

Fusion, Electrical Conductivity, Thermal, and Mechanical Properties of Rigid Poly(vinyl chloride) (PVC)/Carbon Black (CB) Composites

Cheng-Ho Chen, Hsin-Chiung Li, Chih-Chun Teng, Chien-Hsin Yang

Department of Chemical and Material Engineering, Southern Taiwan University of Technology, Tainan County 710, Taiwan, Republic of China

Received 5 September 2003; accepted 15 April 2005

DOI 10.1002/app.22656

Published online 7 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Rigid and conductive poly(vinyl chloride) (PVC)/carbon black (CB) composites were prepared in a Haake torque rheometer. The results illustrate that the fusion torque of the PVC/CB composite is increased as the amount of CB is increased. Both the fusion percolation threshold and the fusion time of PVC/CB composites are decreased when the amount of CB is increased. Two major weight loss stages are observed in the TGA curve of PVC/CB composite. The first thermal degradation onset temperature (T_{onset1}) of PVC/CB composite is decreased as the amount of CB is increased. Both the first and second weight loss stages (ΔY_1 and ΔY_2) of PVC/CB composites are decreased as the amount of CB is increased. The surface

resistivity of PVC/CB composite remains almost constant up to 6 parts per hundred unit weight of resin (phr) CB. When the amount of CB in PVC/CB composite is increased from 6 to 15 phr, the surface resistivity of PVC/CB composite is dramatically decreased from $10^{10} \Omega/\text{sq}$ to $10^4 \Omega/\text{sq}$. Because of the addition of CB, the rigidity of PVC/CB composite is increased and thus the mechanical properties, such as yield strength, tensile strength, and the Young's modulus, are improved. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2167–2173, 2006

Key words: poly(vinyl chloride) (PVC); carbon black (CB); fusion property; surface resistivity; mechanical property

INTRODUCTION

Poly(vinyl chloride) (PVC) is a common and important commodity plastic. PVC products are widely used in the automobile, housing/building construction fields, as well as packaging (everything from food to electronic parts). For use in such wide applications, various additives blended with PVC have been studied.

Suspension polymerization is the major commercial route to produce PVC resins in the industry. Various levels of morphology existed in a suspension PVC powder has been illustrated by Butters.¹ Powder particles, which are stage III particles and visible to the naked eye, are known as grains. Grains are irregular in shape and about 100–150 μm in diameter. Each grain consists of many microparticles, which are stage II particles, and are about 1–2 μm in diameter. The microparticles are loosely packed, and therefore, the grain becomes porous. Each microparticle is assembled by smaller structures that are known as stage I particles (submicroparticles). The stage I particles are

approximately 10–30 nm in diameter and about 5–10% crystallinity.

To achieve good mechanical properties, grain boundaries must be eliminated (pattern I) and the microparticles must be altered and compacted together (pattern II). After significant interdiffusion, the boundaries of submicroparticles disappear and a melt state of polymer (pattern III) is formed. This is referred as the fusion or gelation of PVC.^{2,3} Normally, the fusion mechanism of PVC particles, processed either in an extruder or a batch mixer, is the combination of these three patterns. Optimum values of impact ductility and modulus occur prior to 100% fusion. Benjamin⁴ suggested that although the strength of the material increases monotonically with increasing the degree of fusion, the material reaches the optimum ductility and then becomes easily brittle because of the higher entanglement of the 3-D network.

Electronic components are susceptible to be damaged from electrostatic discharge (ESD) during manufacturing, assembling, storage, and shipping. Electrostatic dissipating thermoplastic compounds have successfully eliminated ESD failures in many applications in the electronic industry. According to Electronic Industry Association standards, conductive materials have a surface resistivity less than $1.0 \times 10^5 \Omega/\text{sq}$, electrostatic dissipative materials have a surface resistivity in the range of 1.0×10^5 to $1.0 \times 10^{12} \Omega/\text{sq}$, and

Correspondence to: C.-H. Chen (chchen@mail.stut.edu.tw).

insulation materials have a surface resistivity greater than $1.0 \times 10^{12} \Omega/\text{sq}$.⁵

There are numbers of mechanisms by which a polymeric material or product can be made conductive, electrostatic dissipating, or antistatic. The conventional methods are through painting, coating, or addition (internal or external) of hygroscopic materials or conductive fillers. For a given polymeric compound, electrical conductivity is determined by the amount, type, and shape of the conductive fillers. A variety of conductive fillers are presently available for material engineers, including conductive carbon blacks (CBs), carbon fibers (CFs), metallic powders, flakes or fibers, and glass spheres or glass fibers coated with metals. CB is the most commonly used filler, because it is much cheaper and lighter than metallic particles. The minimum amount of the filler required to initiate a continuous conductive network is referred as the percolation threshold, which is varied from polymer to polymer for a given CB type.⁵⁻⁸

Fox⁹ reported that the electrical conductivity and melt flow behavior of PVC/CB composites were dependent on the amount of CB. Badawy et al.¹⁰ reported that acrylonitrile butadiene rubber was mixed with different concentrations (1, 3, 5, and 10 phr [parts per hundred unit weight of resin]) of PVC and blended with constant 40 phr of high abrasion furnace black. The obtained unvulcanizates were subjected to electrical conductivity measurements at different values of molding pressures. They found that the molding pressure impacted the electrical conductivity of the composite very much. Noguchi et al.¹¹ studied that the effect of the structure of CB aggregates on the melt behavior and electrical conductivity of poly(vinylchloride-*co*-vinylacetate)/CB composites. They found that the electrical conductivity of the composite was increased as the milling time was increased up to 30 min, then the electrical conductivity was decreased as the milling time was longer than 30 min. They concluded that an optimum aspect ratio and degree of dispersion of the cylindrical CB were aggregated for 30-min milling. Aji et al.¹² compared the pyrolytic CB with the commercial grades as fillers for PVC. The electrical properties of the PVC/CB composites were investigated. For all PVC/CB composites tested, adding up to 10 wt % CB did not significantly change the electrical conductivity. For concentrations higher than 10 wt %, an obvious increase in electrical conductivity was observed. Saad et al.¹³ prepared PVC/dioctyl phthalate (DOP)/CB and PVC/CB composites and studied electrical conductivity properties of these composites. At constant CB content, they found PVC/CB composites had much higher electrical conductivity than the PVC/DOP/CB composites. The electrical conductivity percolation threshold of this PVC/CB system was 20 phr CB. They also

found the PVC/CB composite containing 30 phr CB had the highest electrical conductivity. When the amount of CB was higher than 30 phr, the electrical conductivity of the PVC/CB composite was approximately the same.

In our previous reports,¹⁴⁻¹⁹ the morphological characteristics, the fusion mechanism, and the fusion percolation threshold (FPT) of rigid PVC compounds were studied. The influences of additives on the fusion of rigid PVC composites were illustrated. Since very few papers were related to the effect of CB on the fusion properties of the rigid PVC/CB composites, the conductive PVC/CB composites prepared in a Haake torque rheometer equipped with a three-sectioned mixing chamber and two noninterchangeable rotors under various amount of CB were studied in this research. The fusion characteristics such as fusion torque, FPT, and fusion time, were analyzed. The surface resistivity and mechanical properties of the PVC/CB composite is examined. Thermogravimetric analysis (TGA) was also done to reveal the influence of CB on the thermal degradation properties of PVC/CB composites.

EXPERIMENTAL

Preparation of PVC/CB composites

The materials used in this study were suspension PVC masterbatch powders without any plasticizers, containing 100 parts PVC resin particle (S60®, $M_w = 50,000$; supplied by the Formosa Plastic Co., Taiwan), 20 parts CPE (3615P, supplied by the Dow Chemical Co., USA), 1.5 parts processing aid (PA820), 1.0 part PE wax, 1.0 part calcium stearate, and 1.5 parts heat stabilizer (TM181FS). The PVC masterbatch powders were blended with 0, 3, 6, 9, 12, and 15 phr of CB (PRINTEX XE2-B, mean diameter = 30 nm, supplied by Degussa Co., Germany). All PVC/CB composites were prepared in a Haake torque rheometer (PolyLab 2000) equipped with an electrically heated mixing head and two noninterchangeable rotors. The processing temperature, rotor speed, and blending time were set at 170°C, 60 rpm, and 5 min, respectively. The sample weight for each blending was controlled at 62 g. Fusion curves of PVC/CB composites were analyzed and recorded.

TGA analysis

TGA (Perkin-Elmer, model: TGA 7) was conducted to measure the thermal weight loss of the PVC/CB composites in the temperature ranged from 50°C to 700°C with a heating rate of 10°C/min under a nitrogen stream. The thermal degradation onset temperature and the weight loss of PVC/CB composites were analyzed.

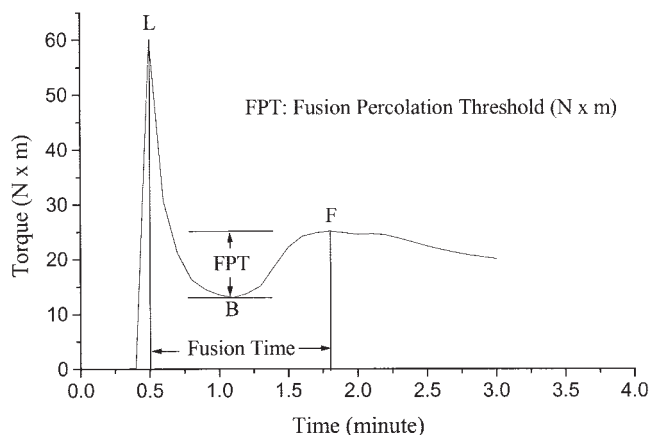


Figure 1 Typical fusion curve of a rigid PVC compound (0 phr CB) melted in a Haake torque rheometer at a temperature of 190°C, a rotor speed of 60 rpm, and a blending time of 3 min.¹⁹

Measurement of surface resistivity

A surface resistivity meter (Zhi Sheng Industrial Ltd., model: RT-1000) was used to measure the surface resistivity of the PVC/CB composite at room temperature.

Mechanical properties

Mechanical properties were evaluated from 3-mm-thick tensile specimens with a 38-mm gauge length, as per ASTM D638 specifications. Yield strength, tensile strength, and the Young's modulus of the PVC/CB composite were analyzed and recorded.

RESULTS AND DISCUSSION

Figure 1¹⁹ demonstrates a typical fusion curve of a PVC compound melted in a Haake torque rheometer at a starting temperature of 190°C, a rotor speed of 60 rpm, and a blending time of 3 min. Three specific points are observed from the curve in Figure 1 that illustrates the relationship between torque and blending time. The first point, L, stands for the sample loading. The second point, B, is generated because of the balance between sample loading and the driving force of free material flow. After that, the torque begins to increase and the third point, F, is generated due to compaction and onset of fusion. At this point, F, the material reaches a void-free state and starts to melt at the interface between the compacted material and the hot metal surface. If the sample is melted and fused in the mixer for a long time, the temperature only slightly increases due to some thermal energy is absorbed by the sample. The higher temperature results in decreasing the melt viscosity of sample, and

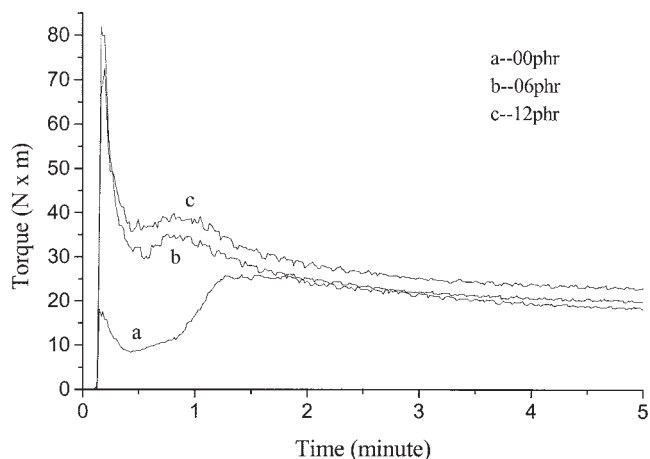


Figure 2 Fusion curves of PVC/CB composites (a: 0 phr CB; b: 6 phr CB; c: 12 phr) melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

therefore, the torque slowly decreases and increases the blending time. Usually, the blending time period between the loading point L and the fusion point F is defined as fusion time. The blending time is defined as the time period between the loading point L and the stopping point.²⁰ In this study, the torque variation between the point B and the fusion point F is defined as FPT of the PVC sample.¹⁹

Figure 2 shows the fusion curves of PVC/CB composites with various amount of CB melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min. Figure 3 illustrates that the fusion torque of the PVC/CB composite is increased as the amount of CB is increased. This is because the CB particles increase the friction in the blending system. This increase results in increase of the fusion torque when the unfused

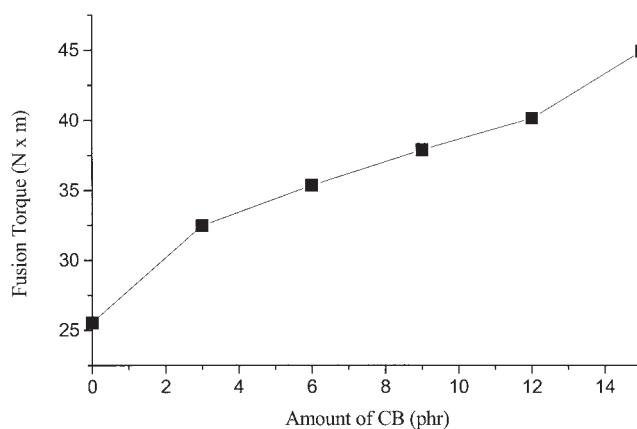


Figure 3 Influence of the amount of CB on the fusion torque of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

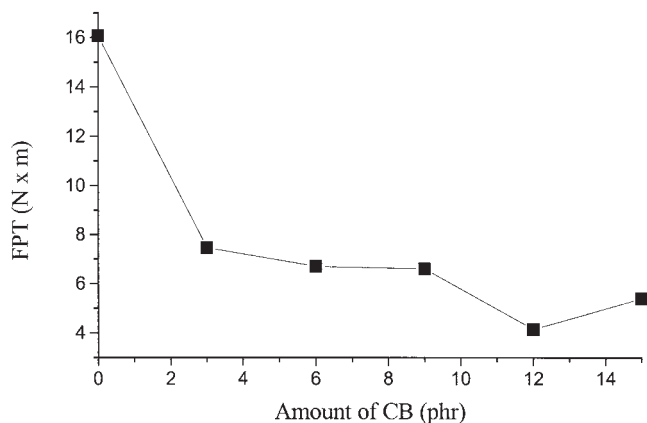


Figure 4 Influence of the amount of CB on the FPT of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

PVC/CB compound reaches a void-free state in the mixer and starts to melt at the interface between the compacted material and the hot metal surface. Meanwhile, the sample weight for each blending was controlled at 62 g. If the amount of CB is increased, the amount of PVC compound is decreased for each blending at constant sample weight.

Figure 4 indicates that the FPT of PVC/CB composite is decreased when the amount of CB is increased. This is because the CB particles can promote the friction in the system, increase the transfer of heat and shear throughout the PVC grains, and then decrease the FPT of PVC/CB composites. Figure 5 demonstrates that the fusion time of PVC/CB composites is decreased as the amount of CB is increased. Since the CB particles can promote the friction in the system and increase the transfer of heat and shear throughout the PVC grains, adding CB particles can assist the

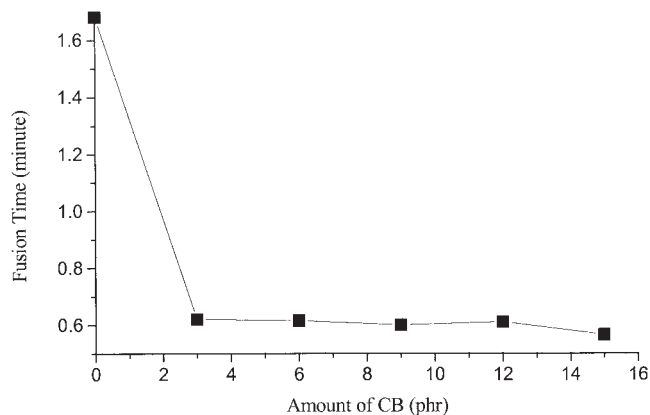


Figure 5 Influence of the amount of CB on the fusion time of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

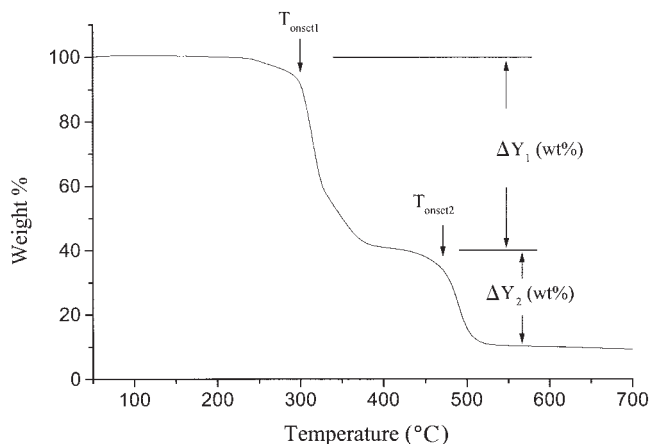


Figure 6 TGA curve of the PVC compound without CB (T_{onset1} : the first thermal degradation onset temperature; T_{onset2} : the second thermal degradation onset temperature; ΔY_1 : the first stage weight loss; ΔY_2 : the second stage weight loss).

fusion process of PVC/CB compound to occur more quickly.¹⁹

Figure 6 shows a TGA curve of the PVC compound without CB (T_{onset1} : the first thermal degradation onset temperature; T_{onset2} : the second thermal degradation onset temperature; ΔY_1 : the first stage weight loss). Two major weight loss stages are observed in the TGA curve. The first weight loss stage within the range of 280–300°C is mainly due to the HCl-elimination reaction of PVC and formation of a polyenes structure.^{21,22} The second weight loss stage within the range of 450–470°C is due to the thermal degradation of carbon chain of PVC that produces flammable volatiles.²³

Figure 7 reveals TGA curves of three PVC/CB composites (a: 0 phr CB; b: 6 phr CB; c: 12 phr CB). The T_{onset2} of PVC/CB composite in Figure 7 is increased

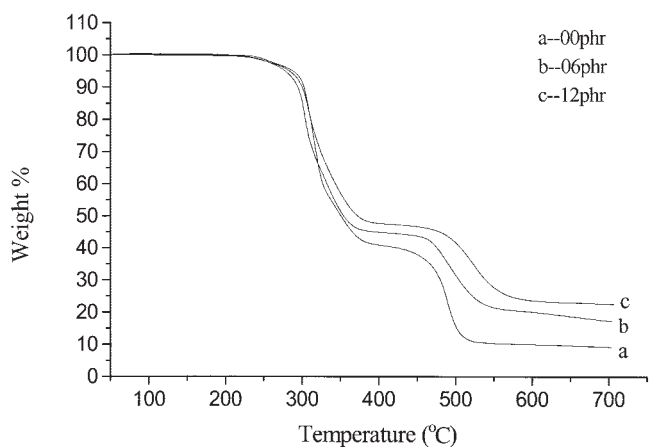


Figure 7 TGA curves of PVC/CB composites (a: 0 phr CB; b: 6 phr CB; c: 12 phr CB).

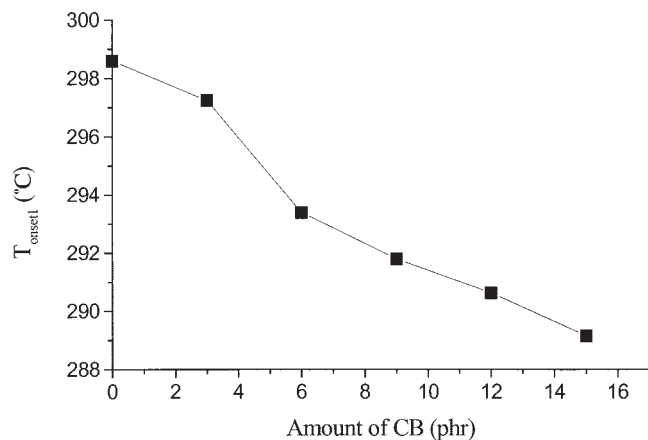


Figure 8 Influence of the amount of CB on the first thermal degradation onset temperature (T_{onset1}) of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

as the amount of the CB is increased. Figure 8 shows the T_{onset1} of PVC/CB composite is decreased as the amount of CB is increased. From this figure it can be inferred that the CB does promote the HCl-elimination reaction of PVC. Figures 9 and 10 indicate the influence of the amount of CB on the first and second weight loss stages (ΔY_1 and ΔY_2) of PVC/CB composites, respectively. Both ΔY_1 and ΔY_2 are decreased as the amount of CB is increased. This is because the sample weight for each blending is controlled at 62 g. If the amount of CB is increased, then the amount of PVC is decreased for each blending at constantly controlled sample weight. Figure 11 exhibits the influence of the amount of CB on the surface resistivity of PVC/CB composites. The surface resistivity of PVC/CB composite remains almost constant up to 6 phr CB. When the amount of CB of PVC/CB compos-

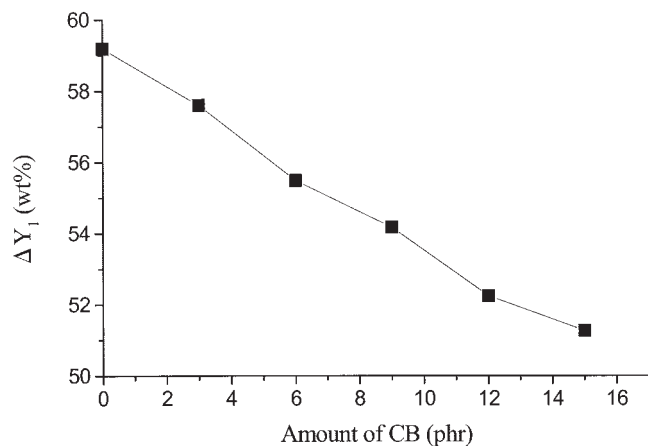


Figure 9 Influence of the amount of CB on the first stage weight loss (ΔY_1) of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

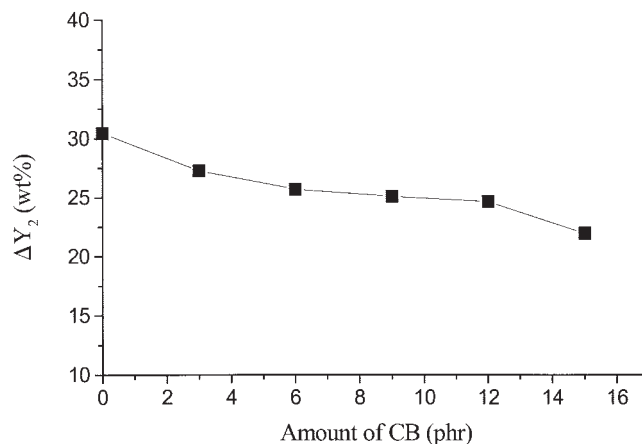


Figure 10 Influence of the amount of CB on the second stage weight loss (ΔY_2) of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

ite is increased from 6 to 15 phr, the surface resistivity of PVC/CB composite is dramatically decreased from 10^{10} to $10^4 \Omega/\text{sq}$. Therefore, the electrical conductivity threshold percolation concentration is about 6 phr in this rigid PVC/CB system and much lower than those of reported results.¹¹⁻¹³ That is based on the fact that the conductive CB with mean diameter of 30 nm are sufficient to come into contact with one another as the filler loading exceeds the threshold concentration.²⁴ This means when the CB is present in abundance in the PVC matrix, the PVC will be saturated with CB, which forms tunnels of electrons between adjacent carbon clusters and through the PVC matrix. If the electric current is applied, it is easier for the current to pass through these tunnels. Accordingly, there will be a dramatically increase in the electrical conductivity for the PVC/CB composite (i.e., the surface resistivity is dramatically decreased).¹³

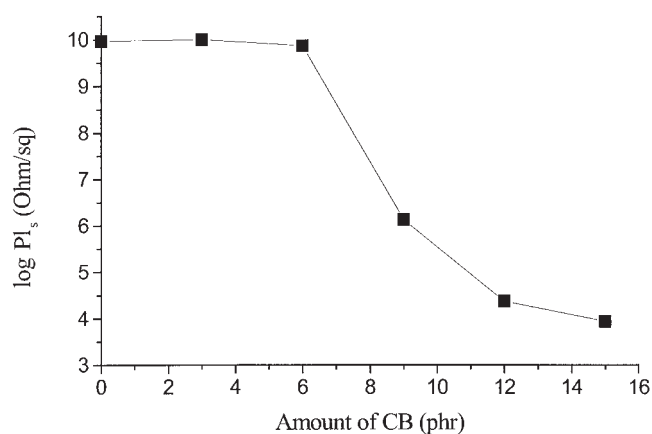


Figure 11 Influence of the amount of CB on the surface resistivity of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

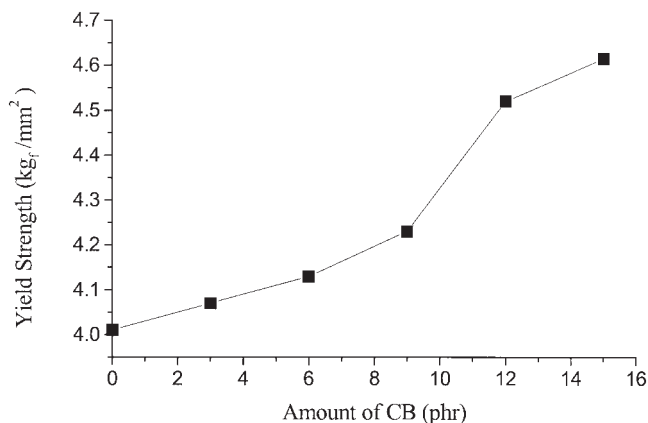


Figure 12 Influence of the amount of CB on the yield strength of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

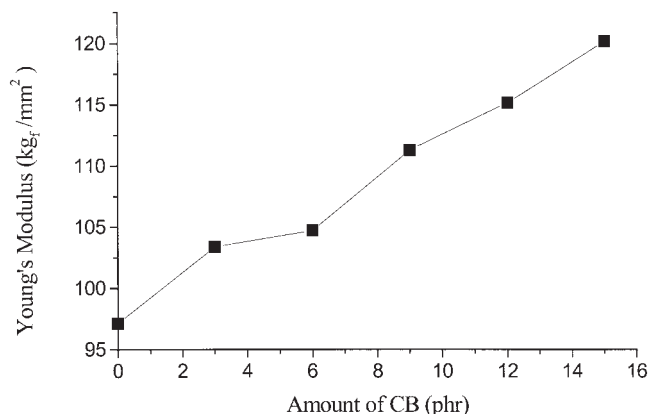


Figure 14 Influence of the amount of CB on the Young's modulus of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

Figures 12–14 indicate the influence of the amount of CB on the yield strength, tensile strength, and the Young's modulus of PVC/CB composites, respectively. All these three figures reveal that the yield strength, tensile strength, and the Young's modulus of PVC/CB composite are all improved as the amount of CB is increased. This is because the addition of CB can increase the rigidity of PVC/CB composite and thus increase the mechanical properties, such as the yield strength, tensile strength, and the Young's modulus.

CONCLUSIONS

Rigid and conductive PVC/CB composites were prepared in a Haake torque rheometer. The fusion torque of the PVC/CB composite is increased as the amount

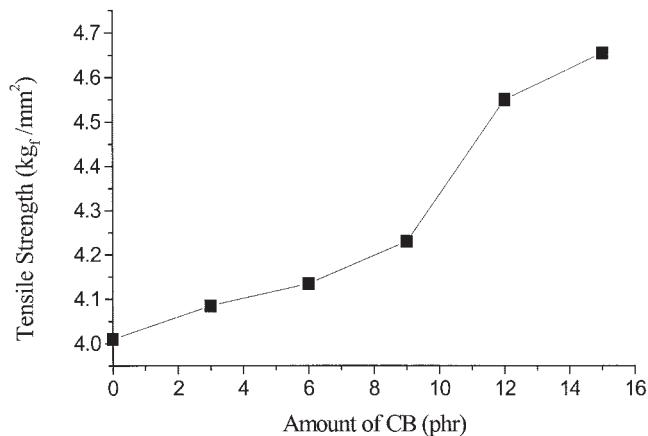


Figure 13 Influence of the amount of CB on the tensile strength of PVC/CB composites melted in a Haake torque rheometer at a temperature of 170°C, a rotor speed of 60 rpm, and a blending time of 5 min.

of CB is increased. However, both the FPT and the fusion time of PVC/CB composites are decreased as the amount of CB is increased. From TGA results, the first thermal degradation onset temperature (T_{onset1}) of PVC/CB composite is decreased as the amount of CB is increased. Both the first and second weight loss stages (ΔY_1 and ΔY_2) of PVC/CB composites are also decreased as the amount of CB is increased. Because of the addition of CB, the rigidity of PVC/CB composite is increased and thus the mechanical properties such as yield strength, tensile strength, and the Young's modulus are increased. The surface resistivity of PVC/CB composite remains almost constant up to 6 phr CB. If the amount of CB in the PVC/CB composite is increased from 6 to 15 phr, the surface resistivity of PVC/CB composite is dramatically decreased from 10^{10} to $10^4 \Omega/\text{sq}$. On the basis of these observations, it may be inferred that PVC/CB composites can be considered potential ESD materials.

References

- Butters, G. Particulate Nature of PVC-Formation, Structure and Processing; Applied Science Publishers Ltd: London, 1982; Chapter 1, p 2.
- Gilbert, M. *Plast Rubber Int* 1985, 10, 16.
- Krzewki, R. J.; Collins, E. A. *J Macromol Sci Phys B* 1981, 20, 443.
- Benjamin, P. Processing of Plastics and Rubber, Institute of International Conference, PVC Processing, Vol. B51, April, Egham Hill, England, 1978.
- Narkis, M.; Lidor, G.; Vaxman, A.; Zuri, L. *J Electrostat* 1999, 47, 201.
- Narkis, M.; Ram, A.; Flashner, F. *J Appl Polym Sci* 1978, 22, 1163.
- Narkis, M.; Ram, A.; Stein, Z. *J Appl Polym Sci* 1980, 25, 1515.
- Narkis, M.; Vaxman, A. *J Appl Polym Sci* 1984, 29, 1639.
- Fox, L. P. *RCA Review* 1978, 39, 116.
- Badawy, M. M.; Nasr, G. M. *Polym Test* 1997, 16, 155.

11. Noguchi, T.; Nagai, T.; Seto, J. *J Appl Polym Sci* 1986, 31, 1913.
12. Dufeu, J. B.; Roy, C.; Aji, A.; Choplin, L. *J Appl Polym Sci* 1992, 46, 2159.
13. Saad, A. L. G.; Aziz, H. A.; Dimitry, O. I. H. *J Appl Polym Sci* 2004, 91, 1590.
14. Comeaux, E. J.; Chen, C. H.; Collier, J. R.; Wesson, R. D. *Polym Bull* 1994, 6, 701.
15. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. *J Appl Polym Sci* 1995, 58, 1089.
16. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. *J Appl Polym Sci* 1995, 58, 1093.
17. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. *J Appl Polym Sci* 1995, 58, 1107.
18. Chen, C. H.; Lo, Y. W. *J Appl Polym Sci* 1999, 74, 699.
19. Chen, C. H.; Lo, Y. W.; Mao, C. F. *J Appl Polym Sci* 2001, 81, 3022.
20. Chung, J. T. Haake Buchler Technical Bulletin, TB-842; 1983.
21. Makherjee, A. K.; Gupta, A. *J Macromol Sci Rev Macromol Chem Phys* 1981, 309, C20.
22. Liebman, S. A.; Reuwer, J. F.; Gollatz, K. A.; Nauman, C. D. *J Polym Sci Part A: Poly Chem* 1971, 9, 1823.
23. Li, B. *Polymer Degrad Stabil* 2000, 68, 197.
24. Xiao, H. Y.; Katsumi, Y.; Hideo, Y.; Toshiro, W.; Shinichi, N.; Mikio, A.; Isa, I. *Jpn J Appl Phys* 1994, 33, 3597.