher extent for samples under conventional vulcanization system when heat aged. Here also the thread samples filled with precipitated $CaCO_3$ along with TiO_2 pigment showed better values compared to the other samples. This may be due to its alkaline behaviour, which is harmless to rubber hydrocarbon. When the NR latex thread is exposed to UV-light and heat, the hydrocarbon gets oxidized to hydroperoxides in the presence of atmospheric oxygen. The hydroperoxides are further decomposed into oxide and a new free radical is formed (Abu Zeid *et al.*, 1986; Carlsson *et al.*, 1979; Scheele and Hillmer, 1970; Bousquet and Fouassier, 1983). The scission of rubber hydrocarbon molecules reduces the properties of the thread samples. The metal components existing in the rubber and filler favour electron transfer and accelerates the production of free radicals which in turn accelerate oxidation (Mei-Chen *et al.*, 1999;

Table 4. **Tensile properties of latex thread after 22 h heat ageing at 100°C**

Formu lation	Modulus 300% (MPa)		Tensile strength (MPa)	
	Original	Heat aged	Original	Heat aged
CV system				
A	1.26	0.73	21	5
B	1.3	1.08	23	4.5
C	1.5	1.00	26	3
D	1.6	1.56	26	8
E	1.5	1.10	26	3.5
EV system				
F	1.2	1.5	18	16
G	1.25	1.6	22	14.5
H	1.5	1.3	25	8
I	1.4	1.8	24	16
J	1.4	1.3	24	10

Ning-Jian *et al.*, 1999). It is also known that active sites like hydroxyl groups, coordinatively unsaturated metal atoms and free radicals present on the surface of fillers are capable of chemical interaction with the polymer (Bryk, 1991). At excited energy conditions like photo irradiation, water molecules co-ordinatively bonded to the filler or pigment surface may participate in hydrolysis and acidolysis of polymers possessing unsaturated bonds.

Based on the above discussion, we can attribute the degradative effects of UV-irradiation on filled NR latex thread sample to a combined action of acidic fillers, water, metal ions present in the filer and also to the high energy radiation. Efficient vulcanized products exhibited very good performance in retaining the physical properties than the conventionally vulcanized products when subjected to heat ageing or photo irradiation.

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