

PVC Filled with Vacuum Pyrolysis Scrap Tires-Derived Carbon Blacks: An Investigation on Rheological, Mechanical, and Electrical Properties

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SYNOPSIS

Pyrolysis of scrap tires produces oil and carbon black (CB). The purpose of this work is to compare pyrolytic CBs with commercial grades as fillers for poly (vinyl chloride) (PVC). Blending of PVC with CB was performed in the melt at 180°C. The compositions prepared were 1, 5, 10, 20, and 30 wt % of CB. The dynamic rheological, mechanical, and electrical properties of the PVC-CB composites were investigated. The results obtained for the storage modulus and complex viscosity of the composites of PVC with the pyrolytic CBs were between those of a high-grade (Monarch 1100) and a low-grade (Sterling R) commercial CBs. Intermediate tensile modulus, elongation at break, and electrical conductivity were also obtained. The specific surface area of the CB was shown to influence the composite properties. Reduction of the volatile matter and ash contents of the pyrolytic CB led to better properties of the PVC composites. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Tire recycling has become a necessity because of the accumulation of discarded tires that are a potential environmental risk. Each year, 24 million tires are disposed of in Canada and about 250 million units in the United States. Although some of these tires are recapped or ground for special uses, most are dumped in rural areas or in landfills. When buried in landfills, they eventually float to the surface. In piles, the nonbiodegradable rubber can cause serious harm if ignited. Tires represent a source of energy and chemicals. By thermal decomposition, it is possible to recover useful products. Tire pyrolysis projects have been reported in the literature.¹⁻³ Oil, gas, and carbon black (CB) are major pyrolytic products and their yields depend on the process pyrolysis conditions used. Under vacuum, tire pyrolysis typically yields 25% CB, 55% oil, 6% gas, and 14% steel and fibers (wt %, as-received tire basis). The process feasibility depends largely on the quality of the py-

rolysis products obtained.⁴ CB obtained during pyrolysis of tires originates from two sources: the CB already present in tires and the one formed during the thermal decomposition reactions.

CBs have been used as fillers in a large number of polymers. Their most common use is with rubbers. The properties of such materials filled with CB depend on CB characteristics such as structure (aggregation state), specific surface area, particle size, and volatile matter content.⁵⁻⁷ A few studies have been performed on CB-thermoplastics composites.⁸⁻¹⁷ Ahuja^{8,9} studied the rheological behavior of styrene/butyl methacrylate copolymer-CB composites. He showed that the storage modulus presents a second plateau at low frequencies and that the dynamic properties were affected by the CB structure, specific surface area, and concentration. He suggested the formation of a CB particles network that depended on temperature and CB surface characteristics.⁸ White^{10,11} and Lakdawala and Salovey¹³ noted the appearance of a yield stress for CB concentrations higher than 20% in polystyrene. According to Dufresne,¹⁷ this yield stress was probably due to particle-particle interactions; changes in particles characteristics, such as a modification of the surface or

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a change in the specific surface area, can result in large effects on the rheology of CB composites.

More recently, Ghandi¹⁶ completed an investigation on polymers similar to those described above. He found that the addition of CB increased the storage modulus G' and, to a lesser extent, the loss modulus G'' . This increase was more important for high concentrations of CB and for CB with higher specific surface area. A yield stress, independent of temperature and polymer matrix, was found for these composites. The existence of a network constituted of CB particles was suggested to explain this behavior. Finally, some investigations with PVC⁶ and polyethylene¹⁷ involved comparison of theoretical predictions using suspension models (Einstein and Mooney models) with experimental data but with little success.

CBs are also used with polymers for their electrical characteristics. Blending CB with polymers increases the electrical conductivity of the composite. Advantages are lower cost, lower weight, and good mechanical properties. However, the increase of conductivity with CB concentration strongly depends on the intrinsic characteristics of the CB. Most of the electrical conduction caused by the addition of CB occurs by channel conduction. For the same CB content, conduction is enhanced when the structure (DBP) of the CB is high. In fact, the presence of large agglomerates allows greater electron mobility along the aggregates and reduces the number of jumps for the channel conduction. A decrease in the size of the particles also allows a better conduction, as well as a high specific surface area because of the higher porosity and the decrease in the interparticle distance.¹⁸

This work investigates the quality (characteristics) of CBs obtained by vacuum pyrolysis of scrap tires as a filler for poly(vinyl chloride). The effect of different conditions of preparation and/or treatments of the CB on the dynamic rheological, tensile modulus, elongation at break, and electrical conductivity of the composites was investigated and comparison with commercially available CB was performed.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) used in this study was a GEON 103 EPF 76 obtained graciously from B.F. Goodrich. Some of its molecular characteristics are given in Table I. To avoid thermal degradation, two

Table I Some Characteristics of PVC and Copolymer

Resin	I.V. ^a	M_w	M_n
PVC	0.92	136,000	66,000
Copolymer	0.60	1,000,000	—

^a Inherent viscosity (Pa.S).

liquid thermal stabilizers based on stain complexes (Mark 694 and 292 from Argus Chemical Corp.) were used. For ease of PVC processing, a copolymer containing 90% methyl methacrylate and 10% ethyl acrylate (obtained from Rohm & Haas Corp.) was also added.

For the CBs used in this study, six were obtained by pyrolysing scrap tires under vacuum. The STAM CB was the direct product of a scrap tire vacuum pyrolysis pilot plant (100 kg/h throughput capacity) located in St-Amable, near Montréal, Québec.⁴ The St-Amable sample was produced at 400–450°C and a total pressure of 10 kPa. The granular CB product was removed from the hot vacuum chamber after forcing it downward across a column of cooling water. The solids were crushed and passed through a 250 micron standard sieve to remove the larger metal and fiber impurities. The STAR is the STAM sample, reheated in the laboratory under vacuum to 500°C to reduce its volatile matter content (including oil residues). The three other CBs were obtained under different conditions in an experimental pyrolysis unit: D02T and D02L, produced at 550°C and 4.6 kPa, were identical, except the second was washed with 1N HCl to reduce its ash and metal content. D06T was obtained at 550°C and a total pressure of 1.3 kPa. The KOBE pyrolytic CB was gratefully supplied by Kobe Steel in Aioi, Japan, and was obtained by atmospheric pyrolysis of scrap tires in a 1000 kg/h commercial unit. Other details regarding the preparation of the pyrolytic CB samples have been published elsewhere.¹⁹ The characteristics of the experimental CBs, together with those of four commercial samples used in this study, are summarized in Table II. Three high-grade commercial CBs (Monarch 1100, Monarch 800, and Vulcan XC 72R) and one low-grade CB (Sterling R) were gratefully provided by Cabot Corp., Boston, MA.

Blending

First, PVC was dry blended with the thermal stabilizers (1 wt % of each) and left at rest for 12 h to allow liquid adsorption by the resin. Then, the co-

Table II Carbon Black (CB) Characteristics

CB	Specific BET Surface Area (m ² /g)	Iodine Index (mg/g)	DBP Structure (mL/100 g)	Volatile Matter (%)	Tint Strength (%)	Ash (%)	pH
Monarch 1100	240	258	65	2.0	115	< 2.0	7.0
Monarch 800	210	258	75	1.5	120	< 2.0	8.0
Vulcan XC 72R	254	253	185	1.5	87	< 2.0	5.0
Sterling R	25	33	70	0.5	58	< 2.0	8.5
D02T ^a	60	144	85	4.9	61	17.0	7.9
D02L ^b	52	60	90	4.7	64	8.5	8.3
D06T ^c	93	151	95	3.3	57	15.5	6.1
STAM ^d		49		7.7		11.4	
STAR ^e		98		3.2		11.8	
KOBE	58	127		3.8	47	9.9	8.6

^a Produced at 550°C and 4.6 kPa.

^b Same as footnote a, and washed with 1N HCl.

^c Produced at 550°C and 1.3 kPa.

^d Produced at St-Amable at 400–450°C and 10 kPa.

^e Same as footnote d, and reheated in the laboratory to 500°C at 0.3 kPa.

polymer (10 wt %) was added. Different amounts of CBs (1, 5, 10, 20, and 30 wt %) were added to the blend in the dry state. Melt blending of the mixture was performed in a Haake Buechler Rheocord batch mixer. The temperatures and speeds used are listed in Table III. The total time of mixing was in all cases about 8 min. These conditions were selected to avoid any PVC thermal degradation. The composites were then compression-molded into plaques 1.3 mm thick. Samples for the different measurements were cut from the plaques. Other experimental details can be found elsewhere.²⁰

Measurements

Rheological Properties

Rheological measurements were carried out on a Rheometrics System-4 rheometer with parallel plate geometry, at 200°C on composites with concentrations from 1 to 30 wt % of CB. The composite samples used were discs of 5 cm in diameter, cut from the plaques. The gap between the parallel plates was

at least 1 mm. The frequency range covered was between 0.01 and 500 rad/s. Preliminary strain sweep experiments were performed to determine the extent of the linear viscoelastic domain. In all cases, 8% strain (even at high frequencies) made it possible to remain in this domain. The fundamental advantage of performing small amplitude oscillatory shear measurements in the domain of linear viscoelasticity is that the microstructure of the system remains homogeneous and stable at a given temperature; then, the tests were performed in a quasi-equilibrium state. Time-sweep experiments did not show any significant degradation at 200°C for plasticized PVC for periods of 30 min. Nevertheless, the samples were not left in the oven for periods exceeding 20 min.

Mechanical Properties

The tensile modulus and elongation at break of composites containing 1, 5, and 10 wt % CB were determined from measurements on an Instron tensile apparatus at room temperature. The drawing speed was 0.5 cm/min and the results were averaged over at least six tests.

Table III Blending Conditions in the Batch Mixer

Operation	Loading	Melting	Homogenization
Time (s)	0 to 60	60 to 180	180 to 480
Temperature (°C)	180	180	160
Mixing speed (rpm)	10	60	50

Electrical Properties

The electrical conductivity of the samples was measured on discs 5 cm in diameter at room temperature according to the ASTM method D 257-83. The electrification time was fixed at 1 min, and a conducting cream (Cardio-cream, Ingram & Bell Medical) was applied on the disc surfaces to have an improved contact between the sample and the electrodes. The measurements were performed by means of a dc amplifier and electrometer (Type 1230-A, General Radio Co.).

RESULTS AND DISCUSSION

Rheological Properties

The results obtained for the samples containing 1 and 5% CB did not show any significant differences between the CBs. The complete results are not shown here for the sake of brevity but can be found elsewhere.²⁰ The results obtained for the 10 and 20 wt % series are presented on Figures 1–3. These figures indicate that the Sterling R CB gives the less viscous composite, and Monarch 800, the most viscous one. The pyrolytic CBs are somewhere between these two. It is noticeable that the viscoelastic behavior of D02T CB is closer to the high-value Mon-

arch 800 CB than to the low-grade Sterling R sample.

Medalia,^{5,6} Lakdawala and Salovey,¹³ and Ghandi¹⁶ reported that differences in CB characteristics were responsible for the differences in the viscoelastic behavior of CB composites. They also noted an important effect of the BET specific surface area. The results presented here are in agreement with this observation. In fact, the highest viscosity is obtained with the CB having the highest BET specific surface area (Monarch 800) and the less viscous composite is obtained with the CB having the lowest BET specific surface area (Sterling R). The BET specific surface area of the STAM and STAR pyrolytic CBs are not known, but their Iodine Index is higher than that of the Sterling R CB. All pyrolytic CBs lie between the two kinds of commercial CBs tested from the point of view of BET specific surface area, as does their viscoelastic behavior.

It seems, however, that the differences in the BET specific surface area do not explain, alone, all the differences in behavior. For example, viscosity of the pyrolytic CB D02T that has an intermediate BET specific surface area is not that far from composites with a much higher BET specific surface area. Structure, particle size, and volatile matter content are also relevant parameters. The volatile matter content, for example, can modify the nature

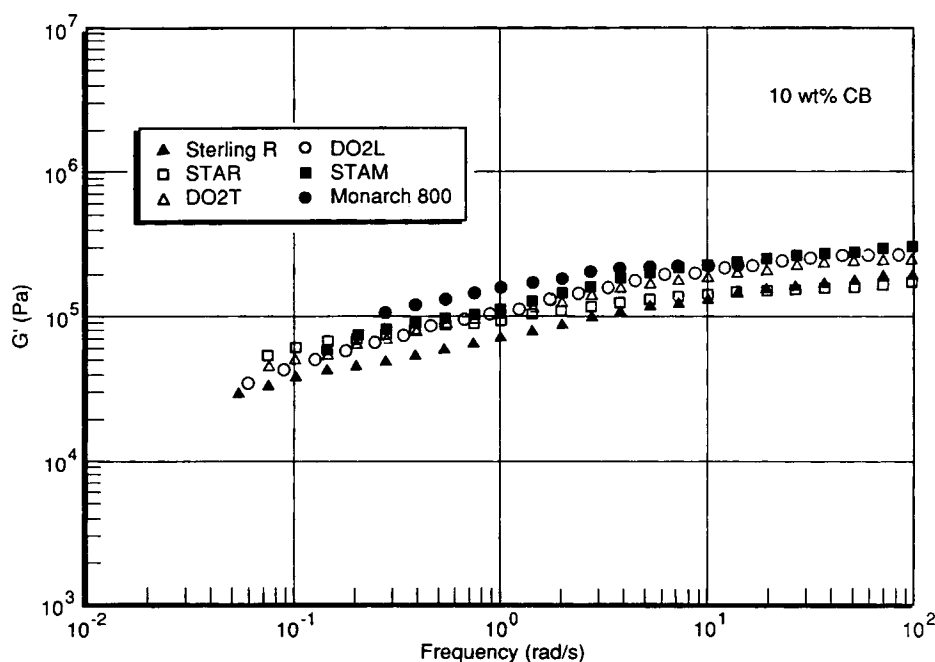


Figure 1 Storage modulus of some PVC-CB composites for a concentration of 10 wt % at 200°C.

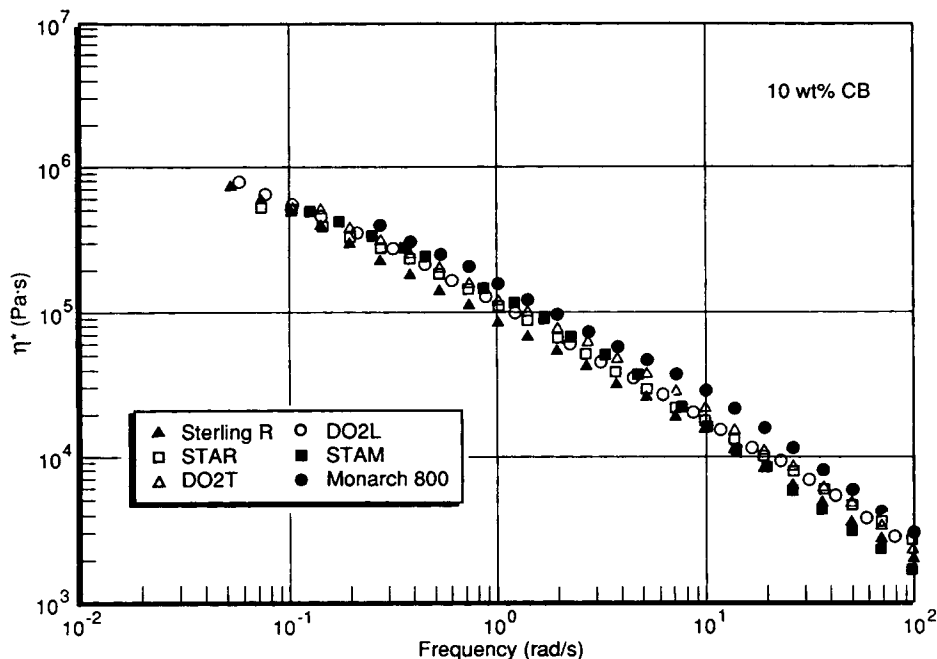


Figure 2 Complex viscosity of some PVC-CB composites for a concentration of 10 wt % at 200°C.

of the interactions between the matrix and the particles and/or act as a lubricant or plasticizer. Thus, in some cases, an increase in the volatile matter content will increase the viscosity (interactions are

predominant), and in other cases, a decrease in viscosity will be observed (lubrication effect).¹⁵

The STAR pyrolytic CB is a STAM reheated to lower the volatile content. It can be observed in Fig-

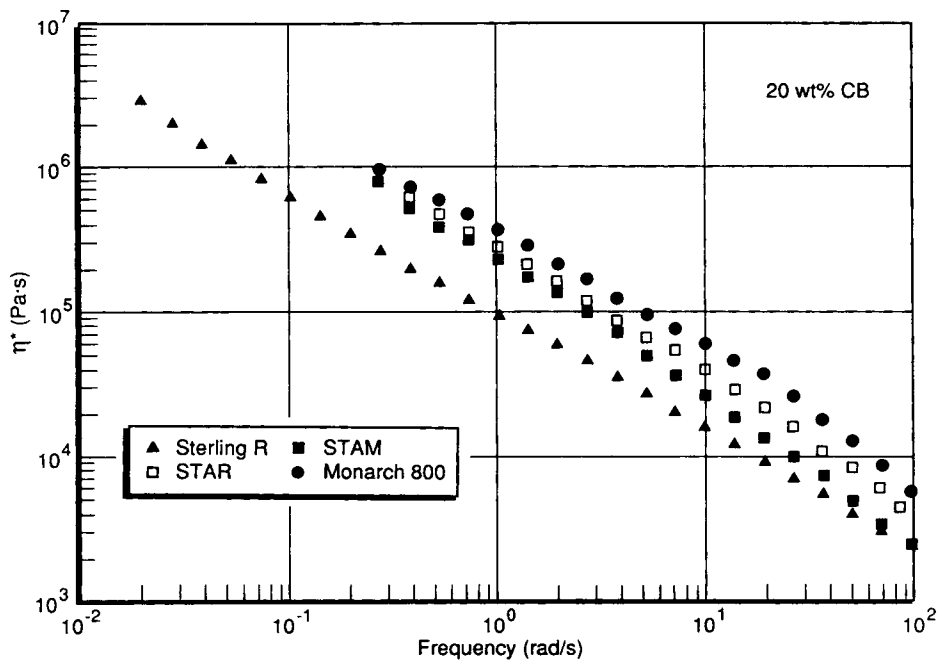


Figure 3 Complex viscosity of some PVC-CB composites for a concentration of 20 wt % at 200°C.

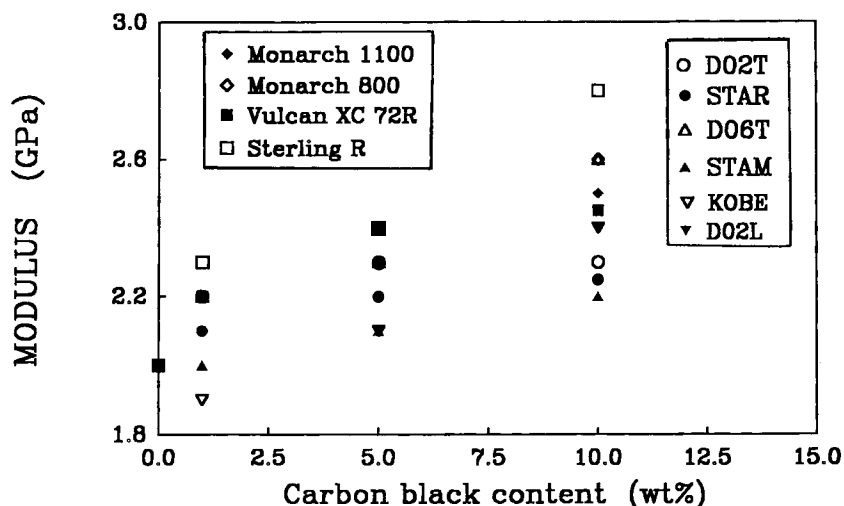


Figure 4 Young's modulus of the different PVC-CB composites as a function of concentration.

ures 2 and 3 that its viscosity is higher in the low-frequencies region where the effects of the interactions are important. At high frequencies, the lubricating effect of the volatile matter is probably more important and a decrease in viscosity is observed. On the other hand, the D02L pyrolytic CB is a D02T washed with an acid to reduce the inorganic matter and ash content. Characteristics of D02L and D02T samples are shown in Table II: Varying changes can be observed in terms of BET specific surface area, structure, and volatile content. Because of the competing effects of the different parameters, the overall observed effect on the viscoelastic properties was negligible, as shown on Figures 1-3.

Mechanical Properties

The results obtained for the Young's modulus and the elongation at break of the composites with the different CBs are presented on Figures 4 and 5, respectively. A constant increase of the modulus and decrease of the elongation at break as a function of CB weight content in the composite are observed. The behavior is strongly dependent on the CB type.

To elucidate the effect of CB characteristics, an analysis of the mechanical results as a function of specific surface area and volatile content was performed. The results are presented in Figures 6 and 7. The effect of the structure on the modulus was

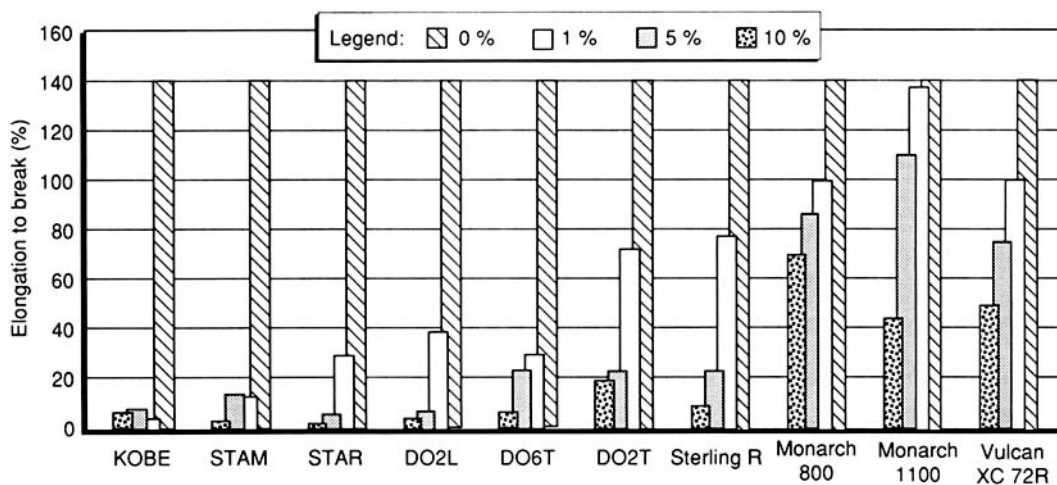


Figure 5 Elongation at break for the different PVC-CB composites as a function of concentration.

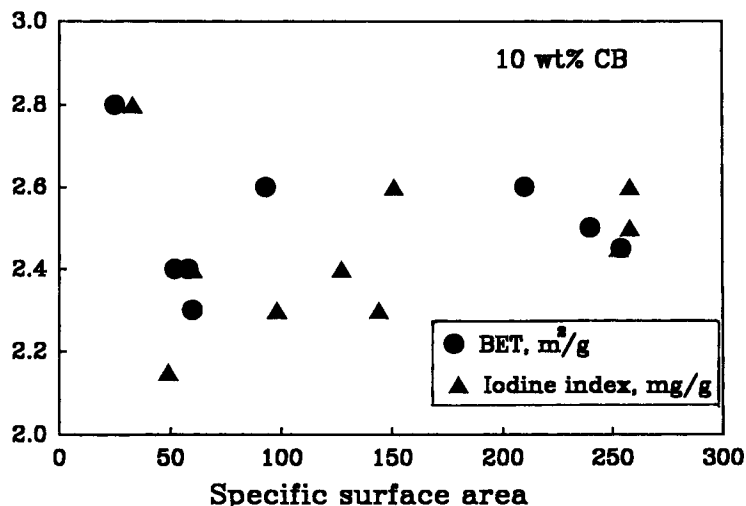


Figure 6 Modulus of the 10 wt % PVC-CB composite as a function of the CB specific surface area.

ambiguous and no particular trend was observed at this point. It is clear from Figures 6 and 7 that the Young's modulus decreased with volatile matter (VM) content. In fact, the VM is essentially composed of oxygen complexes adsorbed on the CB surface that act as a plasticizer for the composite, thus reducing the modulus. These results can be interpreted by the fact that the Iodine Index is related to the macroscopic porosity of the CB and the BET specific surface area to their overall porosity. The effect of the BET specific surface area is less obvious, but a tendency toward a decrease of the modulus as the BET specific area increases can be observed in

Figure 6. On the other hand, an increase of the modulus as a function of the Iodine Index is observed except for the Sterling R sample that has the lowest VM. In fact, a larger contact area between the polymer and the CB will increase the modulus, whereas for a higher CB porosity, the behavior of the modulus will depend on other factors such as diameter of the pores, diffusion, viscosity of the matrix, etc. The CB characteristics' effect on the elongation at break seemed to favor the CBs with higher BET specific surface area, as exemplified by the pyrolytic and the Sterling R CB that led to a sharp decrease of the elongation at break.

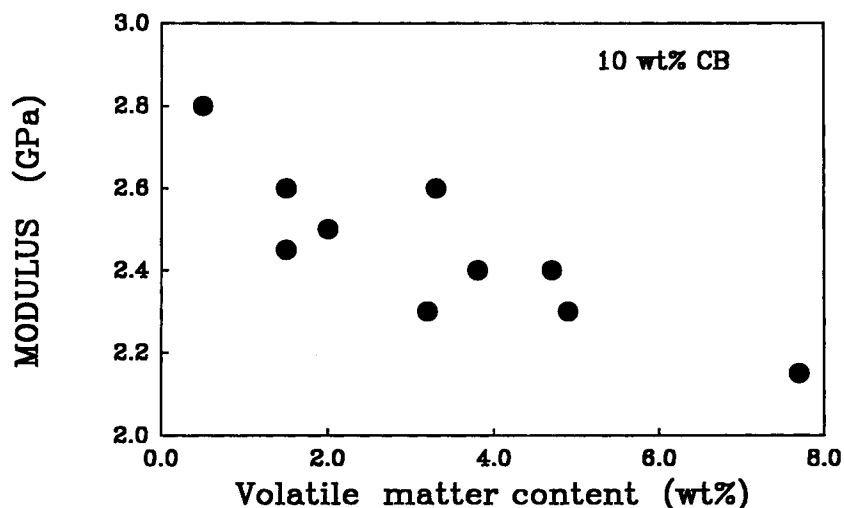


Figure 7 Modulus of the 10 wt % PVC-CB composite as a function of the CB volatile matter content.

Electrical Properties

The results obtained for the electric conductivity of the composites with the commercial and pyrolytic CBs are presented in Figure 8. For all the PVC composites tested, addition of up to 10 wt % CB did not significantly change the conductivity. For concentrations higher than 10 wt %, an important increase in conductivity was observed. This was attributed to the channel conduction as mentioned earlier. The percolation concentration, defined as the mass fraction at which an abrupt change in the conductivity is observed, depends on the CB characteristics. The lowest percolation concentration, giving also the highest conductivity, was obtained with the Vulcan XC 72R CB. Monarch 1100 and Monarch 800 also presented a low percolation concentration and a high conductivity. These three CBs have the highest specific surface area. The Sterling R CB had a percolation concentration much higher than that of the other commercial CB.

The pyrolytic CBs, however, did not yield the same conductivity for the PVC composites. The percolation concentration was not attained for any of them (up to a concentration of 30 wt %). At high CB concentrations (20 and 30 wt %), the acid-washed CB, D02L, presented a conductivity that was lower than that of the untreated sample D02T. Since the inorganics were predominantly composed of metals, particularly iron, their reduction in the CB will decrease the electrical conductivity. Concerning

the effect of the volatile matter content, comparison of the behavior of the STAM and STAR CB showed a slightly higher conductivity for the STAR CB (having a lower residual volatile matter content). This result can be explained by the fact that the volatile matter, which comprised, among other things, oxygen complexes adsorbed on the CB surface, reduced the CB electric conductivity. It should be noted, however, that the most important effects are due to the specific surface area and structure of the CB.

The results obtained for the electric conductivity of the different composites, at a composition of 20 wt %, as a function of the CB BET specific surface area are presented in Figure 9. An exponential dependence of the conductivity as a function of the BET specific surface area was observed. Based on the experimental conductivity values for the STAM and STAR CB, a BET specific surface area of about 100 m²/g is predicted for both. The effect of the structure cannot be assessed precisely since we have just two significantly different structures in the CB used in this study (Vulcan XC 72R and the others).

CONCLUSION

Composites of PVC with CBs obtained during vacuum pyrolysis of scrap tires showed intermediate rheological properties in comparison with the high-

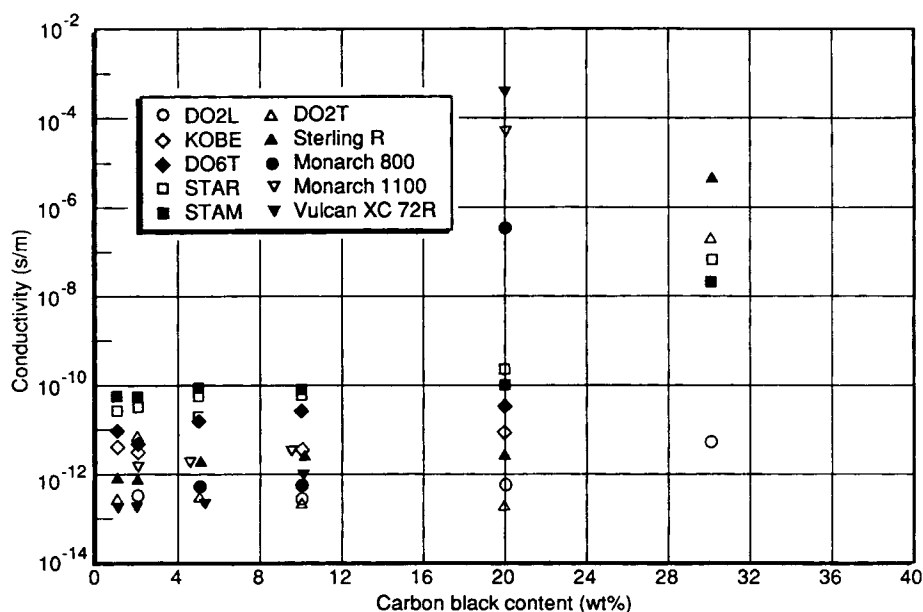


Figure 8 Electrical conductivity as a function of concentration for the different PVC-CB composites.

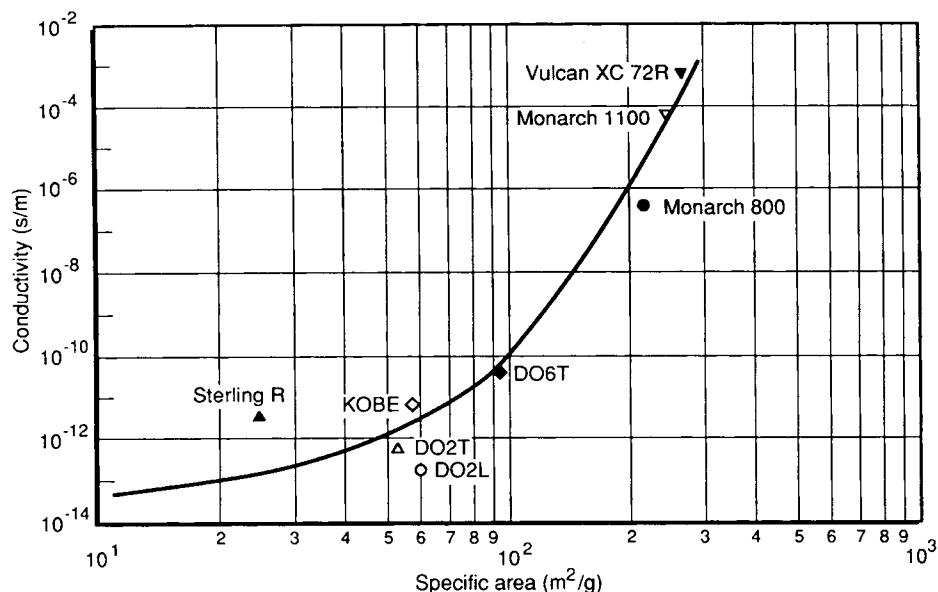


Figure 9 Electrical conductivity of the 20 wt % PVC-CB composites as a function of the CB BET specific surface area.

grade and the low-grade commercial CBs. Intermediate values were obtained for the Young's modulus, elongation at break, and electrical conductivity. The specific surface area of the CB, measured as BET or Iodine Index, was shown to be an important parameter of the properties of the composites (viscosity, modulus, and electrical conductivity). Reduction in volatile matter and ash contents of the pyrolytic CBs resulted in a higher modulus and conductivity. Finally, it appeared that pyrolytic CBs can be used with PVC for the preparation of medium-quality composites (use of pyrolytic CB as a low-cost fillers, e.g.).

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