Effects of Bamboo Charcoal on the Electrical and Rheological Properties of Ethylene Vinyl Acetate Copolymer

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Introduction

Bamboo is one of the world's best known natural engineering materials and perhaps it is also one of the most under-utilized natural resources available abundantly in Southeast Asian countries. Recently, Bamboo and other natural fibers from renewable resources such as pineapple, banana, henequen, sisal, jute, wood and saw dust, coconut (coir), rice husk, and wheat straw are being extensively studied as reinforcing agents in different polymer matrices. Bamboo fiber is the most promising way. Up to now, only mechanical, thermal, and morphological properties of the bamboo reinforced polymer composites have been studied. However, its utilization has not been fully explored. In fact, bamboo charcoal, obtained by pyrolysis of bamboo, gives new properties (prevention from electromagnetic wave, adsorbent, highly caloric fuel, healthcare) [1]. Our work aims to show the effect of bamboo charcoal on the electrical conductivity and rheological properties of ethylene vinyl acetate copolymer.

Experimental

Materials

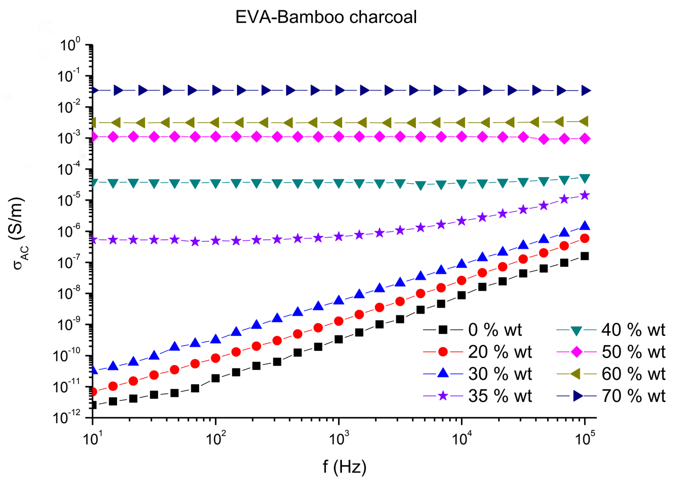
Ethylene Vinyl Acetate :
EVA 2803 (Arkema Evatane ®) containing 28% wt of vinyl acetate
ρ = 0.95 g.cm^{-3}
Melt Flow Index = 3 g/10 min

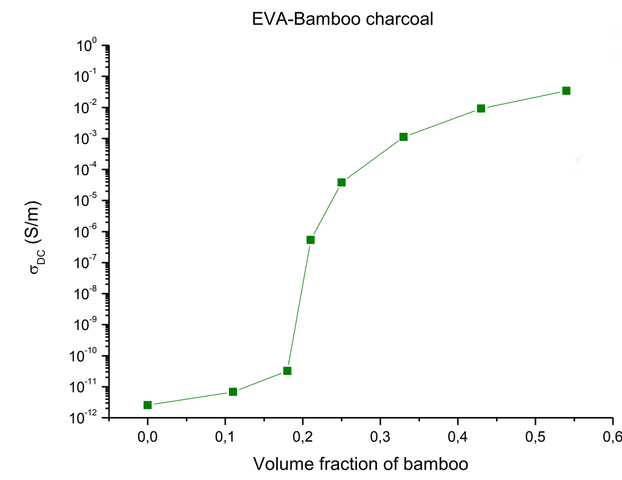
Bamboo charcoal :
Supplied by Bamboo Fibers Technology (Lahonton, France)
ρ = 1.9 g.cm^{-3}
Bulk conductivity = 11 S/m

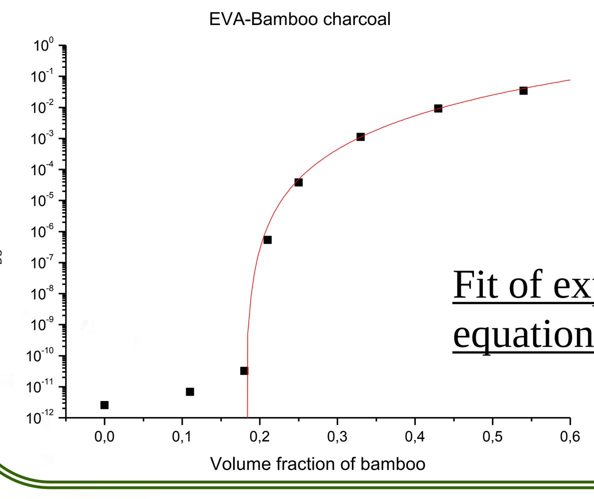
Measurements

The different composites were prepared by dry mix process at 120°C in an internal batch mixer (Haake Rheomix 600) to obtain 20, 30, 35, 40, 50, 60 and 70 %wt of bamboo charcoal containing composites.
The composite's composition was determined by Thermogravimetric analysis from TA Instrument (TGA Q500).
The ac-conductivity of different composites was performed using a TA Instruments DEA 2970 Dielectric Analyzer.
The complex shear modulus (storage modulus G' and loss modulus G") were measured using an AR2000 Rheometer from TA Instruments.
The fillers particles distribution in the EVA matrix was studied by scanning electron microscopy (SEM), HITACHI S800 (HITACHI Corp.).
Mastersizer 2000 was used for measuring the particle size distribution.

Electrical Properties







↑ Φ_{filler} ➔ Conductive filler network formation
At Φc, an abrupt increase of the composite's conductivity is observed.
Φc ➔ insulator-conductor transition
Φc = Electrical percolation threshold

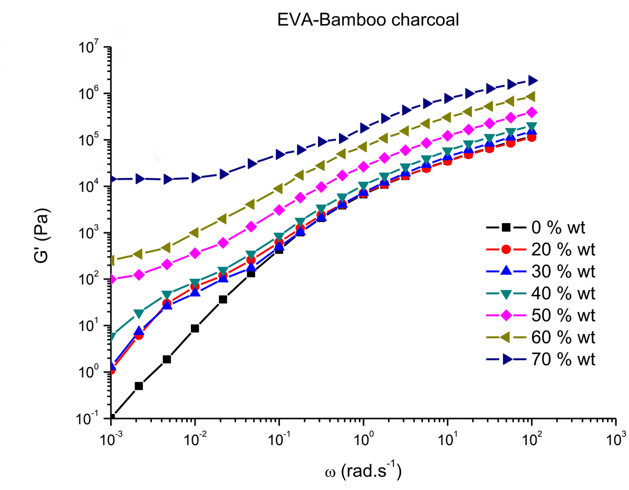
Fit of experimental data with scaling equation for $\Phi \geq \Phi c$:

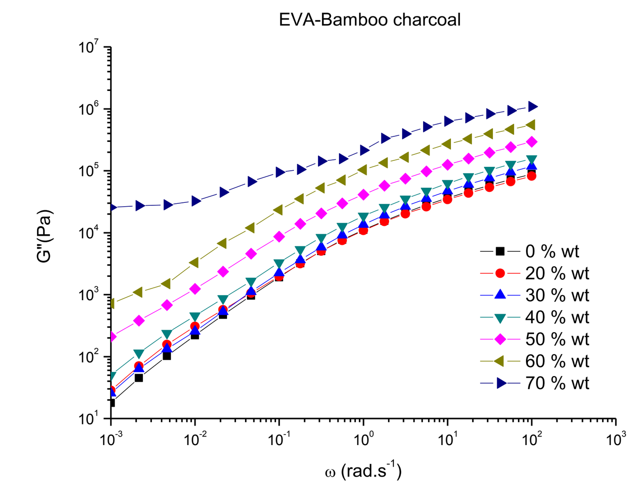
$$\sigma_{dc} \propto (\Phi - \Phi_C)^t$$

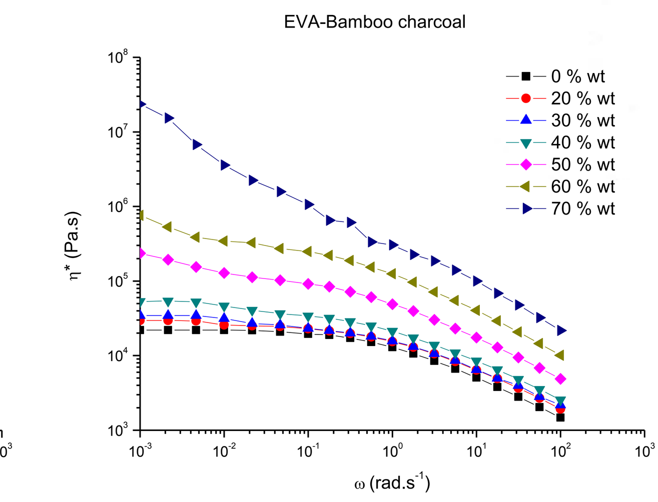
Φc = 18 %v ± 1 %

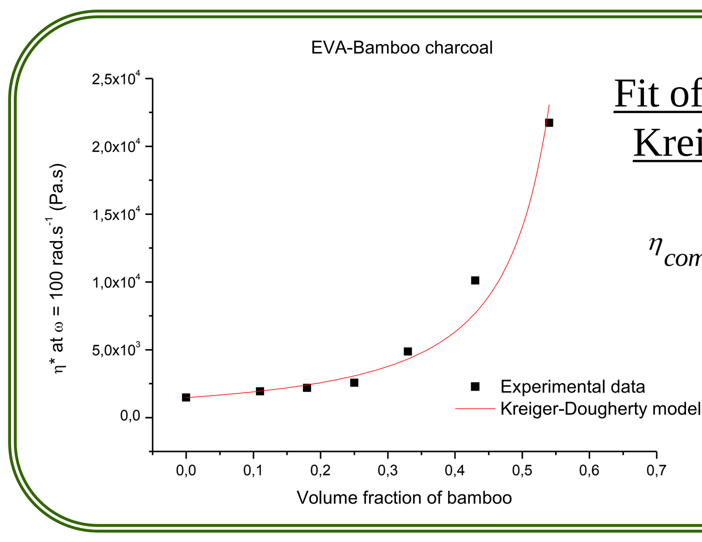
t = 4.1 ± 0.2 ➔ heterogeneous filler's distribution

Rheological Properties









Fit of experimental data with Kreiger-Dougherty model:

$$\eta_{composite} = \eta_{matrix}\left[1 - \frac{\Phi}{\Phi m}\right]^{-[\eta]\Phi m}$$

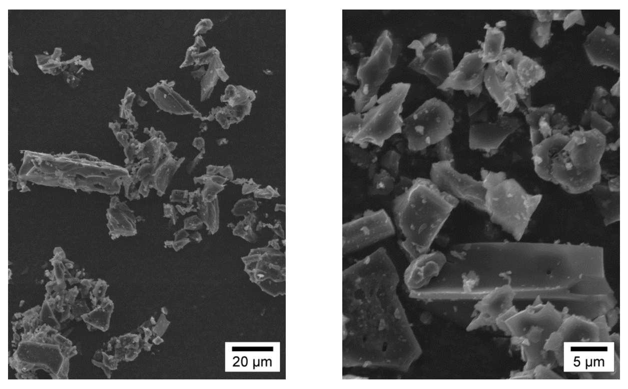
Φm = 0.64 ± 0.05
[η] = 2.32 ± 0.37

↑ Φ_{filler} ➔ Filler network formation
At Φc, the composite melt behaves solid-like rather than liquid-like
Φc ➔ liquid-solid transition
Φc = Rheological percolation threshold

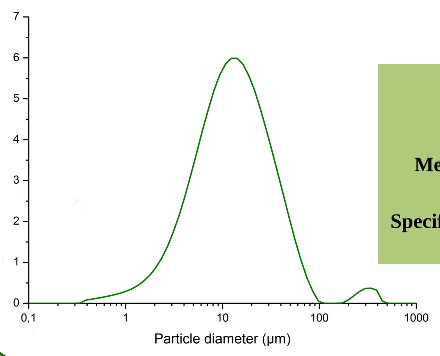
$\Phi c \approx$ 33 %v

Morphology of Filler and Composites

Bamboo charcoal

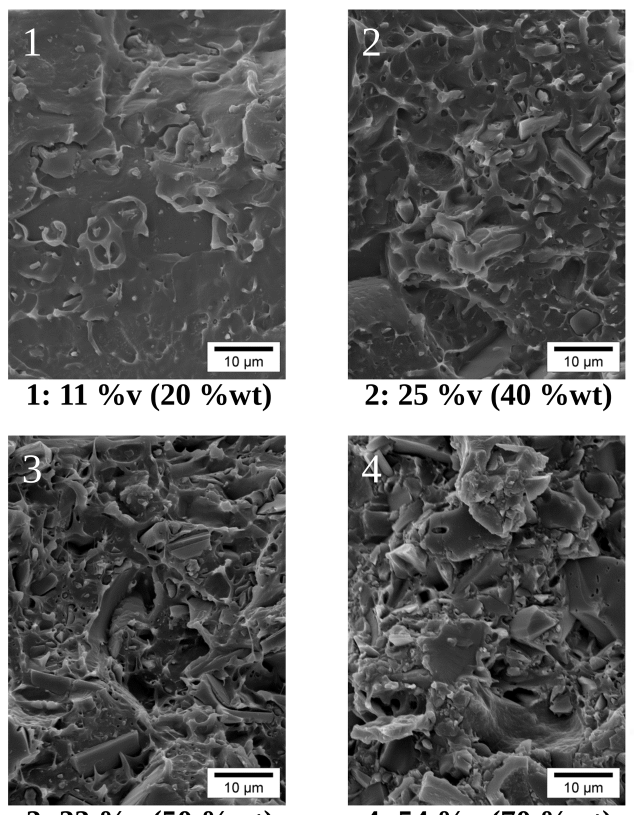


Granulometric analysis of bamboo charcoal



d_{10} (µm)	3,6
d_{50} (µm)	12,7
d_{90} (µm)	39,6
Mean diameter (µm)	21,8
Specific surface area (m²/g)	0,82

EVA-Bamboo charcoal composites



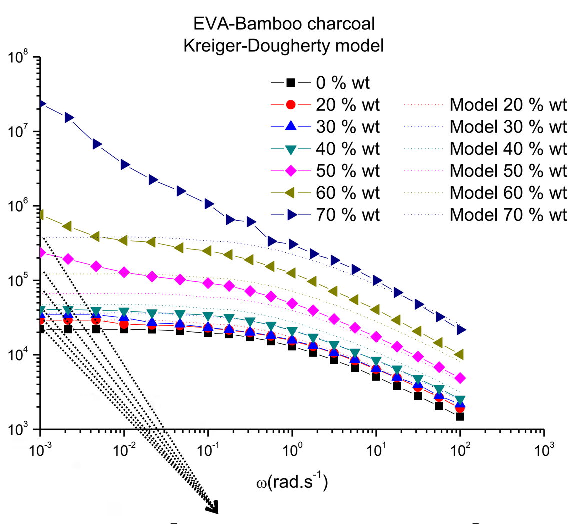
1: 11 %v (20 %wt)
2: 25 %v (40 %wt)
3: 33 %v (50 %wt)
4: 54 %v (70 %wt)

Rheological Models [2]

Kreiger-Dougherty

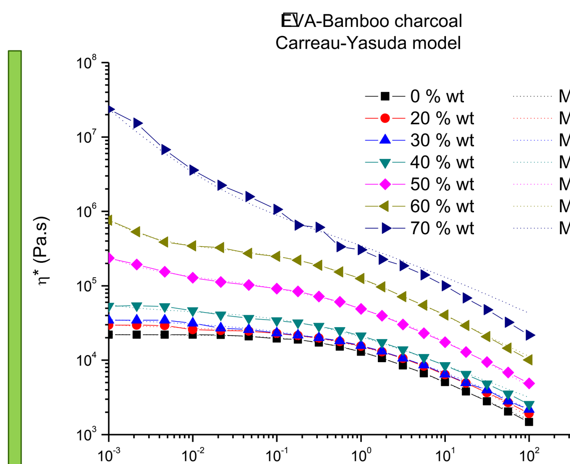
$$\eta_{composite} = \eta_{matrix}\left[1 - \frac{\Phi}{\Phi m}\right]^{-[\eta]\Phi m}$$

Φm = 0.64 ± 0.05
[η] = 2.32 ± 0.37



η_0 according Kreiger-Dougherty

Carreau-Yasuda

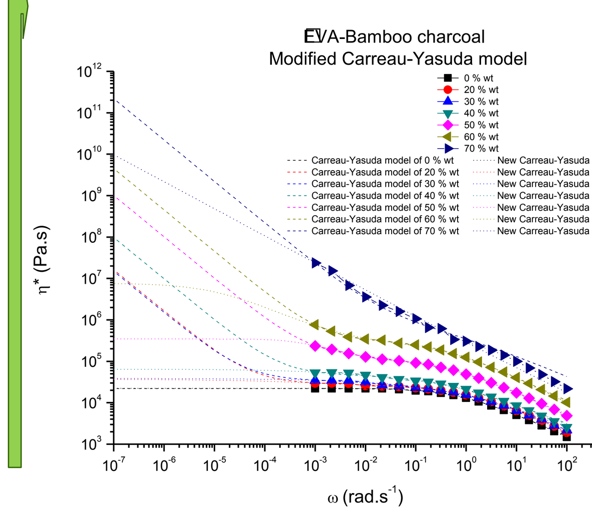


$$\eta^*(\omega) = \frac{\sigma_0}{\omega} + \eta_0\left[1 + (\lambda\omega)^a\right]^{\frac{n-1}{a}}$$

σ_0 is the yield stress.
η_0 is found with the Kreiger-Dougherty's fitting.

%wt of bamboo	0 % wt	20 % wt	30 % wt	40 % wt	50 % wt	60 % wt	70 % wt
σ_0 (Pa)	0,00	1,62	1,49	9,82	101	453	22012
η_0 (Pa.s)	2,20E+04	2,93E+04	3,65E+04	4,70E+04	1,53E+05	3,13E+05	3,00E+06
λ (s)	1,60	0,16	0,29	3,72	0,57	3,71	2,06
a	0,92	0,47	0,39	0,67	0,41	0,83	0,23
n	0,48	0,14	0,29	0,55	0,21	0,44	0,34

Modified Carreau-Yasuda



$$\eta^*(\omega) = \eta_0\left[1 + (\lambda\omega)^a\right]^{\frac{n-1}{a}} + \eta'_0\left[1 + (\lambda'\omega)^a\right]^{\frac{n-1}{a}}$$

Lack of yield stress σ_0

%wt of bamboo	0 % wt	20 % wt	30 % wt	40 % wt	50 % wt	60 % wt	70 % wt
η_0 (Pa.s)	2,20E+04	2,93E+04	3,65E+04	4,70E+04	7,65E+04	2,53E+05	1,44E+06
λ (s)	1,37	0,09	0,36	0,74	2,58	1,92	4,85
a	0,85	0,44	0,36	0,45	1,50	0,76	0,15
n	0,46	0,05	0,35	0,39	0,50	0,38	0,34
η_0' (Pa.s)	318	7439	2127	17700	2,69E+05	7,39E+06	1,41E+17
λ' (s)	9,02	771,70	0,23	173	2415	78825	5,79E+17

Conclusion

Percolation limits mainly depend on the filler's characteristics such as size, shape and aspect ratio. SEM and granulometric analysis showed that bamboo charcoal presents a rectangular shape with low specific surface area. Electrical percolation threshold was obtained at around 0.2 volume fraction while the limit of the electrical conductivity after percolation was observed around 3 x 10^{-2} S/m. In rheology, it is more difficult to define the percolation threshold. Some people define it like the volume fraction of filler when the zero shear viscosity tends to infinity. Another hypothesis suggests that when a yield stress is observed in Carreau-Yasuda's model. In our system, this appears before that the zero shear viscosity tends to infinity. By convention, the three-dimensional filler network formation defined as rheological percolation appears at around 0.3 volume fraction of bamboo charcoal. However, for lower volume fraction, some interactions already exists between filler particles and matrix, which slightly modified the rheological properties at low frequency. Finally, in this work, electrical percolation occurs before rheological percolation. This phenomenon is due to the filler-filler distance required to induce electron transfer in the first case and stress transfer in the latter [3]. Thus, bamboo charcoal confers high electrical properties to polymer matrix without inducing strong changes in its viscolelasticity properties.

References:
1. G. Mingjie, Manual for bamboo charcoal production and utilization, 2004.
2. P. Cassagnau, Melt rheology of organoclay and fumed silica nanocomposites, Polymer, 2008. 49(9): p. 2183-2196.
3. S. Huang, et al., Dynamic Electrical and Rheological Percolation in Isotactic Poly(propylene)/Carbon Black Composites. Macromolecular Materials and Engineering, 2012. 297(1): p. 51-59.

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