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Investigation of reinforcement of the modified carbon black from wasted tires by nuclear magnetic resonance*

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Abstract: Pyrolysis has the potential of transforming waste into recyclable products. Pyrolytic carbon black (PCB) is one of the most important products from the pyrolysis of used tires. Techniques for surface modifications of PCB have been developed. One of the most significant applications for modified PCB is to reinforce the rubber matrix to obtain high added values. The transverse relaxation and the chain dynamics of vulcanized rubber networks with PCB and modified PCB were studied and compared with those of the commercial carbon blacks using selective ^{1}H transverse relaxation (T_2) experiments and dipolar correlation effect (DCE) experiments on the stimulated echo. Demineralization and coupling agent modification not only intensified the interactions between the modified PCB and the neighboring polyisoprene chains, but also increased the chemical cross-link density of the vulcanized rubber with modified PCB. The mechanical testing of the rubbers with different kinds of carbon blacks showed that the maximum strain of the rubber with modified PCB was improved greatly. The mechanical testing results confirmed the conclusion obtained by nuclear magnetic resonance (NMR). PCB modified by the demineralization and NDZ-105 titanate coupling agent could be used to replace the commercial semi-reinforcing carbon black.

Key words: Pyrolytic carbon black (PCB), Nuclear magnetic resonance (NMR), Relaxation, Dipolar correlation effect (DCE), Reinforcement

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INTRODUCTION

Waste tires cannot degrade in the short term; they may cause accidental fire and emit poisonous gases rich in dioxins. How to recycle and utilize them effectively, and prevent secondary pollution to the environment has become a new issue that the reuse of resources is faced with. Pyrolysis is an environment-friendly process for recycling of used tires.

Three products are typically obtained from the pyrolysis of waste tires: gas, oil and char (Gonzalez *et al*., 2001). Pyrolytic oils (a mixture of paraffins, olefins and aromatic compounds) with relatively high heating value (HHV) of approximately 43 MJ/kg and can be combusted directly or added to petroleum refinery feedstock. They can also be used as a source of chemicals in the chemical industry since they contain high concentrations of benzene, toluene, xylene and limonene. The gas fraction contains high concentrations of methane, ethane, butadiene and other hydrocarbon gases with HHV of approximately 37 MJ/m^3, sufficient to provide the energy required by the pyrolysis process. Gebauer *et al*.(1995) found that the chars are a mixture of carbon black, high content of ash, and gritty material (coke) formed by degradation of tire rubber. The economic feasibility of pyrolysis of waste tires depends on to great extent

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the value of the solid residues (Merchant and Petrich, 1993). Pyrolytic carbon black (PCB), the recycling resources, can be used as rubber reinforcement filler (Williams *et al*., 1993; Roy and Darmstadt, 1997). But PCB has only the potential to replace the commercial carbon black in a few certain rubber applications. It was showed that there is large amount of ester and short hydrocarbon grafted on the surface of PCB (Lü *et al*., 2002; Zhou and Yang, 2004; Darmstadt and Roy, 1994). The carbonaceous deposits mainly consist of aromatic hydrocarbons. Although the deposits had low polarity, similar to that of natural rubber, an adequately thick layer could not be formed on the surface of PCB because of the lack of effective active sites.

Rubber is a colloid dispersive system composed of natural rubber, filler, accelerator, and auxiliary agent. Severe constraints on isotropic reorientation of polymer chains are imposed by chemical cross-links in rubber. The reinforcing fillers like carbon black strongly influence the macroscopic material properties. The short transverse relaxation time is influenced greatly as carbon blacks only interact with neighboring chains. A parameter selective nuclear magnetic resonance (NMR) mapping has well established itself as a useful tool for material characterization (Blümich, 2000). Dipolar correlation effect (DCE) is a specific attenuation mechanism of the stimulated echo in microscopically anisotropic solids and has proved to be a new effective tool for study of ultraslow molecular dynamics and the molecular order in polymer networks (Garbarczyk *et al*., 2001).

In this work, methods to improve the structure and micro-dispersion property of PCB were developed. The reinforcement properties of pyrolytic and modified PCB were investigated and compared with those of commercial carbon black by analyzing the transverse relaxation time and the DCE on NMR. The mechanical performance of the vulcanized rubbers with different kinds of carbon blacks was also examined.

EXPERIMENTAL DETAILS

The CHAOYANG brand 650-16 tire tread was provided by Hangzhou Zhongce Rubber Co., Ltd. (China). About 100 g tire shreds (1 cm×1 cm ×1 cm) were set in a quartz tube reactor heated by a tubular furnace in N_2 atmosphere from room temperature to 550 °C at atmospheric pressure. Then the solid residue was collected and ground. PCB was prepared.

The commercial semi-reinforcing carbon black (SRCB) and N330 carbon black as referential fillers were provided by Hangzhou Zhongce Rubber Co., Ltd. (China).

Twenty g PCB samples were mixed with 300 ml nitric acid (20 wt%). The mixtures were heated at 80 °C for 60 min with vigorous stirring and then filtered. The solid residues were washed with distilled water until the pH value of the filtered water was neutral and then were dried to obtain the washed pyrolytic carbon (WPC). The recovered acids can be used three times consecutively. The waste filtrate can be neutralized with alkali and some nitrates can be recovered with appropriate technology.

Coupling agents have been commonly applied to improve the performance of particulate-fill compounds at present (Fuad and Ismail, 1995). The commercial NDZ-105 titanate coupling agent was provided by Nanjing Shuguang Chemical Group Co., Ltd. (China). The dosage of titanate coupling reagent was 1 wt% of that of WPC. NDZ-105 was dissolved with a certain quantity of isopropanol, and then WPC was slowly added into the solution with continuous stirring. After stirring for about 30 min, the mixtures were oven dried to obtain the WPC modified by the titanate coupling agent (TWPC).

The five different kinds of carbon blacks were mixed with natural rubber and other components respectively according to GB/T 3780.18-1998. The mixtures were cured at 140 °C in a plate vulcanizer. The cured rubber pieces for NMR study were about Φ18 cm in diameter and 1 cm thick. The ^1H transverse (T_2) NMR relaxation time of each sample was determined employing Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences, with an echo time of 0.52 ms. T_2 images were created from the spin-echo program using a series of images with echo time (*TE*) of 0.8~1.8 ms. The repetition time was 3 s. The DCE were investigated by a modified stimulated echo sequence with additional π-pulses inserted in the free-evolution intervals as shown in Fig.1 (Grinberg *et al*., 2002); the amplitudes of the primary and the stimulated echo were recorded. Relaxation experiments were performed at 7.05 T on a Bruker DMX

300 spectrometer, and the DCE were measured at 4.7 T on a Bruker DSX 200 spectrometer. All experiments were carried out under room temperature.

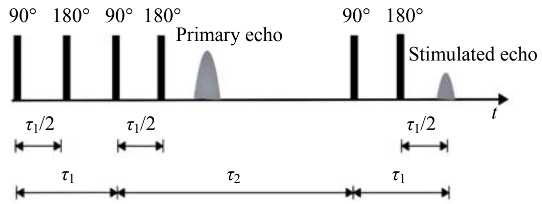

Fig.1 Modified pulse scheme under chemical shift compensated conditions for the acquisition of the primary and the stimulated echo

RESULTS AND DISCUSSION

Characteristics of carbon blacks

The characteristics of the five kinds of carbon blacks together with the content in the natural rubber used and duration of the vulcanization process are given in Table 1. The Brunauer-Emmett-Teller (BET) surface areas S_{BET} of the five kinds of carbons were determined by N_2 adsorption and desorption isotherms measured at 77 K using an automatic adsorption apparatus (Metermetric APAC 2100). The content of carbon black in natural rubber, which is relative to the amount of used natural rubber, is given in phr (parts per hundred rubbers). Table 1 also shows the duration of the vulcanization process.

Table 1 Characteristics of carbon blacks

Sample	Ash content (%)	Surface area (m^2/g)	DBP value ($\times10^{-5}$ m^3/kg)	Content in rubber (phr)	Duration (min)
PCB	16.18	69.23	70	50	30
WPC	7.52	88.62	94	50	30
TWPC	7.45	75.12	80	50	30
SRCB	≤0.5	5~25	47±10	50	30
N330	≤0.5	73~93	102±10	50	30

More than half of the ashes in PCB are removed by washing with acid. Due to the removal of much of ash content and a few carbonaceous deposits between the PCB aggregates, the surface area and DBP value (or structure) of WPC are increased after modification. And the surface area and DBP value of TWPC are decreased slightly because of the grafting of the titanate coupling agent to the WPC surface.

NMR relaxation study of rubber reinforcement with different kinds of carbon blacks

The magnetization decay curves will be shown in double components decay if there are two different components in the matter. Generally, if there are strong interactions between the polyisoprene chains and neighboring carbon blacks in rubber, the magnetization decay is rapid because of the weak molecular movements. This gives rise to a short relaxation time. Whereas the magnetization decay is relatively slow due to small restrictions between the polyisoprene chains and far away carbon black resulted in strong molecular movements, which give rise to a long relaxation time. The magnetization intensity M is given in the appropriate form (Litvinov and de Prajna, 2002; Litvinov and Steeman, 1999):

$$M(t)=C\cdot\exp(-t/T_{2\,\mathrm{short}})+D\cdot\exp(-t/T_{2\,\mathrm{long}}), \quad (1)$$

where $T_{2\,\mathrm{short}}$ and $T_{2\,\mathrm{long}}$ are the fast-decaying and slowly-decaying transverse relaxation time, relating to the interface and matrix, respectively, C and D are both constants.

From the T_2 relaxation component with a much shorter decay time, the contribution of the immobilized units adjacent to the carbon black surface can be determined, whereas the contribution of tightly bound and free rubber can be deduced from the longer decay time. Table 2 gives the value of shorter and longer relaxation components of the samples. Because of the techniques used, it is not possible to detect directly the relaxation time contributed by the immobilized units, which are in the range of 10~30 μm (Fuad and Ismail, 1995). The decay in the total transverse relaxation time implies the decrease of the molecular flexibility introduced by the improvement of the carbon black.

Table 2 Relaxation times of vulcanized rubbers with different kinds of carbons blacks

Sample	PCB	WPC	TWPC	SRCB	N330
$T_{2\,\mathrm{short}}$ (ms)	0.76	0.70	0.54	0.50	0.49
$T_{2\,\mathrm{long}}$ (ms)	4.41	3.74	3.74	2.96	2.90

Moreover, the parameter selective T_2 image of different carbon black filled natural rubber samples were investigated (Fig.2). The variations in T_2 were clearly visible. The T_2 distribution of the sample with coupling agent modified PCB was more homogenous than that of the samples with other PCBs, and was

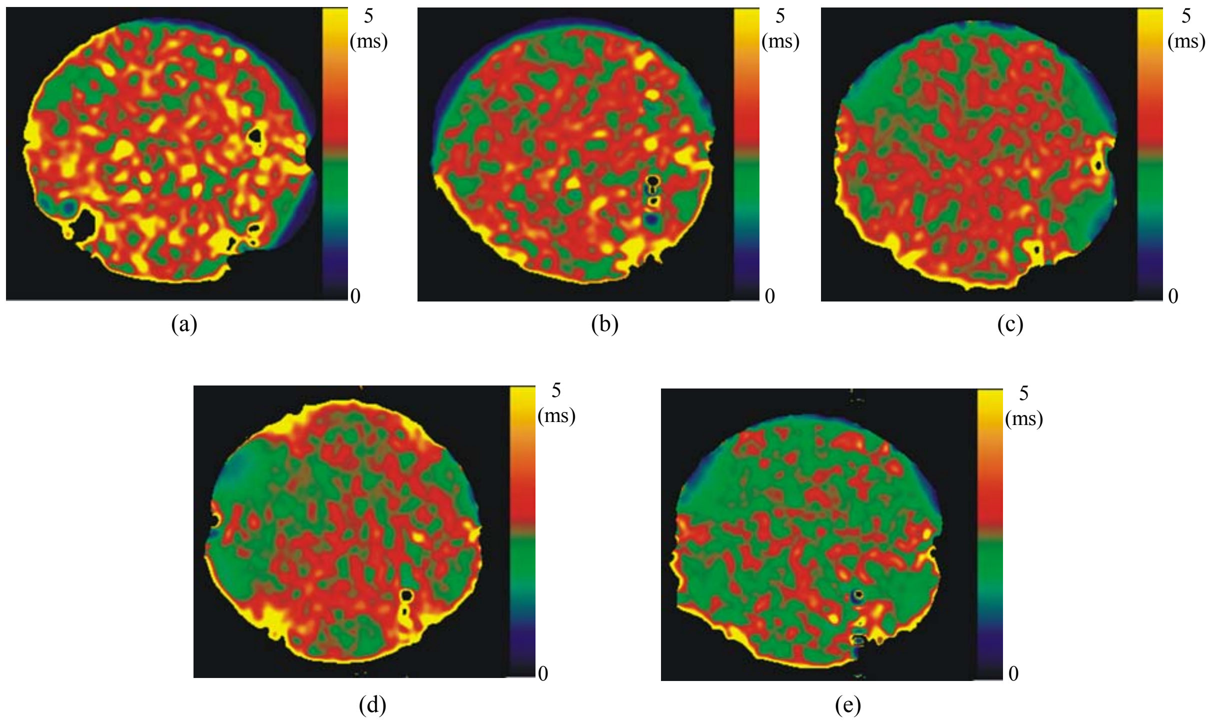

Fig.2 T_2 map of vulcanized rubbers with different kinds of carbon blacks. The resolution is 156 μm×156 μm. (a) PCB; (b) WPC; (c) TWPC; (d) SRCB; (e) N330

similar to that of commercial carbon black. Therefore, one can conclude that the interactions between the carbon black and the neighboring chains are intensified after PCB is demineralized and modified with titanate coupling agent.

DCE study of vulcanized rubber reinforcement with different kinds of carbon blacks

Chain dynamics of polymer networks were studied using the DCE on the stimulated echo. In rubber materials, the relevant dipolar fluctuations are caused by slow reorientations of the long-chain backbones around the local symmetry axis. The latter is determined by the mean positions of permanent chemical cross-links (and/or other topological constraints) restricting isotropic molecular reorientations on the time scale of the NMR experiment. Stimulated echo amplitudes are affected by attenuation mechanisms due to the DCE and spin exchange occurring between the protons of CH and CH_3 (and/or CH_2) groups of polyisoprene chains.

DCE can be separated from other attenuation mechanisms when measuring the quotient of the stimulated and primary echoes as a function of τ_1.

$$\frac{A(2\tau_1+\tau_2)}{A(2\tau_1)} \approx \frac{A_{\mathrm{dc}}(2\tau_1+\tau_2)}{A_{\mathrm{dc}}(2\tau_1)} \equiv Q_{\mathrm{dc}}. \qquad (2)$$

For macroscopically disordered systems like unstretched polymers or rubbers, the dipolar-correlation quotient Q_{dc} is given as (Grinberg *et al.*, 1999)

$$Q_{\mathrm{dc}} = \exp\left\{-\frac{1}{4}\left\langle \delta\Omega_{\mathrm{d}}^2 \right\rangle C_1\right\}. \qquad (3)$$

The coefficient C_1 in Eq.(3) is

$$C_1 = \tau_{\mathrm{c}}^2 (\mathrm{e}^{-\tau_1/\tau_{\mathrm{c}}} - 1)^2 (1 - \mathrm{e}^{-\tau_2/\tau_{\mathrm{c}}}), \qquad (4)$$

where τ_{c} is the characteristic correlation time, and $\left\langle \delta\Omega_{\mathrm{d}}^2 \right\rangle$ is the second moment of the dipolar fluctuation.

Plots of the dipolar correlation quotient $Q_{\mathrm{dc}}(\tau_1)$ in rubbers with different kinds of carbon black are shown in Fig.3. All amplitudes are normalized for the lowest τ_1 value in order to compensate for the spin-lattice relaxation. The curve parameter is τ_2. The set of two experimental curves measured at τ_2=0.05, 0.10 s was fitted at one time. The fitted values of $\langle \delta\Omega_d^2 \rangle$ and τ_c of the experimental curves are given in Table 3.

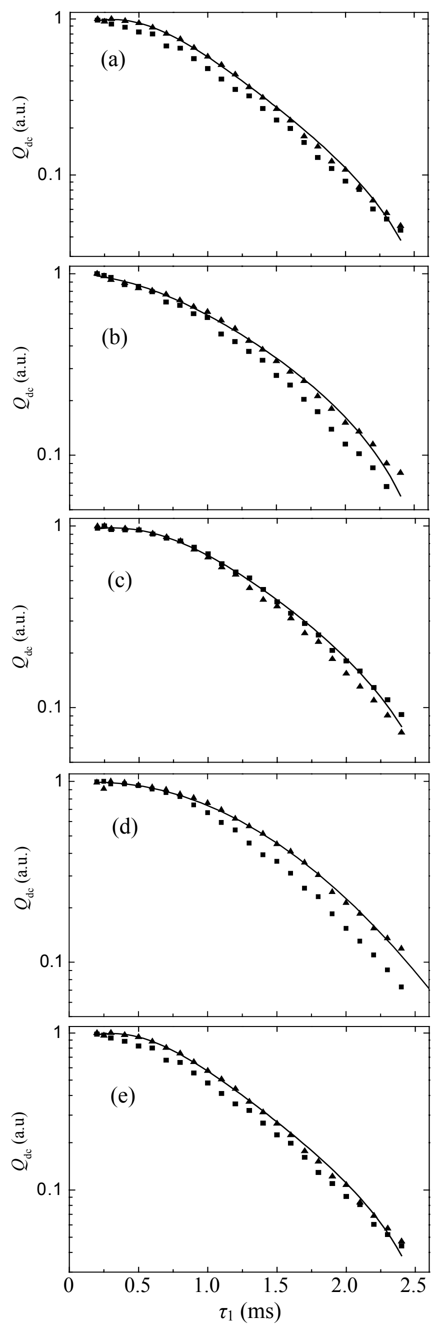

Fig.3 Dipolar correlation quotient Q_{dc} of the stimulated and the primary echo amplitudes of samples as a function of τ_1. (a) PCB; (b) WPC; (c) TWPC; (d) SRCB; (e) N330

Table 3 Parameters of Eq.(3) and Eq.(4) fitted to the data in Fig.3

Sample	$\langle \delta\Omega_d^2 \rangle$ ($\times10^6$ rad^2/s^2)	τ_c (ms)
PCB	1.01	2.21
WPC	1.71	2.14
TWPC	2.54	2.04
SRCB	3.05	2.19
N330	3.27	1.95

A strong sensitivity of $\langle \delta\Omega_d^2 \rangle$ to the density of chemical cross-links had been experimentally proven in the (bulk) DCE experiments for natural rubber (Grinberg and Kimmich, 1995). The values of τ_c tend to decrease with increasing cross-link density γ defined as the inverse of the number of segments N between the nearest neighbor cross-link, i.e., $\gamma \propto 1/N$. In the case of a freely jointed chain of Kuhn segments, the mean-squared fluctuation $\langle \delta\Omega_d^2 \rangle$ scales are proportional to $1/N^2$. So $\langle \delta\Omega_d^2 \rangle$ scales are proportional to γ^2, i.e., $\langle \delta\Omega_d^2 \rangle \propto \gamma^2$. Table 3 shows that the density of chemical cross-links of the rubber with TWPC is greatly improved. And τ_c has similar tendency.

Mechanical performance

Mechanical testing of the rubbers with different kinds of carbon blacks was carried out by Hangzhou Zhongce Rubber Co., Ltd. (China) in electronic pulling equipment. The results are summarized in Table 4. The tensile strength at break of the rubber with TWPC is increased greatly after modification of the PCB. And the mechanical performance of TWPC could meet the need of the SRCB. The tensile strength at break is the load on the unit area of the rubber at break and one of the most important factors for evaluating the quality of the vulcanized rubber. Higher cross-link density and stronger interaction be-

Table 4 Mechanical performance of vulcanized rubbers with different kinds of carbon blacks

Sample	Stress at 300% elongation (MPa)	Tensile strength at break (MPa)	Elongation ratio at break (%)
PCB	−10.9	−7.8	144
WPC	−9.2	−8.4	72
TWPC	−10.73	−5.58	185
SRCB	−8.5±1.6	≥−5.5	≥90
N330	−1.0±1.6	≥−2.5	≥−20

tween the fillers and the polyisoprene chains in the rubber with TWPC resulted in the increase of the tensile strength at break.

Coupling mechanism

The chemical structure of NDZ-105 titanate coupling agent shown in Fig.4 allows the formation of a strong van der Waals attraction and/or the chemical interaction between the organic chains of titanate and the long chains of the polyisoprene chains. Demineralization of PCB recovers a few of the active sites that were originally covered by the inorganic ash and the carbonaceous deposits. The coupling mechanism is shown in Fig.5. The selected NDZ-105 titanate coupling agent's organic chain polarity may be similar to that of the natural rubber. The intensification of interaction between the carbon blacks and the neighboring chains and the increase of chemical cross-link density in vulcanized rubber with TWPC result in improvement of the mechanical performance.

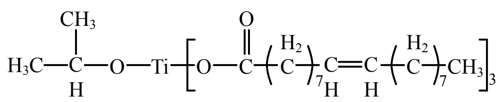

Fig.4 Chemical structure of the NDZ-105 titanate coupling agent

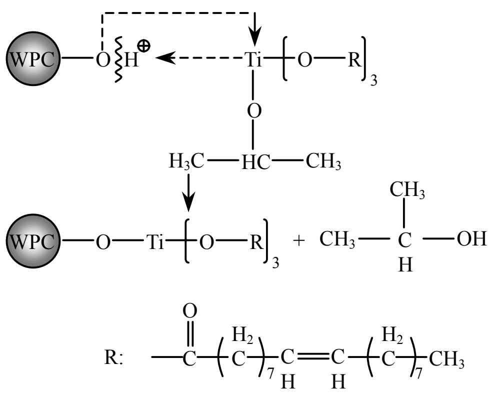

Fig.5 Coupling mechanism of NDZ-105 titanate coupling agent on the surface of WPC

CONCLUSION

Demineralization and modification with NDZ-105 titanate coupling agent not only intensify the interactions between carbon black and the neighboring polyisoprene chains, but also increase the chemical cross-link density of the vulcanized rubber with TWPC. The mechanical testing of the rubbers with different kinds of carbon blacks showed that the strain of the rubber with TWPC is better than that of the rubber with PCB. The mechanical testing results are consistent with the conclusion of the DCE. TWPC could be used to replace the commercial semi-reinforcing carbon black. Modifications in the structure of PCB have shown a little success in making it more attractive to the rubber industry.

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