NOTES

Increase of Mechanical Strength of Hydroxy Terminated Polybutadiene by Adding Small Amounts of Carbon Black

INTRODUCTION

Rubber vulcanizates are commonly reinforced with fillers to increase strength and stiffness.[1-3] Rubbers that do not crystallize on stretching must be compounded with fillers to attain a high strength. The most frequently used fillers are different types of carbon black, with a loading density of about 40–70%. For such high densities other properties, like viscosity and consequently the processability, are also changed considerably. Important characteristics in reinforcements are particle size, structure, and magnitude of the interactions between the surface of the particles and the rubber material. The term structure refers to the joining together of carbon black particles to long chains into a three-dimensional network. Increasing the mechanical strength without changing other properties is impossible; all methods mean compromises in one way or another. If, for example, the crosslink density is increased, the tensile strength and the modulus will increase, but the elongation at break will generally decrease.

The possibility to substantially change the electrical properties of rubbers with only small changes of other properties, has increased a lot due to the introduction of new types of carbon blacks, such as Ketjenblack EC from AKZO, Holland, Black Pearls 2000 from Cabot, USA, and Printex XE-2 from Degussa AG, Germany. They have a very high structure, and they are meant to be used for obtaining electrical conductivity where only small amounts are required compared to conventional electroconductive carbon blacks. In spite of their high structure, nothing has been found in the literature about their reinforcing effects.

In the field of solid rocket motor engineering, a method for increasing the mechanical properties of rubber without changing other properties would be very valuable. In the Skidmore's study,[4] the addition of small amounts of carbon black is recommended to increase the thermal protection ability of rocket motor insulation materials. In other patents addition of small amounts of carbon black to rocket motor materials are recommended for reasons other than improving the mechanical properties.[5]

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The purpose of this work has been to study the effect on mechanical properties of small concentrations of carbon black on the curable rubber, hydroxy terminated polybutadiene (HTPB). This polymer is a frequently used binder material for rocket propellants. It is also a typical low-crystalline, carbon–carbon chain polymer, suitable as a model substance for many rubber materials.

EXPERIMENTAL

Materials

The polymer used was HTPB, type R-45HT (ARCO, USA), with 1.8% of 2,2′-methylene-bis(4-methyl-6-tertiary-butylphenol) (BKF) (Bayer AG, Germany) as antioxidant. The polymer is a liquid prepolymer that can be cured with diisocyanates to a rubber with excellent mechanical properties, even at low temperatures. As curing agent isophorone diisocyanate (IPDI) was used. If not otherwise stated, IPDI was admixed in a molar ratio of 1.0.

The carbon blacks used were types Corax N-375, N-220, and N-115 from Degussa AG, Germany (N-115 is called N-110 in the US), and Ketjenblack EC-600 JD from AKZO, Holland, from now on called KEC. Carbon black notations given are according to ASTM D3912 and D3191. To obtain reproducible results, it is essential to disperse the carbon black thoroughly; and for this reason, for each type of carbon black, a master batch was produced by thoroughly dispersing the carbon black in HTPB on a rolling mill. Then from each master batch samples were taken and diluted with HTPB to the desired concentration.

Measurements

The viscosimeter was a Haake Rotovisco RV 100. The hardness was measured similar to ISO 48-1979 (E), but on a shore A scale on a Zwick 233 apparatus. The tensile test apparatus was an Alvetron TCT 5 from Lorentzen and Wettre AB, Stockholm. The tests were carried out at a temperature of 293 K with a tensile rate of 50 mm/min for every measuring point. Six samples were tested each

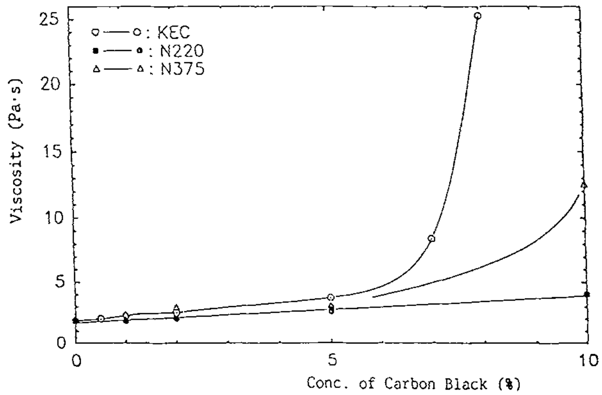

Figure 1 Viscosity at 50°C for HTPB/carbon black mixtures.

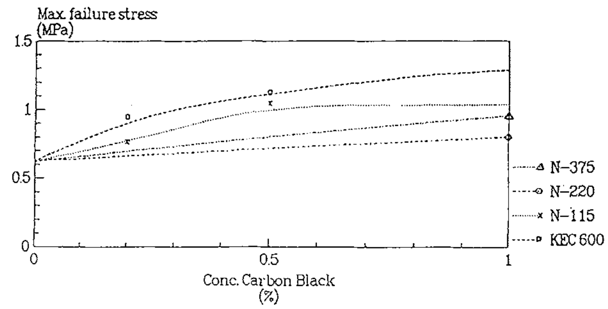

Figure 2 Maximum failure stress vs. concentration of carbon black.

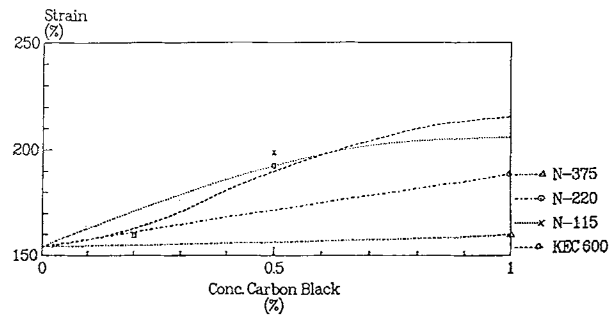

Figure 3 Ultimate strain vs. concentration of carbon black.

time and the average value was calculated. The specimens were measured according to ISO 37-1977 (E), type 2.

RESULTS

Viscosity Measurements

Figure 1 shows the results from the viscosity measurements. At low concentrations, up to 5%, the viscosity is similar for all samples. For concentrations above 5%, however, large differences appear. For the filler with the highest structure, KEC, the viscosity increases by far the most quickly.

Tensile Tests

Table I and Figures 2 and 3 show the results from the tensile tests. In Table I the maximum failure stress is denoted with σ (in MPa) and the ultimate strain with ε (in %). Figure 2 shows the stress at break and Figure 3 the ultimate strain for different concentrations up to 1% carbon black. The tensile strength increases considerably, even at an addition of only 0.2%. The ultimate strain also increases substantially. KEC seems to be the most efficient filler.

Hardness

Table II shows hardness values for HTPB/carbon black mixtures with the two most efficient types of carbon black tested, and for different concentrations of carbon black

Table I Tensile Test Results for HTPB/Carbon Black Mixtures

Type of Carbon Black		Concentration of Carbon Black (%) 0	0.2	0.5	1.0	2.0	5.0	10.0
N-375	σ (MPa)	0.62	—	—	1.00	1.11	1.26	1.86
	ε (%)	154	—	—	157	175	169	241
N-220	σ (MPa)	0.62	—	—	0.62	0.90	0.99	1.39
	ε (%)	154	—	—	189	220	208	205
N-115	σ (MPa)	0.62	0.76	1.04	1.02	1.18	1.35	—
	ε (%)	154	—	198	208	197	222	—
KEC	σ (MPa)	0.62	0.94	1.12	1.32	1.33	2.56	—
	ε (%)	154	—	192	222	200	246	—

Table II Hardness for HTPB/Carbon Black Mixtures

Carbon Black	Concn (%)	Molar Ratio NCO/OH	Hardness Values: Shore A after 1 s	10 s	30 s	Corr. Coeff.
N-115	0.5	1.0	22	21	20	−0.990
	1.0	1.0	24	22	22	−0.991
	2.0	1.0	26	24	24	−0.999
	5.0	1.0	26	24	24	−0.999
	2.0	0.9	15	14	13	−0.990
	2.0	1.0	26	24	24	−0.999
	2.0	1.1	26	25	24	−0.984
	2.0	1.2	20	18	18	−0.991
KEC	0.5	1.0	23	22	21	−0.993
	1.0	1.0	27	26	25	−0.986
	2.0	1.0	29	28	27	−0.999
	5.0	1.0	29	28	27	−0.995
	2.0	0.9	15	13	12	−0.995
	2.0	1.0	29	28	27	−0.999
	2.0	1.1	26	25	24	−0.993
	2.0	1.2	20	19	19	−0.974

and at different curing molar ratios. Each sample was measured after 5, 10, 20, 40, and 80 s and the values were plotted in a shore A/log t diagram. Straight lines were obtained. The values in the table are taken from the diagrams, and the correlation coefficients are given. The hardness increases with increasing concentration of carbon black up to a concentration of about 2%. The highest hardness is obtained for a molar ratio NCO/OH of about 1.0 to 1.1.

DISCUSSION AND CONCLUSIONS

The carbon blacks used were shown to be very efficient as reinforcing agents in very low concentrations, even at concentrations low enough that no noteworthy increase in the viscosity was observed. The rubber used is of the carbon–carbon backbone type with double bonds present, and there should be a similar effect with most materials of this type, for example ordinary styrene butadiene rubber. The most efficient type of carbon black seems to be of the high structure type, KEC. If only very small amounts are to be added, this type seems to be the one to recommend. At the same time, however, the highest increase in viscosity is obtained with this filler.

One important application of these results can be in solid rocket motor technology. To be able to tailor propellants, one wants to be able to change some properties without changing others. In this work it is shown how the strength of the frequently used propellant binder material, HTPB, can be enhanced considerably by adding very small amounts of carbon black.

Thermochemical calculations show that an addition of up to 5% of carbon to solid rocket propellants has a negligible effect on impulse and combustion temperature.[6]

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