

SURFACE ENERGY OF COMMERCIAL AND PYROLYTIC CARBON BLACKS BY INVERSE GAS CHROMATOGRAPHY, COMPARISON WITH SURFACE CHEMISTRY

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Introduction

Pyrolysis of different rubber wastes (e.g. tires) enables the recovery of the carbon black filler. However, the recovered pyrolytic carbon black (CB_P) is different from the virgin carbon black initially present in the rubber. The CB_P contains inorganic rubber components (e.g. ZnO). Furthermore, a portion of the hydrocarbons formed during the pyrolysis from decomposing polymer may react to form carbonaceous deposits on the recovered carbon black.

The largest portion of the inorganic CB_P components can be removed by a demineralization treatment [1]. If the pyrolysis is performed under vacuum the residence time of the hydrocarbons in the reactor is considerably reduced and the formation of the carbonaceous deposits is limited. Previous investigations showed that if the pyrolysis is performed under vacuum the chemistry and morphology of the CB_P resembles that of commercial carbon blacks which was not the case for CB_P from atmospheric pyrolysis [2,3]. In order to make the pyrolysis process economically feasible a commercial application for the CB_P has to be found. Rubber reinforcement is the most important carbon black application. For this application the interaction between the carbon black surface and polymer molecules is very important. By inverse gas chromatography (IGC) the surface energy of the carbon black and the adsorption enthalpy (ΔH) of model compounds for polymers on the carbon black can be measured [4]. The results from IGC correlate with properties of carbon black reinforced polymers [5]. Thus, it is possible to predict the performance of carbon blacks in rubbers from IGC experiments. In this work IGC was used to screen CB_P from different feedstocks as potential reinforcing filler for rubbers in comparison with commercial carbon blacks.

Experimental

The pyrolysis feedstocks consisted of different waste rubbers: cable insulation [6], polyisoprene [7], sidewall

portion of passenger tires [8], whole passenger tires and whole truck tires. The pyrolysis was performed at 500 °C and a total pressure of approximately 10 kPa. For comparison a CB_P from atmospheric tire pyrolysis at 500 °C [9] and a commercial grade N330 were included. Details of the pyrolysis condition can be found in the references. For the IGC experiments a HP 5890 gas chromatograph was used. The experimental conditions were close to those described by Ayala *et al.* [10]. The mathematical treatment followed the procedure given by Wang *et al.* [4].

Results and Discussion

It was found that the adsorption enthalpies of different probe molecules on the recovered CB_P and on commercial carbon blacks were similar (Table 1). The CB_P (Polyisoprene) was obtained from a N330 reinforced polyisoprene rubber. Adsorption enthalpies on the two blacks were practically identical. The adsorption enthalpies may be interpreted as a measure of the strength of the active sites on the carbon black surface. The interpretation of the results would be that the active

Table 1. Adsorption Enthalpies on Carbon Blacks

Sample	ΔH [kJ/mol]		
	n-Hexane	1-Hexene	Benzene
N 330	55.6	61.8	65.2
CB _P (Cable)	50.1	57.6	48.1
CB _P (Polyisoprene)	56.8	63.9	66.6
CB _P (Side wall)	69.2	62.2	58.2
CB _P (Passenger)	61.3	58.3	57.7
CB _P (Truck)	79.2	74.5	67.9
CB _P (Passenger, 1atm)	51.5	52.5	53.3

sites on the recovered CB_P are as strong as on the carbon black initially present in the rubber.

In contrast to the adsorption enthalpies the surface energies of the CB_p were considerably lower than those of commercial carbon blacks (Table 2). The surface energy of the recovered CB_p (Polyisoprene), originating from commercial N330 grade, was about a third smaller

Table 2. Surface Energies (Non-specific Component, γ_s^d) of Carbon Blacks at 150 °C

Sample	γ_s^d [mJ/m ²]	Surface Area [m ² /g]
N 330	150.4	80.0
CB _p (Cable)	125.4	60.0
CB _p (Polyisoprene)	103.7	69.9
CB _p (Side wall)	111.2	48.0
CB _p (Passenger)	113.3	100.0
CB _p (Truck)	109.4	100.0
CB _p (Passenger, 1atm)	28.0	57.0

than the surface energy of the virgin black. For CB_p from atmospheric pyrolysis the decrease of the surface energy was much more pronounced.

This decrease can be explained by the deposition of carbon deposits on the carbon black during the pyrolysis. The surface energy is the excess of the total energy that a solid has over the value it would have if the surface were in the same thermodynamic state as the interior. To minimize the surface energy substances with a lower surface energy may be adsorbed on the surface. During pyrolysis, the atmosphere in the reactor consists of hydrocarbons formed during the decomposition of the elastomers. The hydrocarbons vapors get into contact with the recovered carbon black where they form carbonaceous deposits on the surface. The concentration of these deposits can be measured by ESCA spectroscopy [4].

A good correlation was indeed found between the amount of carbonaceous deposits, measured by ESCA, and the surface energy (Figure 1). Thus, the decrease of the surface energy may be interpreted as a loss of 'active' sites on the CB_p by formation of carbonaceous deposits. To limit this loss of active sites, the formation of carbonaceous deposits has to be reduced. This can be done by performing the pyrolysis at low pressures.

Conclusions

During pyrolysis of rubber waste carbonaceous deposits are formed on the recovered CB_p. These deposits cover a portion of the active sites on the CB_p surface. However, the strength of the active sites which are not

covered or poisoned by the carbonaceous deposits is the same as on the commercial carbon black initially present in the rubber. The formation of carbonaceous deposits can be reduced by conducting the pyrolysis under vacuum. The CB_p from vacuum pyrolysis have an 'active' surface area which is only approximately one third smaller than the virgin black, based on comparison of the γ_s^d values. Thus, CB_p should have the potential to replace commercial grades in some applications.

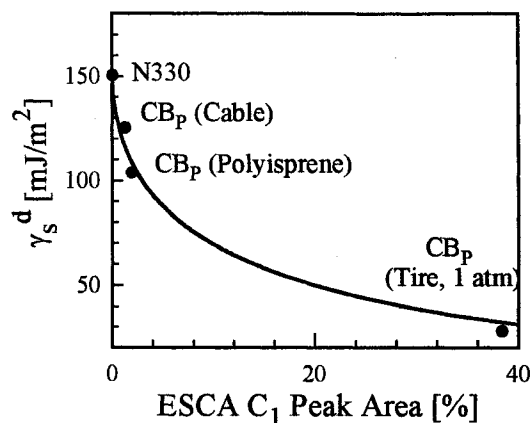


Figure 1. Carbon black surface energy (non-specific portion) vs. amount of carbonaceous deposits measured by ESCA

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