Mechanical and Rheological Properties of Poly(ethylene-*co*-ethyl acrylate) as a Function of Carbon Black Content

Jean-François Feller, Isabelle Linossier*

Polymers & Process Laboratory, South-Brittany University, Rue de Saint-Maudé, 56 325 Lorient, France

Summary: Carbon black (CB) filled poly(ethylene-co-ethyl acrylate) (EEA-CB) is used as conductive phase in conductive polymer composites (CPC). Electrical conductivity of CPC obtained from blends of immiscible polymers results from CB particles localization within the material, which depends on composition and processing conditions. It is particularly important to control viscosity of such systems as this parameter determines both the phase morphology and conductive pathway structure. The small scale, at which CB particle aggregation/dispersion phenomena occur within CPC, makes direct observations difficult. But the effect of carbon black particles/polymers interactions is clearly visible by means of rheological measurements.
A strong reinforcing effect of CB on CPC in both solid and liquid states has been noticed. This phenomenon has been analyzed using classical models as a function of temperature and CB content. The results confirm the necessity of CPC rheology control especially during the process to achieve good reproducibility of electrical properties.

Summary: carbon black; conductive polymer composites; mechanical properties; poly(ethylene-co-ethyl acrylate); rheology

Introduction

Electrically conductive polymer composites (CPC) are obtained by blending insulating polymers with conductive fillers like carbon black, carbon fibers or metal particles. CPC found several application fields such as shielding, switching or heating. The latter takes advantage of CPC self-limiting heating ability for conducting particles above the percolation threshold. This property is based on the so called PTC effect (positive temperature coefficient) which is a conductor-to-insulator transition generally observed as the temperature reaches the melting zone of the polymer in which the conducting particles are dispersed. In CPC, current circulation is obtained through percolation of particles aggregated in conducting pathways. Because the

 DOI: 10.1002/masy.200351335

particles disconnection is the intrinsic mechanism behind the PTC effect, any process that modifies interparticle distance distribution will also affect resistivity of the composite. From this point of view, it is generally accepted that thermal expansion,[1-2] morphology,[3-5] filler characteristics[3,6] and processing conditions[1][7-8] are important factors influencing CPC conductivity. More recently, the use of immiscible polymer blends have brought interesting answers, allowing a decrease in the percolation threshold[3-4,9-10] and an increase in thermal stability. It is particularly important to control viscosity of such systems, as this parameter determines both phase morphology and conductive pathway structure. Viscosity is sensitive to temperature and shear rate during the process[11] but also to carbon black content. CB particles, by their tendency to aggregate and their ability to interact with polymer chains, modify the main characteristics of the CPC.

Therefore, the present study is focused on the influence of carbon black particles on mechanical and rheological properties of a polymer used as CB vector in diphasic CPC, poly(ethylene-co-ethyl-acrylate) (EEA).

Experimental

Materials

Carbon black filled poly(ethylene-co-ethyl acrylate) (EEA-CB) is LE 7704 from Borealis. Main characteristics are listed in Table 1.

Table 1. Polymer characteristics.

	EEA
Alkyl acrylate content w/w	15
T_g (°C) glass transition temperature	- 33±3
T_m (°C) melting temperature	99.5
$T_{c,n}$ (°C) non isothermal crystallization temperature	83
ΔH_m (J.g^{-1}) melting enthalpy	63
MFI (dg.min^{-1}) melt flow index	6.9±0.1

Sample Preparation

EEA/CB blends were obtained by dilution of EEA-CB (37% w/w CB master batch) with EEA in a twin-screw Brabender extruder (L= 400 mm, ϕ= 16 mm) with the following temperature profile (from first zone to die): 220/240/250/260 °C.

Characterization

Rheological properties of polymers were obtained with a ThermoHaake RheoStress 1 rheometer with both cone/plate geometry in steady state conditions and plate/plate geometry in dynamic mode. Capillary rheometry measurements were made during extrusion with instrumented dies of different length/diameter ratio (L/ϕ=15, 20, 30).

Dynamic mechanical analysis was proceeded on a T.A. Instruments 2980 DMA with a simple cantilever accessory, a frequency of 1 Hz, and an amplitude of 10 μm.

Results and Discussion

Rheological measurements are often used to determine polymer behavior under different types of mechanical solicitations, either steady or dynamic. Their sensitivity to any parameter that affects macromolecules motion is valuable to determine interaction phenomena between chains or particles. This is why we have used these techniques to study the behavior modifications of EEA in both liquid and solid states as a function of carbon black content.

Flow Properties

Flow properties have been studied by cone/plate rheometry in steady mode with shear rates from 0.01 and 50 s^{-1} and in capillary rheometry with shear rates from 100 to 5000 s^{-1}. Data from both techniques where combined to obtain viscosity evolution on a wide range of shear rates after usual corrections of Bagley and Rabinovitch. Several blends of 0, 5, 18.5, 23.13, 27.75, 31.31 and 35 % w/w of carbon black have been studied. For heating applications, it is necessary to work with carbon black contents somewhat above the percolation threshold (close to 18% w/w, 0.1 v/v, in this system) to obtain the desired level of conductivity. The fact that above 10% w/w of CB, the Newtonian plateau usually observed at low shear rates is absent shows the necessity of viscosity measurement and control. For highly CB filled samples, viscosity increases roughly with decreasing shear rates revealing that strong interactions between CB aggregates occur to form a structured network. Flow curves of all blends have been superposed and the relative viscosity η/η_0 has been plotted versus carbon black content for three different representative shear rates (0.1, 5 and 500 s^{-1}). Experimental points have been fitted with Maron & Pierce[12] model (Eq. 1) which is derived from the Einstein model for suspensions.

$$\frac{\eta}{\eta_0} = \frac{1}{\left[1 - \frac{\phi}{\phi_m}\right]^2} \qquad (1)$$

η is the viscosity of EEA-CB, η_0 is the viscosity of EEA ϕ_m is the maximum packing fraction.

Several comments can be made on the results presented in Fig. 1. First, the reinforcing effect of CB is much more important at 0.1 s^{-1} than at 500 s^{-1}; second, the Maron & Pierce model describes quite well this phenomenon in the hole shear rate range and fitting experimental data provides interesting values of ϕ_m, the maximal packing fraction that can be interpreted in terms of particle anisotropy. As reported in Table 2, an increase in ϕ_m from 0.21 to 0.55 with increasing shear rate corresponds to a decrease in the aspect ratio *L/D* of CB aggregates. This result is consistent with the fact that at low shear rates aggregates structure can become more important and that, on the other hand, high shear rate destroys aggregates giving them a more spheroid shape.

Table 2. Relations between ϕ_m/*L/D*[12] and ϕ_m/shear rate (present study).

L/D	ϕ_m	$\dot{\gamma}$ (s^{-1})	ϕ_m
30	0.173	0.1	0.21
16	0.303	5	0.29
8	0.476	500	0.55

From Fig. 1 it is also clear that the Einstein model, $\eta/\eta_0 = 1+2.5\phi_m$, is not adequate for describing the viscosity increase for increasing fillers content at least at low shear rates or for particles which tend to aggregate. Moreover, in the processing conditions of CPC by extrusion, $0.1<\phi<0.17$ and $1<\dot{\gamma}<15$ s^{-1}, the composite viscosity can be 4 to 8 times that of the polymer.

Dynamic Mechanical Properties

Curves of storage and loss modulus (respectively *E'* and *E"*) evolution with temperature have been plotted for different carbon black contents and superposed. Analysis of the plateau modulus at 34 °C and 135 °C allows obtaining the curves of Fig. 2 and Fig. 3 in which the relative modulus has been plotted versus CB fraction. As expected, *E'*(34 °C), the storage modulus increases rapidly with CB content. Less obviously E''(34 °C), the loss modulus and surprisingly E'(135 °C) and E''(135 °C) have same tendency. This means that CB increases the mater cohesion in both solid and liquid state and also increases energy dissipation. More precisely, a plateau appears only in E'(135 °C) and E''(135 °C) curves for the CB content above 0.05 v/v which is consistent with the end of Newtonian behavior observed in flow curves. Data have been interpreted using the Guth & Gold model[13-15] according to Eq.

$$E = E_0\left(1 + a\phi + b\phi^2\right) \qquad (2)$$

with E_0 the modulus of the matrix without CB and ϕ the CB volume fraction.

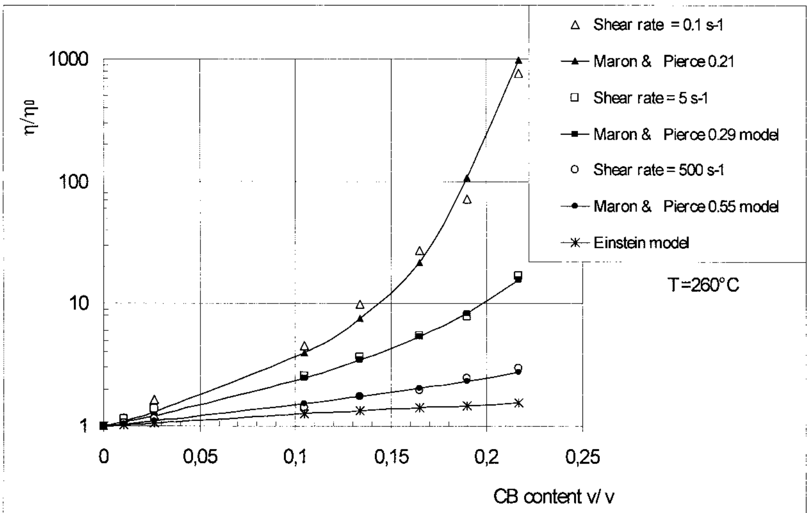

Fig. 1. Relative viscosity (η/η_0) increase of EEA-CB as a function of CB content v/v at 260°C.

In this model, for spherical reinforcing particles, a=2.5 and b=14.1 whereas for rod-like particles, $a=c.f$ with c=0.67 and $b=d.f^2$ with d=1.62. ϕ is the filler volume content and f is an adjustable parameter called aspect ratio. Assuming that particles can interact and form elongated aggregates, we have fitted experimental data with the previous model taking c=0.67. For both E'/E_0 and E''/E_0 at 35 °C, the results are presented in Table 3; d values are rather different from the predicted one (1.62) which shows that the model underestimates the reinforcement behaviour. Thus, it is necessary to find another formulation, which takes into account molecular interactions and complex shapes the aggregates may have. Moreover, it is also clear from Fig. 2 that this phenomenon is temperature-dependent and cannot be described by the Guth & Gold model at high temperatures. In fact, the increase in modulus at 134 °C as a function of the CB content, follows an exponential law instead of a second-order polynomial law.

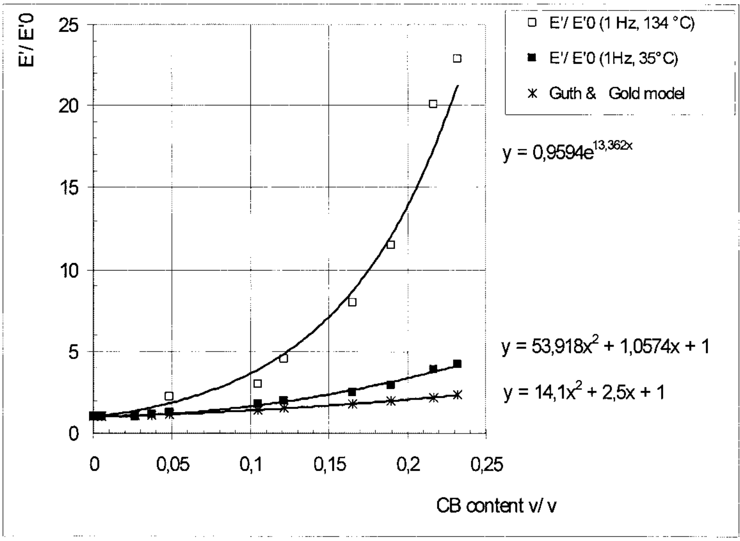

Fig. 2. Relative storage modulus of EEA-CB, E'/E'_0 as a function of CB content v/v for 35 °C and 134 °C (f = 1Hz).

Table 3. *a, b, c, d* and *f* coefficients of Eq. 2.

	a	*b*	*c*	*d*	*f*
Guth & Gold model	2.5	14.1	-	-	-
E' (35 °C)	1.06	53.92	0.670	21.59	1.58
E" (35 °C)	4.44	13.43	0.670	0.3064	6.62

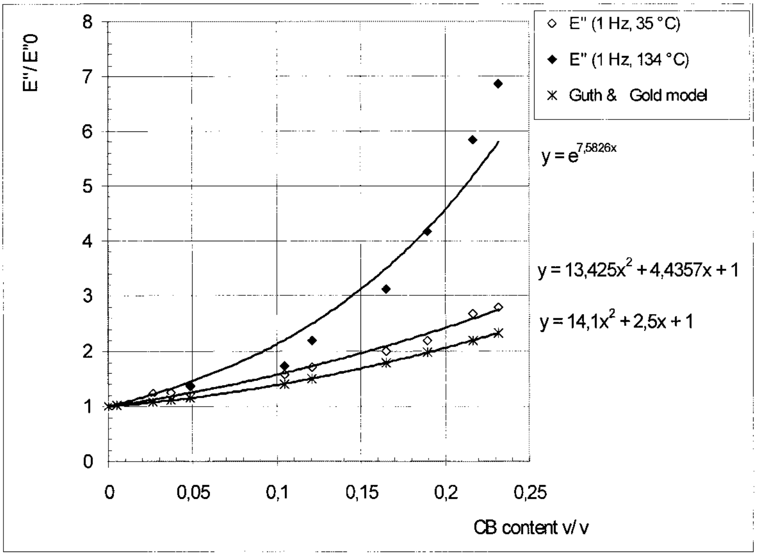

Fig. 3. Relative loss modulus E''/E''_0 of EEA-CB as a function of CB content v/v for 35 and 134 °C (f = 1Hz).

Conclusion

Evolution of viscosity and modulus of carbon black (CB) filled poly(ethylene-co-ethyl-acrylate) (EEA-CB) has been studied as a function of the CB content. In the melt, we have noticed that the Newtonian plateau of flow curves disappears above 10% w/w CB and that the reinforcing effect of CB is much more important at 0.1 s^{-1} than at 500 s^{-1}. Moreover, the Maron & Pierce model describes quite well the viscosity increase in the whole shear rate range and fitting experimental data provides interesting values of ϕ_m the maximal packing fraction that can be interpreted in terms of particle anisotropy. Analyzing the evolution of plateau moduli at 34 °C and 135 °C obtained by dynamic mechanical measurements, reveals interesting features of the reinforcement behavior. As expected, E'(34 °C), the storage modulus increases rapidly with the CB content. Less obviously E''(34 °C), the loss modulus and surprisingly E'(135 °C) and E''(135 °C) have the same tendency. Interpreting data using the Guth & Gold model shows that the reinforcement is underestimated especially at high temperatures. This means that CB increases the matter cohesion in both solid and liquid state and also increases energy dissipation.

Acknowledgements

The authors thank F. Auffret, S. Catoire and H. Béllégou for their contribution to this work. This project was supported by the French Ministry of Research & Technology.

[1] X. S. Yi, G. Wu, D. Ma, *J. Appl. Polym. Sci.*,**1998**, 67, 131.
[2] M. B. Heaney, *Physica A*, **1997**, 241, 296.
[3] F. Gubbels, R. Jérôme, P. Teyssié, E. Vanlathem, R. Deltour, A. Calderone, V. Parenté, J. L. Brédas, *Macromolecules*, **1994**, 27, 1972.
[4] J. C. Lee, T. Hikehara, T. Nishi, *J. Appl. Polym. Sci.*, **1998**, 69, 193.
[5] M. A. Knackstedt, A. P. Roberts, *Macromolecules*, **1996**, 29, 1369.
[6] Y. Luo, G. Wang, B. Zhang, Z. Zhang, *Eur. Polym. J.*, **1998**, 34, 8, 1221.
[7] K. Cheah, M. Forsyth, G. P. Simon, *J. Polym. Sci., Part B*, **2000**, 38, 23, 3106.
[8] M. Narkis, A. V. Tobolsky, *J. Appl. Polym. Sci.*, **1969**, 13, 2257.
[9] O. Breuer, R. Tchoudakov, M. Narkis, A. Siegmann, *Polym. Eng. Sci.*, **2000**, 40, 4, 1015.
[10] C. Lagrève, J. F. Feller, I. Linossier, G. Levesque, *Polym. Eng. Sci.*, **2001**, 41, 7, 1124.
[11] J. F. Feller, I. Linossier, A. Charpentier, *18th International Congress of the Polymer Processing Society,* June 22-26, **2002**, Guimarez.
[12] L. P. Fox, *Carbon Black Polymer Composites*, **1982**, 6, 163, E. K. Sichel Ed., Marcel Dekker, New-York.
[13] S. Wolff, M. J. Wang, *Carbon Black Sci. & Technology*, **1993**, 9, 289-355, J. B. Donnet, R. C. Bansal, M. J. Wang Ed., Marcel Dekker, New York.
[14] S. S. Hamza, *Mater. Lett.*, **1997**, 30, 1 53.
[15] L. Flandin, A. Hiltner, E. Baer, *Polymer*, **2001**, 42, 827.