Conducting Rubberlike Copolymer–Carbon Fiber Composites

ELI RUCKENSTEIN* and LIANG HONG

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

SYNOPSIS

Electrically conductive rubberlike copolymer–carbon fiber composites have been prepared by either a solution method or a concentrated emulsion method. In the former procedure, carbon fibers were introduced with stirring in a copolymer–toluene solution, and the polymer–fiber composites were precipitated by extracting the solvent with methanol. In the latter procedure, a pastelike concentrated emulsion of copolymer–toluene solution in an aqueous solution of sodium dodecylsulfate (SDS) was first formed, and the carbon fibers were mechanically blended with the concentrated emulsion. The polymer–carbon fiber composites were precipitated by extracting the toluene and water with methanol. Four kinds of rubberlike copolymers have been used: styrene/ethylene–butylene/styrene triblock copolymer (SES), styrene/butadiene/styrene triblock copolymer (SBS), ethylene/propene/ethylene triblock copolymer (EPE), and ethylene/vinylacetate copolymer (EVA). Short (L = 0.1 mm)- and medium (L = 5 mm)-length carbon fibers were employed. The composites were hot-pressed in a Laboratory Press to form a sheet. The effects of the two methodologies on the electrical conductivity and mechanical properties of the sheets were investigated by changing the type of polymer, the size of the carbon fibers, the volume fraction of the carbon fibers in the composites, and the hot-pressing temperature. Composites with electrical conductivities in the range of 5–14 S/cm, tensile strengths in the range of 10–17 MPa, and elongations at break point larger than 200% were obtained. The conductivities of the composites prepared with the short fibers were by two orders of magnitude smaller than those prepared with medium-size fibers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The initial attempts to develop conducting polymers had the scope to achieve a conductivity as large as that of copper combined with the processability of polyethylene. Their highly conjugated structure made, however, most conducting polymers insoluble and infusible, hence, unprocessable, and, in addition, vulnerable to degradation.[1] These factors have stimulated efforts in preparing processable polymer composites,[2] one of the general methodologies being the embedding of conductive materials such as metal powders in insulating polymer matrixes. In such systems, the electrical conductivity and mechanical properties rely not only on the intrinsic properties

of the polymer and the conductive filler, but also on the surface chemistry of the two and on the mixing operation. Indeed, since the electron transfer in a conductive polymer composite occurs mainly through the physical contact among the conductive filaments, the polymer matrix–filler adhesion becomes important in preventing the formation of free spaces between them in which moisture could condense, thus generating disconnections in the conductive network. For this reason, many patents suggested the use of fine particles of carbon black as filler due to its ability to generate a conductive material that is not degradable by ultraviolet light, moisture, and temperature.[3,4] This capacity, which distinguishes the carbon black from most metal powders, is due to a better adhesion due to a surface polarity closer to those of the organic polymer matrixes. Recently, Guigon[5] examined the interface of a carbon–epoxy composite by transmission electron

Table I The Weight Percent and Volume Percent of Carbon Fibers (CF) in the Conductive Composites[a]

Notations	CF Introduced (g)	Wt %	Vol %
a	0.25	7.2	4.2
b	0.5	13.5	8.0
c	1.0	23.8	14.8
d	2.0	38.5	25.8
e	3.0	48.4	34.3

[a] A copolymer, 3.2 g, in 35 mL toluene was used for each sample. The calculation is based on the approximate densities 1.0 g/cm^3 for the polymer and 1.8 g/cm^3 for the carbon fibers.

microscopy and concluded that the carbon–matrix interpenetration is essential for good adhesion. In addition to a suitable polarity, the high surface area possessed by carbon black constitutes a key element in the generation of a diffuse interface. One of the major problems with carbon black is that the conductivity of the composite cannot be controlled, because of its sharp percolation behavior.[6]

Carbon fibers have replaced carbon black in the preparation of conductive polymer composites quite recently.[7] Although they provide a much lower surface area than does carbon black, they generate a higher conductivity at lower fiber/polymer weight ratios and allow for a fine tuning of the conductivity. In addition, they can, for sufficiently small contents, reinforce the polymer composites.

In the present article, results are reported regarding polymer–carbon fiber composites prepared via both a solution method and a concentrated emulsion method. In the former method, a toluene polymer solution was mixed with carbon fibers and the mixture was introduced into methanol, which is a poor solvent for the polymer but is miscible with toluene. The extraction of toluene by methanol led to the rapid contraction of the polymer chains that entrapped the carbon fibers suspended in the solution among the expanded polymer chains, thus generating a composite. In the latter method, a pastelike concentrated emulsion of a toluene polymer solution in an aqueous surfactant solution was first prepared

and then mixed with carbon fibers. Removing the toluene and water with methanol from the mixture, polymer latexes were generated from the emulsion droplets that were deposited on the carbon fibers. Four kinds of rubberlike copolymers (SES, SBS, EPE, and EVA, see the section Materials for the symbols), were employed to prepare conducting composites. Because these copolymers possess toughness and elasticity, the prepared polymer–fiber composites have also good mechanical properties.

EXPERIMENTAL

Materials

The four kinds of copolymers used, styrene–ethylene/butylene–styrene triblock copolymer (SES) (28 wt % polystyrene); styrene–butadiene–styrene triblock copolymer (SBS) (29 wt % polystyrene); ethylene–propene–ethylene (EPE) triblock copolymer (60 wt % polyethylene), and ethylene–vinylacetate copolymer (EVA) [9 wt % poly(vinyl acetate)], were purchased from Polymer Science Co. The short carbon fibers employed (average length $L \sim 0.1$ mm, diameter = 15 μm) were of grade CARBOFLEX P-100 (Ashland) and the medium carbon fibers ($L \sim 5$ mm, diameter = 10 μm) were of grade P 25-X (Union Carbide). Carbon graphite sheets (99.9%, Johnson Matthey) were employed in the measurement of carbon–liquid contact angles. The surfactant sodium dodecylsulfate (SDS) (98%, Aldrich), toluene (99+%, A.C.S. Reagent, Aldrich), and methyl alcohol (99.9% A.C.S. reagent, Aldrich) were also used in the preparation of the samples.

Preparation of Samples

Sample Preparation Based on the Concentrated Emulsion Method

The Concentrated Emulsion. A concentrated emulsion[8] differs from the conventional emulsions in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of

Table II Contact Angles of Various Liquids on Graphite

Liquid System	H_2O	SDS (aq) (0.36 g/2 mL H_2O)	Toluene	SES in Toluene (0.2 g/2 mL)	EVA in Toluene (0.2 g/8 mL)
θ (degree)	63.5	10.5	8.0	46.7	32.3

Figure 1 SEM pictures of the EVA–CF_m-d before hot pressing: (a) EVA particles are deposited on carbon fibers (the emulsion method); (b) EVA particles agglomerate to a large extent among themselves (the solution method).

spheres of the same size) and may be as high as 0.99. The continuous phase has a low volume fraction and for large values of ϕ is in the form of a network of thin liquid films that separate polyhedral droplets.

Preparation Procedure. A copolymer, 3.2 g (one of the four copolymers) was introduced in 35 mL toluene and the system was stirred at about 50°C until a uniform polymer solution was obtained. A solution of SDS (0.36 g) in 2 mL water was prepared in a 100 mL round-bottom flask equipped with a mechanical stirring blade. The polymer toluene solution was introduced slowly with vigorous stirring into the flask, to form a pastelike concentrated emulsion. Various amounts of carbon fibers were then dispersed into the concentrated emulsion with mechanical stirring. The mixing continued for about 10 min to maximize dispersion. The mixture was added, in small portions, to a 250 mL beaker containing 150 mL methanol under stirring. In this step, the polymer chains and the carbon fibers precipitated, while the water and toluene were extracted by methanol. The liquid was then decanted, and the precipitate was washed several times with fresh methanol followed by water, both with stirring and pressing to remove any remaining toluene and free SDS. The black flakes were air-dried in a fume hood overnight, and approximately 2.0 g of the dry sample was hot-pressed in a Laboratory Press (Fred S. Carver Inc.) at about 150°C to form a sheet. The various weight and volume percents of carbon fibers are listed in Table I. The following abbreviations are used in this article for the various carbon-fiber polymer composites: (1) CF_s and CF_m stand for the short and medium carbon fibers, respectively; and (2) SBS-CF_s-c (see Table I), as an example, stands for the composite that contains the polymer SBS and 23.8 wt % of short carbon fibers.

Samples Preparation Based on Solution Method

A copolymer, 3.2 g (SES or EVA) was introduced in 35 mL toluene and the system was stirred at about 50°C until the polymer dissolved completely. To this polymer solution, various amounts of carbon fibers were added. The next steps were the same as those for the concentrated emulsion method.

Measurement of Electrical Conductivity

The samples were cut into rectangular shapes (5 × 1.5 cm) and the conductivity measured at room temperature by the four-point technique.
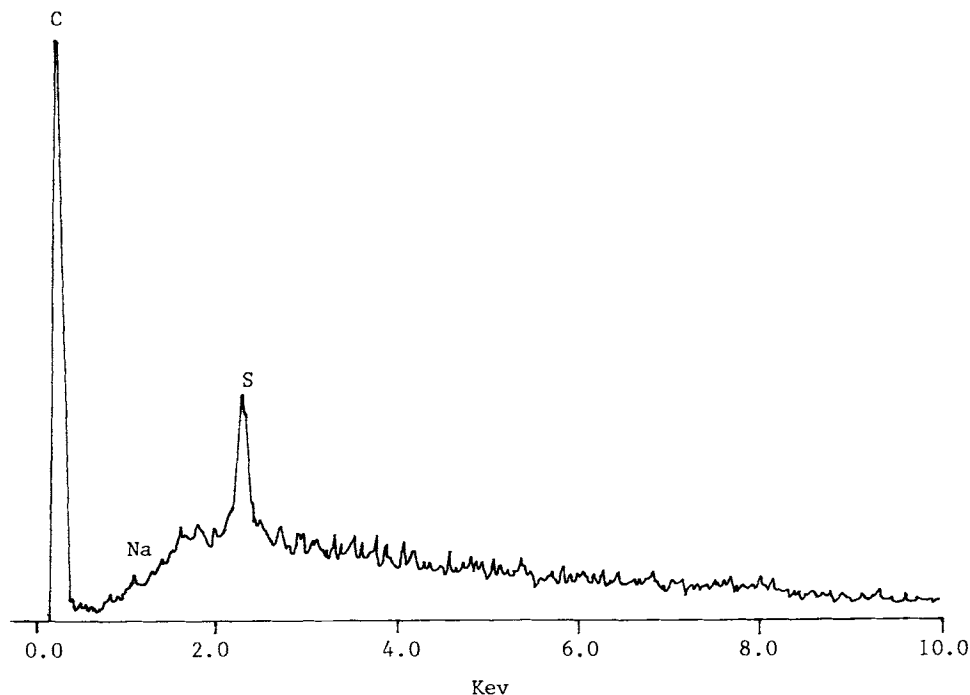
Figure 2   The energy-dispersive spectroscopy (EDS) of sample (a) of Figure 1.

Tensile Testing

The sample sheets were cut to the size required by ASTM D.638-58T. The tensile testing was performed with an Instron universal testing instrument (Model 1000) at room temperature. The elongation speed of the instrument was 20 mm/min.

Scanning Electron Microscopy (SEM) Analysis

The SEM micrographs were obtained with a Hitachi S-800 instrument. The sample was coated with carbon before investigation. Energy-dispersive spectroscopy (EDS) was performed with a PGT/IMIX field emission microscopy equipment.

Table III   Effect of the Hot-Pressing Temperature on Electrical Conductivity (S/cm)[a]

	T (°C)				
	25	50	95	120	150
EVA-CF$_m$-d (emulsion)					
1st	7.8	9.0	26.5	25.9	18.8
2nd			24.4	24.6	18.0
3rd			22.3	22.5	20.8
Average	7.8	9.0	24.4 (8.6%)	24.3 (5.1%)	19.2 (6.2%)
EVA-CF$_m$-d (solution)					
1st	2.5		26.1	25.1	27.0
2nd			14.1	17.5	21.4
3rd			17.8	20.8	26.4
Average	2.5		19.3 (32%)	21.1 (18%)	24.9 (12.4%)

[a] 1st, 2nd, and 3rd mean that measurements have been carried out on various samples of the same sheet. The percentages in the parentheses represent the standard deviation from the arithmetic average value.
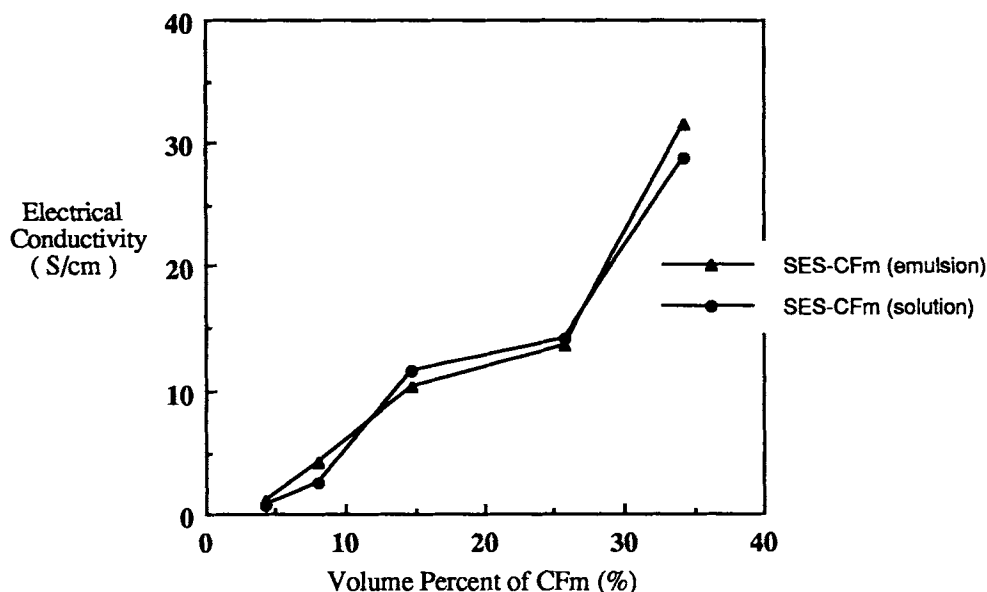
Figure 3 Effect of carbon–fiber concentration in vol % on the electrical conductivity: SES–CF_m (emulsion) represents composites prepared by the emulsion method; SES–CF_m (solution) represents composites prepared by the solution method.

Contact Angle Measurements

The contact angles of various liquids on graphite sheets were measured to gain qualitative information about the wetting ability of these liquids on carbon fibers. The measurements were carried out with a Rame-Hart NRL contact angle goniometer instru-

Table IV Effect of the Short Carbon Fibers, CF_s, on the Conductivity and Mechanical Properties of Various Composites[a]

Polymer–CF_s Composites	Electrical Conductivity (S/cm)	Tensile Strength (MPa)	Elongation at the Break Point (%)
SES	Insulator	15–20	∞
SES–CF_s-c	1.5×10^{-2}	17.4	470
SES–CF_s-d	4.4×10^{-1}	12.5	247
SES–CF_s-e	2.0×10^{-1}	4.7	82
SBS	Insulator	10–15	∞
SBS–CF_s-e	1.0×10^{-2}	6.7	16
EPE	Insulator	15–20	∞
EPE–CF_s-e	1.6×10^{-1}	5.4	12
EVA (9% VA)	Insulator	25–30	500
EVA–CF_s-e	3.1×10^{-2}	33.4	6

[a] The samples were prepared by the emulsion method, and the hot-pressing temperature was 150°C. CF_s stands for the short carbon fiber having $L = \sim 0.1$ mm and $D = 15$ μm; the symbols c, d, and e indicate the volume percent of CF_s in the composite (see Table I).

ment (Model 100). The results are listed in Table II.

RESULTS AND DISCUSSION

Effects of the Concentrated Emulsion Method on EVA-CF_m Composites

In concentrated emulsions, small droplets of toluene, with diameters between 1 and 10 μm, containing the polymer are separated by thin liquid films of aqueous sodium dodecylsulfate (SDS) solution; the electrical repulsion among the anion head groups of the emulsifier molecules adsorbed on the surface of the droplets ensures the kinetic stability of the pastelike emulsion.[9] When the copolymer EVA was used to prepare the composites, our observations indicated that the composites based on the concentrated emulsion method exhibited a stronger adhesion between polymer and the fiber than did those based on the solution method. Although before hot pressing it was relatively easy to separate the polymer from the fiber in the latter case, it was more difficult in the former. The SEM pictures of the composites EVA-CF_m-d (Fig. 1) show that the average agglomeration number of polymer particles in (a), which is based on the emulsion method, is smaller than in (b), which is based on the solution method.

Because the aqueous solution better wets the fiber (see Table II) (has stronger interactions with the
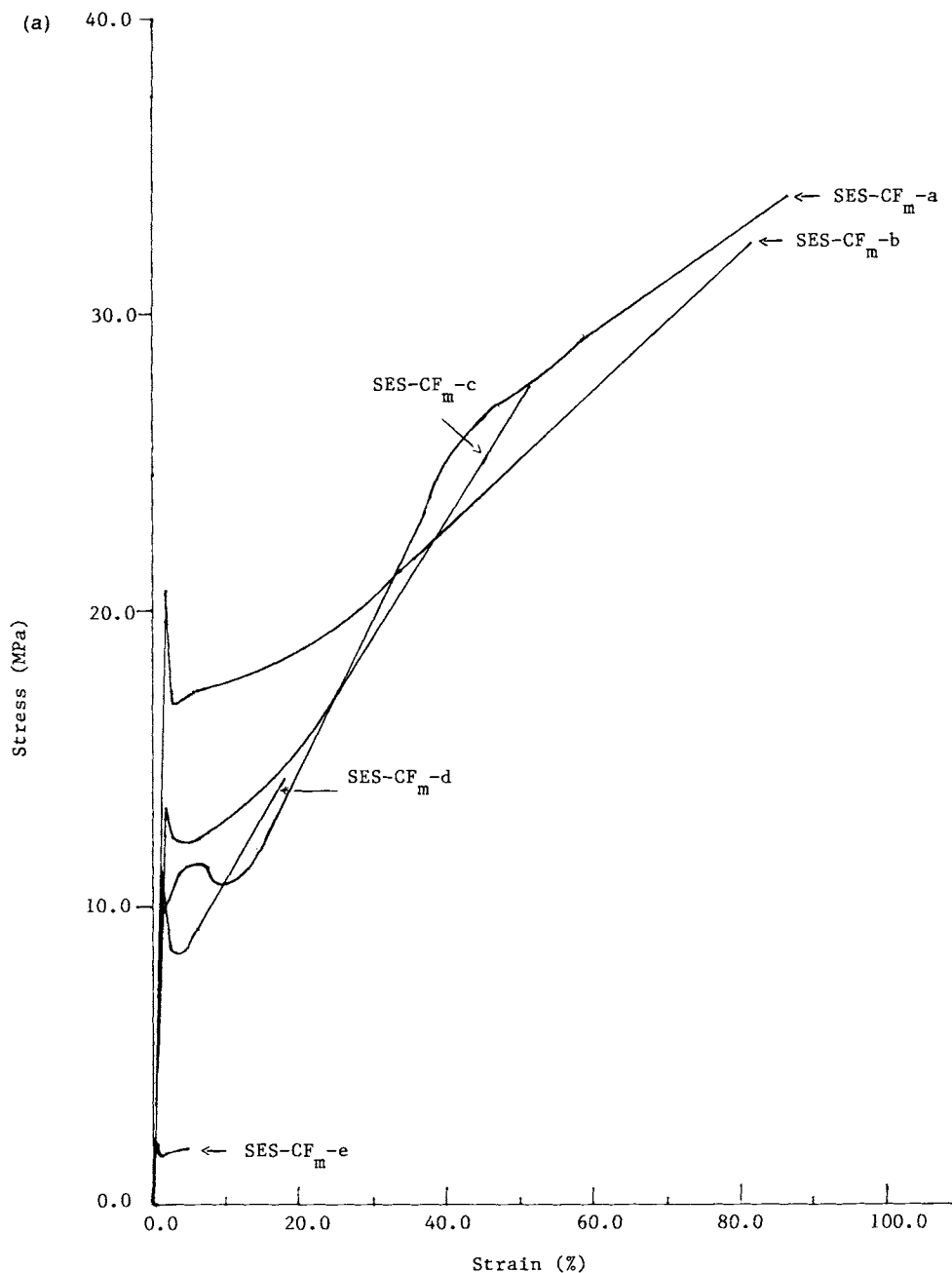
Figure 4 Stress–strain curves: (a) composites prepared by the emulsion method; (b) composites prepared by the solution method (the tensile strength of SES-CF$_m$-a is 36.2 MPa, and of SES-CF$_m$-b, 27 MPa, and the strain at the breaking point of the former is 90%, and of the latter, 66%).

fibers) than does the polymer–toluene solution, the fibers have the tendency to distribute more uniformly in the emulsion, in order to achieve some contact with the water-solution films. Therefore, during the extraction of toluene and water, the agglomerates of polymer coils find more easily, in their neighborhood, carbon fibers for deposition. The adhesion between polymer and fiber is enhanced by the surfactant because their head groups interact with the oxygen sites always present on carbon fibers and their hydrocarbon chains interact with the polymer chains. The K_α absorption peaks of sulfur
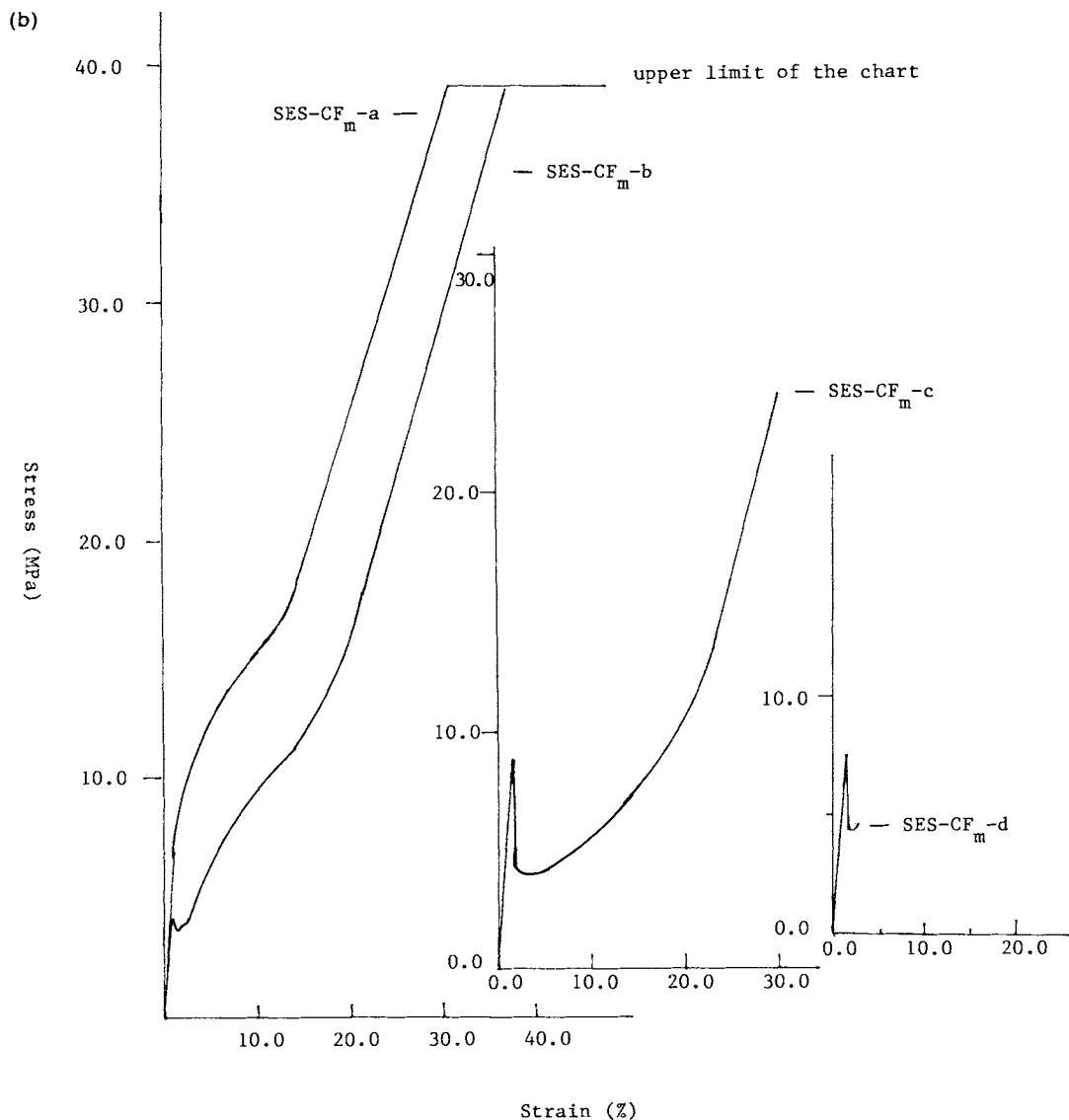
(b)

Stress (MPa)

Strain (%)

Figure 4   (*Continued from the previous page*)

and sodium in the EDS spectrum indicate the presence of SDS in the composites (Fig. 2). When, however, the mixture of the EVA–toluene solution and carbon fibers CF_m was introduced in methanol, the random EVA coils contracted and tended to agglomerate among themselves to a higher extent than in the concentrated emulsion case (see Fig. 1). This tendency occurs because the solution of EVA in toluene (about 1 g of polymer/10 mL of solvent) is a gel at room temperature, in which a physically crosslinked polymer network traps solvent molecules. The carbon fibers are not as well wetted by the toluene–polymer solution as they are by the aqueous solution of surfactant and are therefore less uniformly distributed. Consequently, during the extraction of the solvent by methanol, the polymer is more likely to form aggregates of polymer particles than polymer–fiber entanglements.

To investigate the effect of the different methods, namely, via emulsion and via solution, on the electrical conductivity of the EVA-containing composites, the conductivities of the samples prepared by different methods and at different hot-pressing temperatures are listed in Table III. This table shows the following: (1) The different methods lead to different electrical conductivities. The distribution of carbon fibers in the samples is more uniform in the emulsion method than in the solution method, since

Table V Effect of the Medium Carbon Fibers, CF_m, on the Conductivity and Mechanical Properties of Various Composites[a]

Polymer–CF_m Composites	Electrical Conductivity (S/cm)	Tensile Strength (MPa)	Elongation (%)
SES–CF_m-c	10.0	27.8	500
SES–CF_m-d	13.6	13.4	215
SES–CF_m-e	31.6	1.8	18
SBS–CF_m-c	5.0	17.1	775
SBS–CF_m-d	16.3	29.3	15
EPE–CF_m-c	9.4	10.6	584
EPE–CF_m-d	30.0	34.5	14
EVA–CF_m-c	4.2	27.9	10
EVA–CF_m-d	19.1	36.5	6

[a] The samples were prepared by the emulsion method. CF_m stands for the medium carbon fibers having $L = 5$ mm and $D = 10$ μm; the symbols c, d, and e indicate the volume percent of CF in the composite (see Table I).

the conductivities measured in various regions of the same sheet are less different in the former than in the latter processing. The standard deviations from the arithmetic averages are between 6.9 and 8.6% in the first case and between 12 and 32% in the second. The adhesion between polymer and fiber is stronger in the emulsion pathway. As a result, the more uniform distribution achieved during precipitation will be maintained later during the hot pressing, since the fiber and the adjacent polymer will displace together. (2) Because EVA is sensitive to temperature and melts in a range of temperatures around 95°C, the effect of the hot-pressing temperature is important, the conductivity being much larger for a hot pressing at 100°C than at room temperature. For emulsion processing, Table III suggests that an optimum pressing temperature around 100°C exists.

Electrical Conductivity and Mechanical Properties of the SES-CF_m Composites

Because the triblock copolymer SES contains both glassy thermoplastic and elastomeric blocks, it possesses both toughness and elasticity. The electrical conductivity curve vs. volume percent of carbon fibers in the SES-CF_m composites prepared by both emulsion and solution methods are presented in Figure 3. The average electrical conductivities of the composites based on both methods are close. This implies that both methods can achieve similar carbon fiber distributions for the SES-CF_m systems.

The stress/strain curves of the composites SES-CF_m-a to SES-CF_m-e based on the emulsion method are ploted in Figure 4(a) and those based on the solution method in Figure 4(b). One can note that (i) the curves in (a) have a sharp yield point, whereas those in (b) exhibit below 14 wt % fibers a rather smooth transition to the ductile region and a less sharp yield point above 14%; (ii) the samples in (b) can be much less elongated than those in (a), particularly, the samples with high volume percent of CF_m; and (iii) the tensile strength is reinforced by small amounts of fiber after which it decreases for both kinds of samples with increasing content of carbon fibers. The main difference between the mechanical properties of samples (a) and (b) consists in the glassy thermoplastic–elastomeric behavior in the former case and the elastomeric behavior in the latter one for fiber contents below 14 wt %. This behavior is a result of the processing method. Indeed, since SES is a block copolymer, there are two kinds of microphases that correspond to polystyrene and poly(ethylene/butylene) blocks, respectively. When the SES–toluene solution is dispersed into a surfactant aqueous solution to form a concentrated emulsion, the polystyrene microphase, which is more polar than the poly(ethylene/butylene) microphase, will tend to accumulate at the water–polymer interface. Since the polystyrene phase

Table VI Comparison of the Theoretical Conductivity (σ_{max}) with the Largest Experimental Values in Each Series of Composites

Composites	ϕ_{CF} (%)	σ_{max} (S/cm)	$\sigma_{exp}/\sigma_{max}$ (%)	Tensile Strength (MPa)	Elongation (%)
SES–CF_m-e	34.3	48.5	65.2	1.8	18
SBS–CF_m-d	25.8	36.5	44.7	29.3	15
EPE–CF_m-d	25.8	36.5	82.2	34.5	14
EVA–CF_m-d	25.8	36.5	52.3	36.5	6

Table VII   Comparison of the Theoretical Conductivity σ_{max} with the Next to the Largest Experimental Conductivity in Each Series of Composites

Composites	ϕ_{CF} (%)	σ_{max} (S/cm)	$\sigma_{exp}/\sigma_{max}$ (%)	Tensile Strength (MPa)	Elongation (%)
SES-CF$_m$-d	25.8	36.5	37.2	13.4	215
SBS-CF$_m$-c	14.8	20.9	23.9	17.1	775
EPE-CF$_m$-c	14.8	20.9	44.9	10.6	584

surrounds the poly(ethylene/butylene) phase, the finally obtained polymer will have a glassy thermoplastic behavior in the initial range of deformations. This explains why, when concentrated emulsions are employed, the glassy thermoplastic behavior is more noticeable.

There is a difference between the behavior of the composites based on EVA and SES. In the former, the emulsion procedure generates materials with a more uniform conductivity. In contrast, for the latter, the emulsion and solution procedures provide comparable conductivities. Although, as already noted, it is likely that the carbon fibers are more uniformly distributed in the emulsion-based composites, this effect is more prominent in the EVA composites than in the SES-based composites. This is probably because EVA generates in toluene a physically cross-linked network of a gel. The concentrated emulsion cuts this gel in small droplets with fibers located among the droplets. During precipitation, the polymers deposit on the fibers located in the vicinity of the droplets. In the solution procedure, the deposition process is not restricted to small regions and nonuniformities in precipitation can more easily occur.

Effects of the Length of Carbon Fiber and of the Nature of the Polymer on the Electrical Conductivity and Mechanical Properties of the Carbon Fiber–Polymer Composites

When short carbon fibers (CF$_s$) have been used, the electrical conductivities of the composites (Table IV) acquired values as low as those obtained when mixing colloidal size carbon black particles with thermoplastics[10,11] even for wt % near 50. In addition, as for the carbon black, the mechanical properties of the polymers were damaged by the introduction of CF$_s$ into the polymers. The short carbon fibers have a behavior similar to that of carbon black[12] concerning both the electrical conductivity and the mechanical properties, even though the ratio between the length of the fiber to its diameter is

relatively large ($\sim$ 10) and the diameters for the fiber and carbon black are about 10 and 0.1 μm, respectively.

The medium carbon fibers (with average length L = 5 mm and diameter D = 10 μm) were found to be effective in generating relatively high electrical conductivities as well as in reinforcing the mechanical properties of the composites for not too large fiber contents (Table V). From Table V one can see that composites containing the same percent of carbon fibers but different polymers can have very different conductivities. This has probably its origin in the hot-pressing process, since at the same hot-pressing temperature (150°C), each polymer has a specific rheological behavior, which affects the motions of the fibers inside the polymer, leading to different conductive networks.

The maximum conductivity (σ_{max}) of a composite containing randomly oriented fibers can be calculated using the expression[13]

$$\sigma_{max} = (2/3\pi) \cdot \phi_{CF}\sigma_{CF}$$

where ϕ_{CF} and σ_{CF} are the volume fraction and the conductivity of the carbon fibers, respectively. The ratio of the experimental value of the electrical conductivity σ_{exp} to σ_{max}, using σ_{CF} = 666 S/cm (Ref. 7), is given in Table VI. The composites listed in this table provide the highest electrical conductivity in each of their series, but their mechanical properties are not always adequate. However, one can find (see Table VII) polymer composites that have good mechanical property with somewhat lower electrical conductivities.

CONCLUSION

Rubberlike polymer–carbon fiber composites were prepared by both a concentrated emulsion and a solution processing. In the former, a concentrated

emulsion containing a solution of a polymer in toluene as dispersed phase and an aqueous solution of sodium dodecylsulfate as the continuous phase was mixed with carbon fibers, and a polymer–carbon fiber composite was precipitated by introducing methanol into the system. In the latter processing, a polymer–toluene solution was directly mixed with carbon fibers, and the next steps were the same as in the emulsion method. The composites were hot-pressed to obtain sample sheets. The effects of these two methodologies on the electrical conductivity and mechanical properties of the composites were investigated by changing the type of polymer, the size of the carbon fibers, the volume fraction of the carbon fibers in the composites, and the hot-pressing temperature. The main conclusions are as follows:

1. In the concentrated emulsion, the polymer solution is divided into micrometer-size regions. This methodology is suitable for polymers with strong internal interactions among the polymer chains, like EVA, because the agglomeration of the contracted polymer coils can be restricted during precipitation to small regions.

2. The presence of the surfactant molecules at the fiber–matrix interface when the composite is prepared via the concentrated emulsion enhances the adhesion between them.

3. The morphology of SES (styrene–ethylene/butylene–styrene) triblock copolymer–fiber composites can be controlled such as to have glassy thermoplastic blocks surrounding elastomeric blocks when its toluene solution is dispersed into an aqueous surfactant solution. After precipitation in methanol and hot pressing, the glassy thermoplastic blocks constitute the continuous phase and are responsible for the glassy thermoplastic behavior in the initial range of deformations.

4. When the average length of carbon fiber increases from 0.1 to 5 mm, the electrical con-

ductivity of the composites increases by two orders of magnitude from about 2×10^{-1} to 3×10 S/cm.

5. Composites that have electrical conductivities in the range of 5–14 $(\Omega \ cm)^{-1}$ and good mechanical properties with a tensile strength in the range of 10–17 MPa and an elongation at the break point larger than 200% were prepared.

REFERENCES

1. N. C. Billingtram and P. D. Calvert, *Adv. Polym. Sci.*, **90**, 1 (1989).
2. J. Delmonte, *Metal/Polymer Composites*, Van Nostrand Reinhold, New York, 1989, p. 77.
3. E. Galli, *Plast. Compound.*, **March/April**, 22 (1982).
4. J.-B. Donnet and A. Voet, *Carbon Black*, Marcel Dekker, Inc. New York, 1976.
5. M. Guigon, *J. Mater. Sci.*, **27**, 4591 (1992).
6. B. Wessling, *Kunststoffe Ger. Plast.*, **76**(10), 69 (1986); E. N. Dannenberg, L. Paquin, and H. Gwinnell, in *Encyclopedia of Chemical Technology*, 4th ed., J. I. Kroschwitz and M. Howe-Grant, Eds., Wiley, New York, 1991, Vol. 4, p. 1063.
7. P. B. Jana, S. K. De, S. Chaudhuri, and A. K. Pal, *Rubber Chem. Tech.*, **65**, 7 (1991).
8. E. Ruckenstein and K. J. Kim, *J. Appl. Polym. Sci.*, **36**, 907 (1988).
9. E. Ruckenstein, G. Ebert, and G. Platz, *J. Colloid. Interface Sci.*, **133**, 432 (1989).
10. A. I. Medalia, *Rubber Chem. Technol.*, **59**, 432 (1986).
11. P. Kathirgamanathan, in *High Value Polymers*, A. H. Fawcett, Ed., Redwood Press, Melksham, Wiltshire, 1991.
12. G. Kraus, in *Chemistry and Technology of Rubber*, A. Vidal and J. B. Donnet, Eds., Applied Polymer Symposia 39, Wiley, New York, 1984, p. 75.
13. A. R. Blythe, *Electrical Properties of Polymers*, Cambridge University Press, 1980, p. 126.