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Influence of Morphology on PTC in Conducting Polypropylene-Silver Composites

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Summary: Blends of polypropylene with silver particles of controlled morphology are performed to elaborate polymer-metal conductive composites which can present a PTC effect to be used for a specific current limited function. The samples present quite low percolation threshold around 22% in volume of Ag and a resistivity at room temperature around 100 ohm.cm. Looking at the results of the analysis of the PTC effect, it can be observed that the electrical behaviour of the samples is depending of the crystalline morphology of the systems which is governed by the specific nucleation effect of the silver filler on the polypropylene matrix.

Keywords: conductive composite; metal filler; percolation; PTC effect; thermoplastic

Introduction

The study of conductive polymer composites is of large interest considering their industrial applications.[1–3] Such materials consist of a thermoplastic or thermosetting matrix filled with fillers such as metals[1,2], carbon[3–5] or intrinsically conductive polymers.[6] A specific feature of such composites is the presence of a transition insulating/conductive state at the so-called percolation threshold.

One of the peculiar characteristics of the filled semi-crystalline polymers is the existence of the significant positive temperature coefficient of resistance (PTC) which has reversible character.[7–9] During last years the study of the PTC effect attracted the attention of researchers due to the perspectives of applications, namely in temperature sensors, thermistors, self-regulating heaters, disruptor devices etc.[9–15] The origin of the PTC effect is not definitively clear : it is assumed that the sharp increase of resistance with temperature is due to the volumic expansion of the thermoplastic matrix in the melting zone. The PTC effect depends on many factors : nature, size, shape and hardness of fillers, [10,14,16–18] volume fraction in the composite[19,20] chemical nature and viscosity of the polymer matrix,[18] polymer-filler interactions.[21,22]

In this field the objective of our research is the better understanding of the parameters which control this electric transition. We have chosen to elaborate specific conductive polymer composites by using metallic filler[23]. For this, blends of polypropylene PP with silver particles (Ag) were performed and the paper focus on the influence of the morphology of the propylene matrix on the PTC effect. The key point is the nucleating effect of the metallic filler which has to be controlled to monitor the electrical properties of such composites.

Experimental Section

Materials

The composites under study were prepared by mixing spheric silver particles quite monodisperse (DC 100 (Engelhard) with an average diameter about 1 micron) with polypropylene PPg2 (Exxon Mobil

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Chemical) with MFI 2g/10 min which is a commercial polypropylene without any other specification from the producer to which is added in this work 10% by weight microcrystalline talcum (S.A. Talc de Luzenac) of 1 μm to modify the nucleation of polypropylene.[24] Talcum was added to PPg2 in extruder before to introduce silver filler.

Processing

Different processing machines were used as batch mixer Haake Rheocord, Scamia calander or DSM micro 15 Twin-Screw compounder. Blends of PPg2 and Ag particles were proceeded in batch mixer or in the twin-screw extruder at $T = 473$ K with 50 rpm rotation speed in the two cases. The filler is added slowly during 7 mn then still mixed about 5mn then the blends were pressed as a 1 millimeter thick foil after the batch mixer procedure or were under 3 millimeter diameter extrudate form before granulation. The mixtures obtained with calander were performed at $T = 448$ K by a 10 mn long addition of the filler in the melted matrix between the 2 cylinders. 5 mn blending was additionally done to insure a good homogenization. The blends were first pressed as a 1millimeter thick foil before granulation.

It was noticed that the process of blending with the twin screw extruder was easier and leads to the more homogeneous composites.

Observation of the Morphology

In situ analysis of the cristallization during cooling was observed in polarized light of Leitz Orthoplan optical microscope equipped with an Mettler heating plate under the same conditions of cooling, preparing samples for electrical analysis.

Scanning electron microscopy (SEM) was performed with a Hitachi S-800 at 15 kV microscope in order to visualize the morphology of the samples prepared by cryogenic fracture and gold plated.

Electrical Analysis

The samples for electrical analysis were 22 mm thick and 24.5 mm in diameter. They were obtained from the prepared granules melted between two types of electrodes to optimize the contact of the material under test. So two aluminium plates or two stainless steel grids 150 microns thick and 200 microns net sized were used. The procedure was to heat the mold at 463 K, first slowly per 5 mn step then under a pressure of 300 bars during 5 mn. The samples were then cooled under pressure 3 bars. Voltage source Keithley 237 was used to perform the automatic electrical measurement in a Polymer Laboratories cell during thermal cycles with an heating (3K/min) and cooling rate (5 K and 30 K/min).

It was verify that the samples present an ohmic behavior in the range of applied voltage to perform the measurements.

Thermal and Dilatometric Analysis

DSC measurements were performed with TA 2920 modulated analyzer to determine the crystallinity degree as well as the temperature of crystallization of the materials. PVT "Pression-Volume-Temperature" analysis were performed on a PVT100-SWO-Polymertechnik GmbH to register the specific volume changes during controlled thermal cycle under 200, 500 and 800 bars pressure of the melted polymer. The samples are first melted 2 mn under 200 bars at $Tmax = 503$ K to arise the thermal history of the samples then they are cooled down at 20 K/mn at $T = 323$ K and then heated up to Tmax under the pressure values indicated previously.

Results and Discussion

Different composites were prepared with different contents of filler in volume to establish the classical percolation curves of the dc conductivity versus volumetric fraction of the filler. Generally the percolation threshold depends of the natures of polymer and filler used as well as of the type of blending. Samples prepared with polypropylene and silver present more or less aggregated filler with a quite low percola-

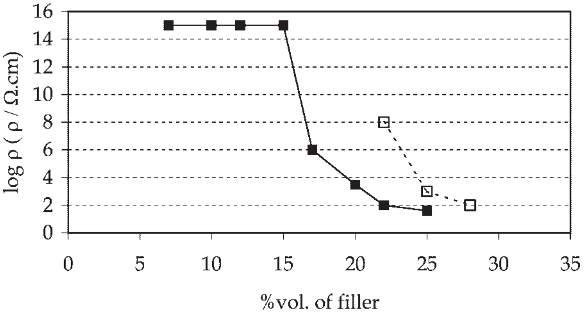

Figure 1.
Influence of the tool of processing on the percolation threshold of composites filled with 1 μm Ag particles. (■) PPg2 calander, (□) PPg2 mini extruder.

tion thresholds about 16% volumetric fraction of conductive filler in the case of a calander processing but around 22% with a twin-screw one as shown in Figure 1. Such higher percolation threshold is due to the fact that the dispersion of the metallic filler is better in this case, which is confirmed by optical analysis. The resistivity at room temperature is around 100 Ω̃cm whatever the type of blending PPg2-Ag systems.

Looking at the results of the analysis of the PTC effect, it can be observed in Figure 2 that electrical behavior of the composites is different. The PPg2–25% Ag composite does not present any clear conductive-resistive transition contrary to the other conductive composite based on PPg2 + 10%w.talcum + 25% Ag which presents a relevant variation of resistivity of height decades and the commutation temperature at about 418 K.

As PPg2 + 10%w.talcum + 25% Ag composite has been proceeded in the same way that PPg2 + 25% Ag composite and as MEB studies of these samples indicate the same state of dispersion of the filler, the difference observed in their electrical behavior can be supposed to be due to the role of nucleating agent and consequently of the size of the superstructure.

It was necessary at this level of the study to characterize the thermal properties, the morphology, as well as the volumetric expansion of the matrices which governs the PTC effect. First, specific investigations of the nucleation of the matrix were performed by in situ observation under microscope to evidence the size of the crystalline entities developed in the PPg2 matrix and by DSC to characterize the crystallinity ratio and the crystallization temperature of the system. Crystallization analysis of the PPg2 matrix pure or with 0.05% of Ag particles under optical microscope is presented in Figure 3. It is shown that the number of the spherulites of the PPg2 without or in presence of Ag particles is quite different. The nucleation of polypropylene matrix starts in part on the silver acting as nucleating agent and giving a finer morphology. Additionally some silver particles are isolated inside the spherulites of polypropylene matrix during the crystallization and consequently are not contributing to the conductive paths.

When talcum is added to the polypropylene matrix, the (PPg2 + 10%talcum + 25% Ag) composite can crystallize from the nucleating agent present in the polymer and the nucleation from the silver filler is consequently limited contrary to what happened in the polypropylene matrix of the (PPg2 + 25% Ag) composite. As a direct consequence, (PPg2 + 10%talcum + 25% Ag) shows in Figure 2b a sharp and reproducible electrical behavior.

DSC thermograms of four systems were registered during the first heating of the samples after they were molded and are presented in Figure 4. The heating rate was 3 °C/mn like the one performed for the electrical measurements. The temperature

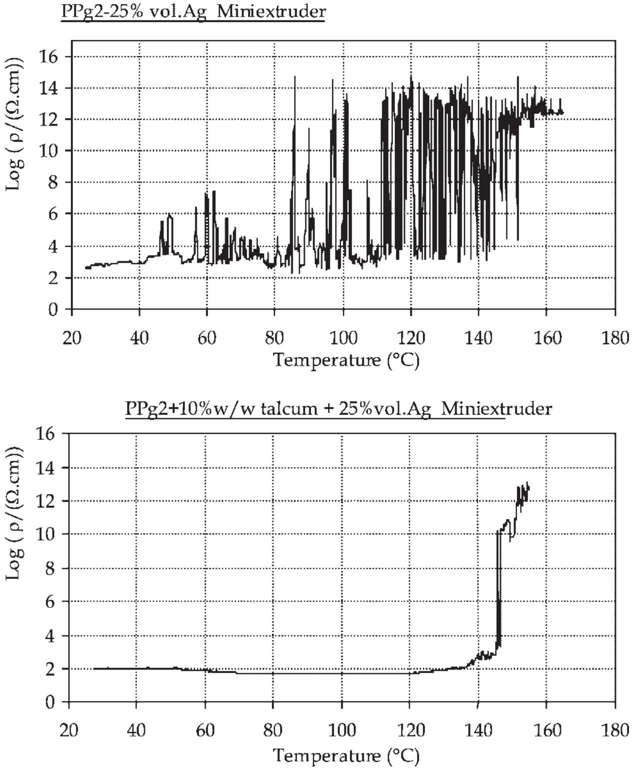

Figure 2.
PTC effect in different conductive composites based on Ag and Polypropylene matrices (PPg2 + 25%Ag, PPg2 + 10%w.talcum + 25%Ag).

of the beginning of the melting corresponds very well to the temperature of commutation observed for the PTC. Then it is not observed a huge difference in the temperature of the melting peak of the different materials : only 4–5 degrees of shift in the case of (PPg2 + 25%Ag) or with (PPg2 + 10%talcum + 25%Ag) samples. It is only

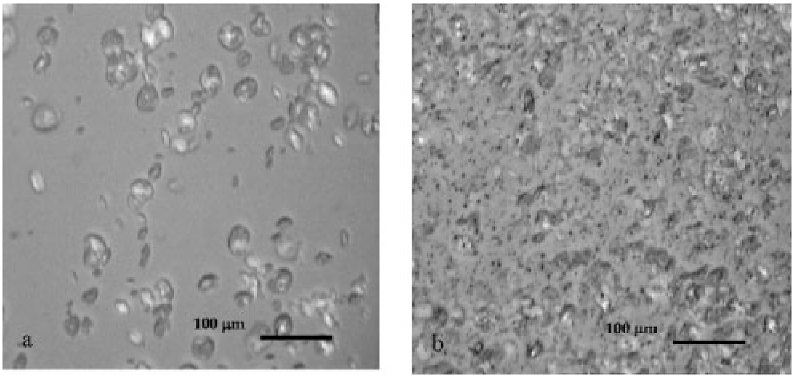

Figure 3.
Optical microscopy images of : a) PPg2 pure and b) PPg2–0.05% Ag.

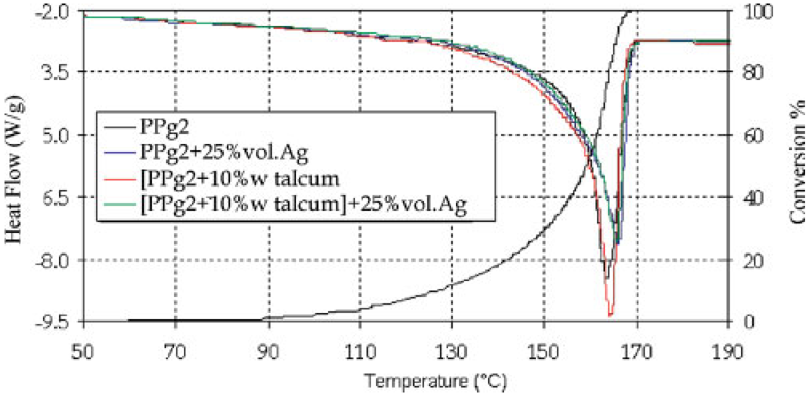

Figure 4.
DSC Thermogram of extruded samples listed in order of increasing temperature of their melting peak : samples based on pure PPg2, PPg2 filled with talcum, PPG2 filled with silver and PPg2 filled with talcum and Ag. Heating rate 3 °C/min.

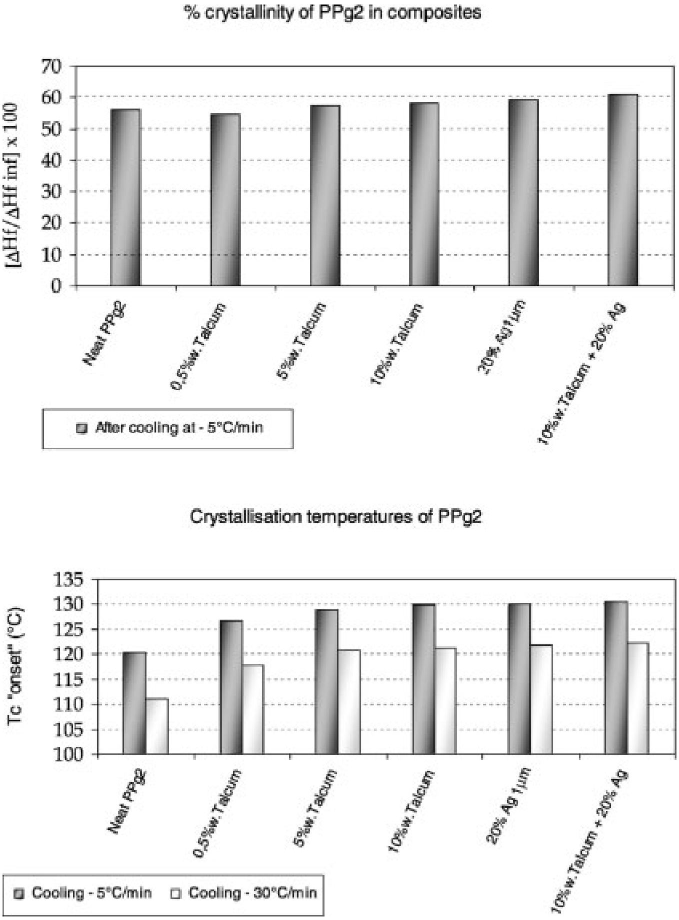

Figure 5.
Values of crystallinity ratio and crystallization temperatures for neat PPg2 matrix filled with 0.5, 5, 10% talcum, filled with 20% Ag and with 10% talcum + 20% Ag.

possible to say that silver seems to promote spherulites with thicker lamellae.

Crystallinity ratio calculated from the thermograms and crystallization temperatures are presented in Figure 5. It is no significant change in the value of the degree of crystallinity which is about 55%, what ever is introduced 0,5, 5 and 10% talcum or 20% Ag or 10%talcum + 20%Ag. On the contrary, it is observed the increase of the crystallization temperature Tc up to 1OK in accordance with the effect of nucleating agent (talcum or Ag or both talcum + Ag). In this last case, when the polypropylene has the possibility to nucleate first on the talcum, it nearly does not nucleate on Ag particles as the Tc is not changing any more. It means in other terms that the silver does not act anymore as a nucleating agent of the polypropylene PPg2 when the10% talcum is added.

As this composite presents a PTC effect it has to be concluded that the nucleating effect is the major point of control of the electrical properties in polypropylene. It is worth to notice that in parallel to the present study on polypropylene based conductive composites, the same work has been performed in polyethylene matrix for which the PTC behavior was always observed[25] whatever the type of processing, the size and the nature of filler. Possible explanation of such difference is to notice that polyethylene crystallization is not influenced by silver contrary to polypropylene. The two polyolefines have different behavior regarding the crystallization in presence of the metallic filler.

It is to conclude that the increase of the crystallization temperature in the case of polypropylene matrices in presence of nucleating agent (talcum or silver or both) is a proof of the Ag contra productive effect during the crystallization to get PTC behavior as seen in Figure 2 and as studied in PE filled in the same way with silver filler too.

The second factor which can govern the PTC transition is the variation of the volumetric expansion coefficient in the melting domain.[27] As shown in Figure 6, PVT analysis of the different polypropylene matrix PPg2 pure, with talcum and with Ag present the same expansion behavior with the same amplitude which therefore confirms also that the global crystallinity is independent of the formulation. Again such result cannot explain the difference of PTC behavior in these different systems and confirms that the hypothesis formulated about the importance of the crystallization effect to control the morphology.

The different analysis presented in this work underline that the quality of dispersion of the filler, the value of the heating peak, the degree of crystallinity and the volumetric expansion coefficient behavior do not explain the huge difference in the PTC behavior of the different blends of silver based composites. It has been evi-

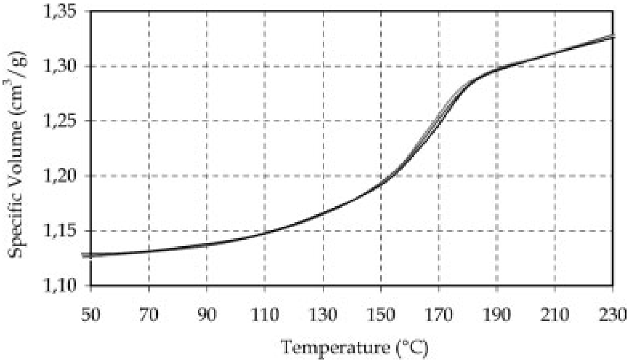

Figure 6.
PVT diagrams under 200 bars of the different polypropylene matrix (PPg2, PPg2 + 25%Ag, PPg2 + 10%w. talcum, PPg2 + 10%w. talcum + 25%Ag) processed with mini extruder.

denced that it is the nucleation effect of the silver which governs the crystalline morphology and finally is the main control parameter of the PTC effect. By using a classical nucleating agent as talcum added to the PPg2 matrix with silver, it is possible to decrease the nucleating capacity of the silver particles, hence avoiding their individual insulation and thus promoted a well reproducible PTC effect.

Conclusion

The present study of the PTC effect in conductive polypropylene-silver composites is unique and very interesting as it has allowed to explain the quite negative results obtained at the beginning of the work. It was not in the literature any serious work on the effects of the crystallization and of the crystalline morphology in the metal filled composites as the filler limits the optical microscopy analysis. The rare publications[28–30] dealing with the influence of the filler on the morphology of the matrix concern only carbon black which is said to have no effect on specific thermoplastic matrix.

The presence of silver filler influences the morphology of the PP matrix acting as a nucleating agent, losing its capacity to create the conductive paths inside the matrix. It is a very important point to control the crystallization of the matrix to understand the different PTC behavior of such conductive composites which is not only dependant of the filler dispersion but also of the size of the crystalline superstructure.

If the elaboration of such extrinsic conductive material is well controlled, they can exhibit the Positive Temperature Coefficient (PTC) effect upon heating, it means very strong resistivity ‘‘jump’’ at the so-called commutation temperature Tc at 413 K. Such adaptative or so-called smart materials can be used as an efficient disruptor due to 8 decades increase of the resistivity under heating. Further paper will present the results of the phD study[26] on PPg2 or its blends with copolymers based on polyamides filled with iron filler instead of silver.

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[1] S. K. Bhattacharya, ‘‘*Metal-Filled Polymers (Properties and Applications)*’’, Marcel Dekker ed, New-York, Basel 1986.

[2] J. Delmonte, ‘‘*Metal/Polymer Composites*’’, Van Nostrant Reinhold ed., New York 1990.

[3] E. K. Sichel, ‘‘*Carbon black-polymer composites, The physics of electrically conducting composites*’’, Marcel Dekker ed., New-York, Basel 1982.

[4] J.C. Huang, *Advances in Polymer Technology* **2002**, *21*, 299.

[5] M. Narkis, J. Yacubowicz, A. Vaxman, A. Marmur, *Polym. Eng. Sci.* **1986**, *26*, 139–143.

[6] R. B. Seymour, ‘‘*Conductive Polymers*’’, Polymer Science and Technology Volume *15*, Plenum Press ed., New York, 1981.

[7] J. E. Martin, M.B. Heaney, *Phys. Rev.* **2000**, *B 62*, 9390.

[8] I. Mironi-Harpaz, M. Narkis, *Polym. Eng. Sci.* **2001**, *41*, 205.

[9] R. Strumpler, *J. Appl. Phys.* **1996**, *80*, 6091.

[10] R. Strumpler, J. Glatz-Reichenbach, *J. Electroceramics* **1999**, *3*, 329.

[11] X-W. Zhang, Y. Pan, Q. Zheng, X-S. Yi, *J. Appl. Polym. Sci.* **2000**, *78*, 424.

[12] S. Srivastava, R. Tchoudakov, M. Narkis, *Polym. Eng. Sci.* **2000**, *40*, 1522.

[13] M. Narkis, S. Srivastava, R. Tchoudakov, O. Breuer, *Synth. Metals* **2000**, *113*, 29.

[14] W. Wenyuan, L. Bingzhi, S. Yunzhi, *Radiat. Phys. Chem.* **1995**, *46*, 1015.

[15] J.F. Feller, D. Langevin, S. Marais, *Synth. Metals* **2004**, *144*, 1, 81.

[16] H. Bar, M. Narkis, G. Boiteux, *Polymer Composites* 2005, 12.

[17] G. Boiteux, J. Fournier, D. Issotier, G. Seytre, G. Marichy, *Synth. Metals* **1999**, *102*, 1234.

[18] A. Maaroufi, K. Haboubi, A. El Amarti, F. Carmona, *J. Mater. Sci.* **2004**, *39*, 265.

[19] F. Carmona, C. Mouney, *J. Mater. Sci.* **1992**, *27*, 1322.

[20] C-M. Chan, C-L. Cheng, M. M. F. Yuen, *Polym. Eng. Sci.* **1997**, *37*, 1127.

[21] G. Yu, M. Q. Zhang, H. M. Zeng, Y.H. Hou, H.B. Zhang, *J. Appl. Polym. Sci.* **1999**, *73*, 489.

[22] S. J. Park, H-C. Kim, H-Y. Kim, *J. Colloid Interf. Sci.* **2002**, *255*, 145.

[23] Mamunya , Y. P., Muzychenko , Y. V., Pissis , P., Lebedev , E. V. and Shut , M. I.*J. of Macromol. Sci., Part B Physics.* **2001**, *B40*, (3 & 4) pp.591.

[24] E. Ferrage, F. Martin, A. Boudet, S. Petit, G. Fourty, F. Jouffret, P. Micoud, P. De Parseval, S. Salvi, C. Bourgerette, J. Ferret, Y. Saint-Gerard, S. Buratto, J.P. Fortune, *Journal of Materials Science*. **2002**, *37*, 1561.
[25] Ye.P. Mamunya, Yu. Muzychenko, P. Pissis, E.V. Lebedev, M.I. Shut, *Polym. Eng. Sci.* **2002**, *42*, 90.
[26] C. Boullanger, phD thesis of University Claude Bernard Lyon1, n°212 2004, 26 November **2004**.
[27] Fulchiron , R., Koscher , E., Poutot , G., Delaunay , D. and Régnier , G. ''Analysis of the pressure effect on the crystallization kinetics of polypropylene : dilatometric measurements and thermal gradient modeling''. *J. of Macromol. Sci., Part B Physics*. **2001**, *B40* (3&4), p.297.
[28] T. M. Wu, J.C. Cheng, M.C. Yan, *Polymer* **2003**, *44*, 2553
[29] J. C. Lee, T. Ikehara, T. Nishi, *Journal of Appl. Polym. Sci.* **1998**, *69*, 193
[30] J. C. Lee, K. Nakajima, T. Ikehara, T. Nishi, *J. of Appl. Polym. Sci.* **1997**, *64* (4), 797.