

Magnetic Resonance Investigations of Carbon Black Charge Acceptance in Xerographic Toners

Richard P. N. Veregin

Xerox Research Centre of Canada, Mississauga, Ontario, Canada

Carbon black (CB) plays an important role in the triboelectric charging of xerographic toners.¹ While the salient effect of carbon black chemistry on triboelectrification and contact potential is well known, the nature of the charge exchange, and the electron accepting sites on the carbon black are not well understood. Carbon black is also well known to give rise to Electron Spin Resonance (ESR) signals, due to the presence of unpaired electrons. This paper is a review of recent work that has been done to utilize the magnetic resonance techniques of Electron Spin Resonance (ESR) and Electron-Nuclear Double Resonance (ENDOR) Spectroscopy to understand the nature of triboelectric charging involving carbon black.

ESR and ENDOR have been used to follow the charge exchange involving both oxidized and unoxidized carbon blacks.²⁻⁶ The electrochemical reduction was done *in situ* in the ESR spectrometer, so that the generated ESR signal could be followed during the reaction. The electrochemical reduction of the carbon black in an electrolyte results in electron transfer to the carbon black, generating a paramagnetic resonance signal.² Each carbon black generates a characteristic signal. In the case of the unoxidized carbon black, the accepted electron is a charge carrier, part of the conduction band of the carbon black, as shown by an ESR intensity that is nearly invariant with temperature (the accepted electrons follow Fermi statistics).⁶ The accepted electron is, however, in a different environment compared to that of the bulk conduction electrons in the carbon black. These bulk states are inherent in the carbon black, and appear unaffected by the electrochemical reduction. As will be shown later, the accepted electrons are most likely in surface conduction states, rather than in bulk states.

In the case of the oxidized carbon black, the accepted electron from electroreduction goes into a localized surface state, that is associated with the oxygenated sites on the carbon black.⁶ The localized nature of the site is observed as an ESR intensity that increases with inverse temperature. However, the intensity increases faster than the linear dependence with inverse temperature expected for Curie law behaviour of localized electrons. This superlinear temperature behaviour most likely arises from an equilibrium between the electrons in the bulk state conduction band of the carbon black, and the electrons accepted into the localized surface states.

Thus the nature of the accepted electrons on electroreduction in both carbon blacks is very different, and is characteristic of the carbon black, although in both carbon blacks these electrons are in surface states. While the

accepted electrons on the carbon black are relatively stable at low temperature, at room temperature they slowly dissipate. Alternately, the electrooxidation of the carbon black can also be used to remove the electrons produced by electroreduction of the carbon black. The electron transfer to and from these sites appears to be completely reversible. Thus the electrochemical reduction does not appear to cause any irreversible chemical changes to the carbon black.

Melt-mixing of a carbon black with a toner resin also generates an ESR signal. While this behaviour has been known since the early 1960's,⁷⁻⁹ the nature of this ESR signal has been very unclear. It has been variously suggested that this signal arises from the carbon black itself, perhaps due to mechanical forces from the mixing operation, or due to generation of macroradicals from the resin, causing an electroreduction of the carbon black. For the same unoxidized and oxidized carbon blacks used in the electroreduction studies, the melt-mixing of the carbon black with a styrene copolymer resin does generate an ESR signal. The ESR signal observed is the same characteristic signal that was observed on electrochemical reduction of the same carbon black. Thus the unoxidized black/resin composite gives rise to an ESR signal that arises from a charge carrier in a surface conduction state. The oxidized black gives rise to an ESR signal that shows a the superlinear inverse temperature dependence, arising from surface localized states that are associated with oxygenated sites. Except for differences in the intensity of the ESR signals, resulting from differences in the number of electrons transferred, the signals from electroreduction and melt-mixing are identical.

Thus it can be concluded that melt-mixing of the CB into the toner resin results in an electron acceptance by the carbon black from polymer donor sites. The interface between the carbon black and the resin can be pictured as containing paired positively charged sites on the resin, and negatively charged sites on the carbon black. These paired sites are much more stable than the negatively charged site in the electrochemically reduced carbon black, as the former are stable for years at room temperature, becoming unstable only at temperatures that are considerably higher than the glass transition temperature, T_g , of the resin. The observed ESR signal arises from surface states of the carbon black, whose nature depends on the carbon black properties. In the unoxidized black the electron is accepted by a surface conduction state that is delocalized. In the oxidized black, the possible electron delocalization into a conduction state is prevented, by stabilization of the electron into localized oxygenated sites.

Although it is difficult to quantitate the conduction electron signal from the unoxidized carbon black, the number of electron spins observed for the oxidized CB is 3.5×10^{17} spins/g, approximately six electrons per 10^6 \AA of carbon black/resin interface. This is the number of electrons that the resin can donate, and that the carbon black can accept, at the interface. In comparison, a toner can exchange up to perhaps $100 \mu\text{C/g}$ for a $10 \mu\text{m}$ particle. This corresponds to about five electrons per 10^6 \AA of toner surface, very comparable to the observed donated charge from the polymer. The inference is that the acceptance of electrons by the carbon black, and the donation of the electrons by the resin, in the melt-mixed carbon black resin composite, is the same process as occurs in triboelectrification. The observed electron accepting sites on the carbon black in turn, are the sites that accept electrons in triboelectrification, and are responsible for the negative triboelectric charging imparted by the carbon black to the resin.

Using ENDOR spectroscopy the nature of the interface at the charge acceptance site of the carbon black has been studied.^{4,6} ENDOR observes any NMR active nuclei (in the resins we studied, only ^{19}F and ^1H are detectable) that are interacting with an unpaired electron spin. In the electrochemically reduced carbon black itself, an ENDOR ^1H signal is observed, due to the interaction of surface or defect hydrogen atoms of the carbon black with the accepted electron on the carbon black. That an ENDOR signal is observed for both reduced carbon blacks, and that the interaction appears to be a dipolar electron-nuclear interaction, indicates that the electron and the hydrogen atom must be spatially proximate, with a separation of less than about 1 nm. This suggests that the electron must be in a carbon black surface state, not in a bulk state.

In the melt-mixed carbon black with polystyrene copolymer resin, an ENDOR signal is also observed, arising from the interaction of the electrons accepted by the CB with the hydrogen atom nuclei on the resin. Since this interaction is dipolar, it is very sensitive to both the separation of the electron from the hydrogen atoms in the resin, and also to any relative motion between the two. The observed ENDOR signal indicates that the electron spins, and the resin hydrogen atoms are spatially proximate, showing the resin is in intimate contact with the carbon black. As the temperature is increased through the glass transition temperature of the copolymer, the ENDOR signal decreases rapidly, due to the rapid motion of the hydrogen atoms in the polymer chains at the interface with respect to the unpaired electrons on the carbon black surface.

In partially fluorinated resins, the ^{19}F nuclei, as well as the ^1H nuclei, at the interface with the carbon black surface, produce ENDOR signals. Since a fluorine ENDOR can only come from atoms on the resin, it is clear that the ENDOR interactions in the polymer composites are due to an interaction, at the interface, between electrons in surface states of the carbon black, and atoms of the resin that are proximate to the surface states. As the ratio of the fluorine/hydrogen content of the resin is changed, the relative intensities of their respective ENDOR signals change. Since atoms of the resin that are further away from the electron states on the carbon black will show a much less intense ENDOR signal than those that are closer, the relative intensities of the ^{19}F and ^1H ENDOR signals indicate the relative distances of the atoms to the charge exchange site on the CB.

Comparing different fluorinated polymers shows that the fluorinated part of the molecule is furthest away from the charge exchange site. This suggests that the donor site on the polymer, which would be expected to be proximate to the acceptor site on the CB surface, is closer to the non-fluorinated part of the molecule. This is intuitively reasonable, as fluorination makes a resin charge negatively (accept electrons), rather than donate electrons. Thus the site of the positive charge on the resin, which forms a charge pair with an electron accepted by the carbon black surface, might be expected to prefer to be further from the fluorinated section of the resin.

References

1. P. C. Julien, in "Carbon Black", 2nd Ed., J.B. Donnet, Ed., 1993.
2. J. R. Harbour, M. J. Walzak, *Carbon* **24**, 743 (1986).
3. J. R. Harbour, M. J. Walzak, *J. Coll. Int. Sci.* **119**, 150 (1987).
4. R. P. Veregin, J. R. Harbour, Y. Kotake, E. G. Janzen, *Carbon* **25**, 541 (1987).
5. R. P. Veregin, J. R. Harbour, Y. Kotake, E. G. Janzen, *J. Coll. Int. Sci.* **132**, 542 (1989).
6. J. R. Harbour, M. J. Walzak, R. P. Veregin, *J. Coll. Int. Sci.* **138**, 380 (1990).
7. A. K Chatterji, *Amer. Chem Soc. Div. Polym. Chem Prepr.* **7**, 535 (1966).
8. A. B. Sullivan, R. W. Wise, in *Proceedings, 5th International Rubber Conference*, Brighton, 1967, p. 235, Maclaren, London, 1968.
9. M. A. Waldrup, G. Krause, *Rubber Chem. Technol.* **42**, 1155 (1969).