

Surface Active Sites of Carbon Black Characterized by Inverse Gas Chromatography/Temperature Programmed Desorption Method

Ching-Shiun Chen¹, Chen-Yin Hsu², Jarrn-Horng Lin^{3,} and Hsiu-Wei Chen²*

¹ *Center of General Education, Chang Gung University, 259 Wen-Hwa 1st Rd., Kwei-shan, Tao-Yuan, Taiwan, 333, Republic of China.*

² *Dept. of Chemistry and Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Kaohsiung, Taiwan 804, Republic of China.*

³ *Dept. of Material Science, National University of Tainan, 33, Sec. 2, Shu-Lin St., Tainan, Taiwan, 700, Republic of China.*

Abstract

We combined Inverse Gas Chromatography and Temperature Programmed Desorption as in-situ IGC/TPD, and employed polar and nonpolar monomer as probe molecules for investigating the surface energy distribution of carbon blacks. We found the surface energy distribution of carbon black measured by aromatic molecules identified as first order desorption have a well linear relationship in compounding properties, such as wear abrasion, rolling and skid resistance. We propose a new analysis technique which combines with two conventional methods for identifying the surface active sites of carbon blacks and revealing their functions in elastomer reinforcement. In addition, it is easy to apply this method in characterizing the surface structures of other nano-materials.

Introduction

Carbon black is the most widely used nano-scale materials in diversely applications, such as filler for tire, pigment for ink and paint, anti UV and conductive shielding for cable and plastic application.

Surface physicochemical structures, for example particle size, aggregate structure and functional groups, of carbon black are the dominant factor to influence on its applications. There are numerous articles has been published to develop methods to investigate the surface structures, such as Nitrogen Surface Adsorption (NSA), Iodine Adsorption, CTAB adsorption, acid-base titration, FT-IR-ATR, STM/AFM, HRTEM and PGC-MASS techniques, however there is still lack of a reliable method to quantify the real active sites of carbon black in any application fields.

In our previous study, we has developed a significant parameter-Surface Activity Index (SAI) of carbon black and used it to successfully predict its reinforcement interaction in filler-elastomer system, even in real tire applications. However our final goal is to quantify the active sites of the carbon black by a more simple method and to tailor-make them as requirements in any application fields. So in this study, we employed we combined two traditional methods-Inverse Gas Chromatography (IGC) and Temperature Programmed Desorption (TPD) as In-situ IGC/TPD to investigate the surface active sites by using probe molecule, such as benzene, toluene and xylene. The structures of these molecules are part of elastomer segment, so we choose them as probe f molecules for simplifying our studying system.

We try to reveal the chemical and physical sites of carbon black by using this method through the desorption energy distribution and to link the correlation of them with the dynamic properties, for instance, the rolling resistance and wet traction, of carbon filled elastomer system.

Methods

Carbon blacks used in this study were supplied by China Synthesis Rubber Corp., they are produced under well controlled in the same reactor with the same configuration and the same hydrocarbon feedstock. The samples were dried in oven at 120°C without any further treatment by solvent extraction.

In-situ IGC/TPD measurements are executed in a fixed-bed reactor attached with a flame ion detector, the heating system is a hand-made furnace with a temperature controller Eurotherm 818p. The equipment is illustrated in Fig. 1.

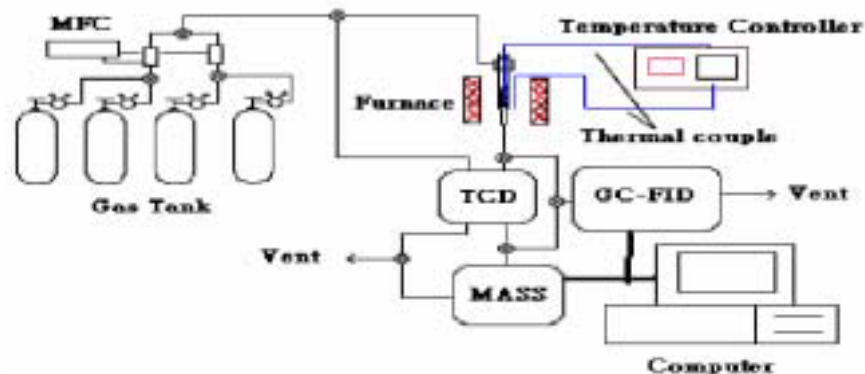


Fig. 1 The instrumental diagram of Temperature Programmed Desorption Method

The weight size of each sample is controlled at fix specific surface area for comparing with the different kind of carbon black. Methane is used as the blank molecule for IGC testing, because the interaction of methane and carbon black is small and insignificant. Each dose of probe mole, such as benzene, toluene and xylene, is 1 μL injected at elevated temperatures higher than the boiling temperatures of each probe molecule for excluding the probe molecule condensed on carbon black surface. The surface energy distribution of IGC measurements will be obtained when integrated the diagram of each probe molecule from FID signal. We recognized the IGC diagram shows the weak interaction between the probe molecule and carbon black, so the energy distribution will be near the physical adsorption energy of probe molecule on carbon black surface. However, we found that even the adsorption temperature is higher than the boiling temperature of each probe molecules, there are part of them still strongly stuck on the carbon black surface. We executed TPD measurements to investigate the stronger adsorption interaction and also calculated the energy distribution of each probe molecule on carbon black surface. Helium is the carrier gas for TPD measurements at a flow rate 30 cc/min by a mass flow controller-MKS 247C the ramp is at 1 K/s and linear controlled by a temperature controller.

In-situ IGC/TPD measurements will show the weak and strong active sites of carbon black for interacting with the probe molecules, in this study, we try to set up the correlation between the surface energy distribution of carbon blacks refereeing to the interaction with elastomer molecules. We hope to deduce a model to explain the interaction mechanism of filler-realstomer system through our results.

Results and Discussions

Benzene, toluene and xylene are three probe molecules used in this study for in-situ IGC/TPD measurements, because the phenyl group is most popular structure in the elastomer molecule segment, especially in the automobile tire formula-such as SBR. So we used the dynamic testing results, for example $\tan\delta@ 0^\circ\text{C}$ and $\tan\delta@ 70^\circ\text{C}$, to deduce the correlation of surface adsorption energy of each probe molecule with them. The former refer to the wet traction of the tire properties and the latter is well accepted as the rolling resistance of the tire performance.

The results of IGC measurements refer to the surface adsorption energy of probe molecules, and them of TPD measurements will show the surface desorption energy of the same molecule, the former represents the weaker sites of carbon black interacted with the probe molecule and the latter means the stronger sites of them to anchor the probe molecules.

In our results, we find that the IGC measurements shown no well correlation of surface adsorption energy along with the dynamic properties of carbon black reinforced elastomer system, it means that the weaker energy sites of carbon black only have miner influence on interacting with the elastomer molecules, even there were numerous papers have been published to demonstrate the merit of this method.

Therefore, we only use the surface desorption energy measured by TPD method to explain the active sites of carbon black surface when it interacted with elastomer molecules.

In Fig. 2, it is clearly to find that the surface desorption energy of toluene has well acceptable linear correlation with the dynamic properties $\tan\delta@0^\circ\text{C}$, the higher adsorption energy will show higher value of $\tan\delta@0^\circ\text{C}$, it means that the surface sites of carbon black have stronger interaction with the toluene-like molecule will have better wet traction in tire performance. In the real application of an automobile tire, the higher surface energy sites of carbon black have large energy hysteresis effect when the traction behavior have been occurred for softening the filler-elastomer system to grasp wet ground better for safety driving.

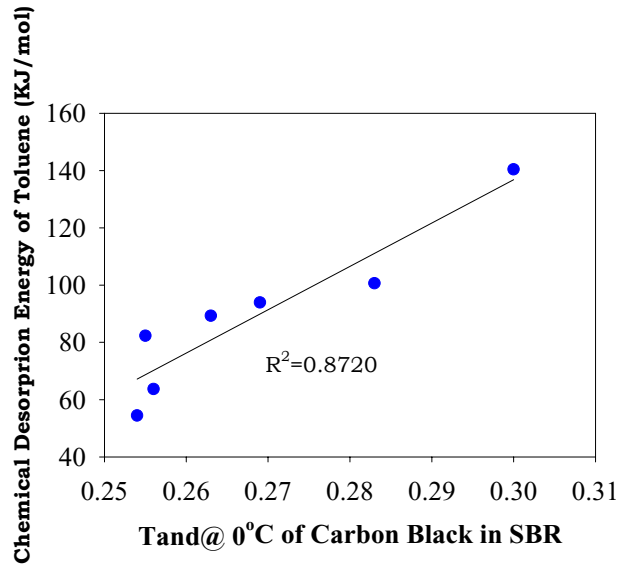


Fig. 2 The surface desorption of toluene v. s. the dynamic properties of $\tan\delta@0^\circ\text{C}$ of carbon black-SBR system.

However, in Fig. 3, it shown that the higher energy sites of carbon black will result in poor rolling resistance depending on the value of $\tan\delta@70^\circ\text{C}$. The higher value of $\tan\delta@70^\circ\text{C}$ stands for the higher energy hysteresis when the automobile tire running on the road surface, generally it need smaller is better for saving oil consumption, in other word decrease the exhausting of carbon dioxide. How to improve the rolling resistance is to increase the filler-elastomer interaction, the better way is to establish chemical bonding between filler and elastomer, such as SiO_2 and silane-69 in the green tire application.

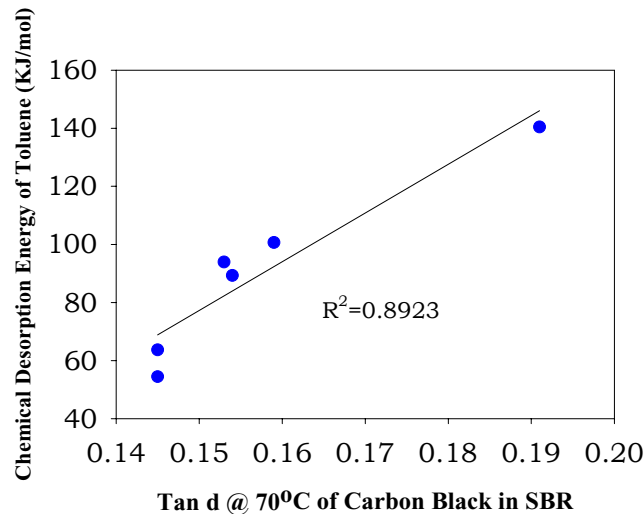


Fig. 3 The surface desorption of toluene v. s. the dynamic properties of $\tan\delta@70^\circ\text{C}$ of carbon black-SBR system

Base on the results of $\tan\delta@0^\circ\text{C}$ and $\tan\delta@70^\circ\text{C}$, it is reasonable to propose that the higher energy sites measured by toluene are the surface defect structure of carbon black. These structures have higher energy level than other sites, however the interaction with the toluene is still not a chemical bonding so they could merely improve wet traction not to rolling resistance. Fig. 4 and 5 also evidenced that higher surface area measured by nitrogen or iodine adsorptions will show higher surface desorption energy, because higher surface energy have more defect sites on surface in the same particle size.

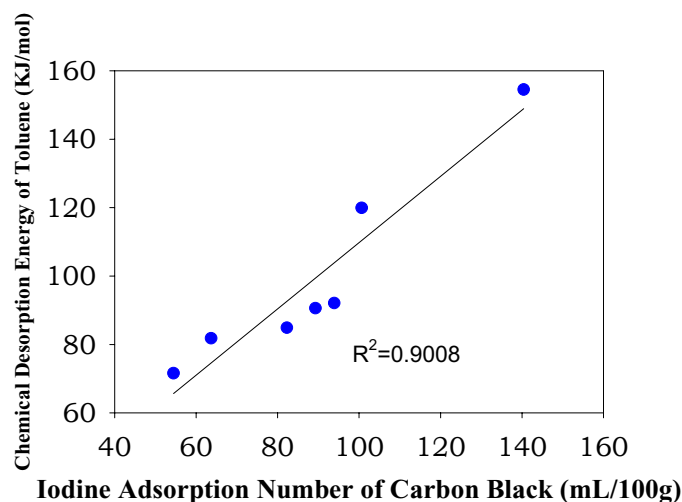


Fig. 4 The surface desorption of toluene v. s. Iodine adsorption value of carbon black

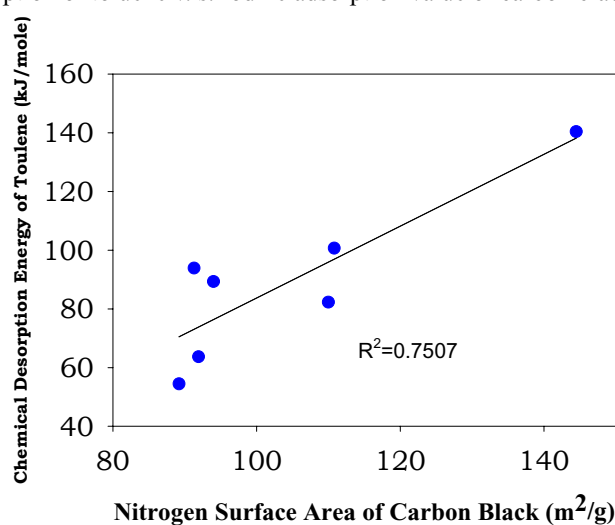


Fig. 5 The surface desorption of toluene v. s. Nitrogen Surface Area of carbon black

Conclusions

In-situ IGC/TPD measurements show a good correlation along with the dynamic properties of filler-elastomer system, the higher energy sites measured by toluene, in this study, will refer to the defect structure of carbon black surface which will have better wet traction in tire application. In this study, our results have shown a useful information to explain the filler-elastomer interaction. This technique could be applied to a reliable tool to measure the surface active sites for any solid materials, especially in nano-scale materials.

Acknowledgements

C.-S. Chen (NSC-95-2113-M-182-003-), H.-W. C. and J.-H. L. (NSC-95-2113-M-110-006) would like to express their sincere appreciation to the National Science Council of Republic of China for supporting this study financially.

References

1. J. B. Donnet et. al. Carbon Black; Marcel Dekker: New York, 1991.
2. O. Smidsrod, J. E. uillet, *Macromolecules* **1969**, 2, 272.
3. H. Hadjar, H. Balard, E. Papirer, *Colloids and Surfaces A* **1995**, 99, 45.
4. E. Brendle, E. Papirer, *J. Colloid Interface Sci.* **2001**, 22, 451.
5. E. Papirer, E. Brendle, F. Ozil, H. Balard, *Carbon* **1999**, 37, 1265.
6. J. H. Lin *Carbon* **2002**, 40, 183.