Conductive Polymer Composites (CPC): Influence of Processing Conditions, Shear Rate and Temperature on Electrical Properties of Poly(butylene terephthalate)/ poly(amide12-b-tetramethyleneglycol) - Carbon Black Blends

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Summary: Conductive Polymer Composites (CPC) have been obtained by blending two immiscible polymers, poly(butylene terephthalate) (PBT) and poly(amide12-b-tetramethyleneglycol) (PEBAX) with carbon black (CB). The extrusion process allows to obtain anisotrope co-continuous structures of various morphologies depending on composition and experimental conditions. It is possible to enhance CPC conductivity with appropriate processing temperature (T_p) and screw speed (Ω), without changing the composition of the blend. The best results are obtained with Ω =5 rpm and T_p=260°C. PBT/PEBAX-CB resistivity evolution with T_p and Ω doesn't follow a linear law as expected from previous studies with poly(butylene terephthalate)/poly(ethylene)-CB and poly(butylene terephthalate)/poly(ethylene-co-ethyl acrylate)-CB systems. CB distribution has a more important impact on conductivity than polymers phase morphology. A good control of these parameters is essential to reproduce and optimize electrical properties.

Keywords: blends; carbon black; conductive polymer composites; electrical properties; processing conditions; shear rate

Introduction

Blends of poly(butylene terephthalate)/poly(amide12-b-tetramethyleneglycol)-carbon black (PBT/PEBAX-CB) lead to conductive polymer composites (CPC) with smart properties for heating applications. CB is initially dispersed in PEBAX to constitute the conductive phase whereas PBT provides the system with both thermal stability and mechanical properties. Although the positive temperature coefficient (PTC) is lowered by PBT thermal expansion, no negative temperature coefficient (NTC) can be observed up to 220°C, temperature over which PBT begins to melt. To guaranty the reproducibility of electrical properties of such materials, it is necessary to control every influential parameter. The influence of processing conditions,

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temperature and shear rate, on both morphology and carbon black distribution has already been shown.[1,2] In most works reported in literature, electrical properties of CPC are measured from samples prepared by mixer and compression molded, i.-e., rarely close to industrial processing conditions as extrusion or injection.[4,5] It is therefore difficult to find unique interpretation of the influence of processing temperature, shear rate and blending time which depend widely on the considered techniques and polymer systems. Nevertheless, it seems that for monophase systems, increasing mixing time or mixing speed increases resistivity of the CPC as a result of a better conducting particles dispersion.[4,6-7] For multiphase systems, the previous parameters can lead to the opposite behavior, the migration of conducting particles to the interface between the two polymers leading to a decreases of resistivity.[8-9] The effect of an increase of blending temperature is generally to favor particle agglomeration in the melt and to decrease resistivity as also evidenced with isothermal electrical measurements.[10]

In this work we have studied the resistivity evolution of extruded blends of PBT/PEBAX-CB with temperature as a function of different processing conditions and analyzed the results as a function of morphologies and carbon black distribution.

Experimental

Materials

Poly(butylene terephtalate) (PBT) is VESTODUR® 3000 from DEGUSSA-HUELS, carbon black poly(amide12-b-tetramethyleneglycol) (PEBAX-CB) is from ATOFINA. Main polymer thermal charactéristics can be found in Table 1.

Table 1. Polymers characteristics.

	PBT	PEBAX
T_g (°C)	50±3	-75/-40
T_m(°C)	225±3	165
$T_{c,n}$(°C)	185	145
ΔH_m($J.g^{-1}$)	140	16,7
Melt Flow Index ($dg.min^{-1}$)	7.7	-

Samples Preparation

PBT was blended with PEBAX-CB in a single screw FAIREX extruder ($L = 600$ mm , $\Phi = 30$ mm) with three temperature profiles: 220/240/240/240°C, 240/260/260/260°C, 260/280/280/280°C, corresponding to processing temperature of respectively 240, 260 and 280°C. All polymers were dried for 24 hours at 90°C under vacuum before processing. We used 2x10x70 mm^3 samples for electrical measurements. In this study only one CPC as been used, a blend of 60 % w/w PBT / 40% w/w PEBAX (initially containing 40% w/w of carbon black).

Characterization

Electrical resistivity was measured by a four-probe technique described in a previous work.[11] All samples for analysis were cut from extruded tapes. Cycles are applied in loops to the samples (heating from 30°C to 220°C at 0.6 °C.min^{-1} and cooling from 220°C to 30°C at 0.6 °C.min^{-1}). In order to get rid of PEBAX cristalline phase and PBT amorphous phase thermomechanical history, only the second heating/cooling cycles were used.

Morphologies were observed with a JEOL JSM-6031 scanning electron microscope (S.E.M.) after fracture of the samples in liquid nitrogen followed by extraction of PEBAX phase by DMSO for 12 hours in a KUMAGAWA. The etched surfaces were then coated under vacuum by a thin gold layer.

Results and Discussion

In CPC with conductive particles content over the percolation threshold, a more or less sharp conductor to insulator transition is sometimes observed, called PTC (positive temperature coefficient) effect. This non-linear evolution of resistivity with temperature corresponds to the disconnection of carbon black particles due to the polymer matrix expansion. Many parameters can influence PTC effect characteristics, among which crystallinity, thermal expansion coefficient, reticulation and composition, as already discussed in a previous work,[11] but its exact origin is not yet fully understood especially for multiphase systems. PTC effect amplitude corresponds to the resistivity difference between room temperature and end of PTC transition and it can be seen on Fig. 1, that the curves are not necessarily surperimposable during heating and cooling. In fact, the conduction phenomena are different during crystallization and melting of PEBAX which explains the observed hystheresis. Thus the right part of the curves corresponds to heating and the left part to cooling.

Influence of Processing Temperature on Resistivity

Curves of Fig. 1 show the evolution of resistivity with temperature for several processing temperatures. For a screw speed of Ω = 25 rpm, increasing processing temperature from 240°C to 260°C decreases resistivity. The decrease in resistivity is about 0.3 decade for an increase of processing temperature of 20°C, which is rather significant. The same behavior was observed for experiments realized with a screw speed of Ω = 50 rpm (Fig. 2). A resistivity decrease with increasing processing temperature was also observed in a previous work for PBT/poly(ethylene-co-ethyl acrylate)-CB (EEA-CB) and PBT/poly(ethylene)–CB (PE-CB) systems in similar experimental conditions.[1]

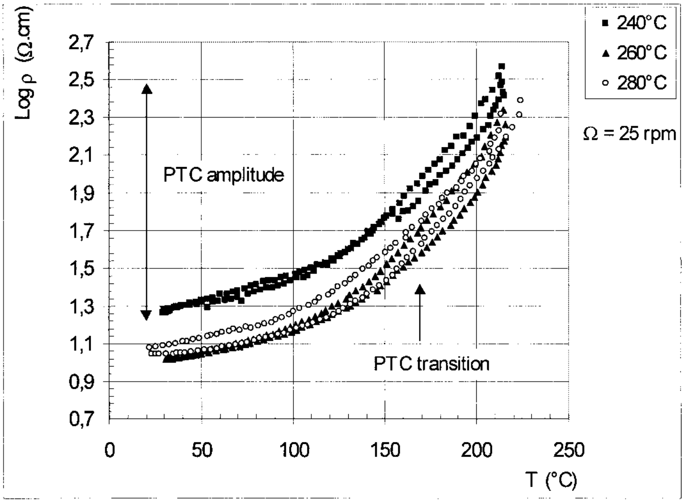

Fig. 1. Resistivity versus temperature as a function of processing temperature for a screw speed of Ω= 25 rpm.

This phenomenon was interpreted in terms of viscosity variations of the all polymers of the blend. A viscosity decrease in the conducting phase EEA (or PE) increasing carbon black mobility and aggregation at the interface, leading to conductivity increase. Moreover, PBT viscosity decrease makes possible EEA (or PE) channels shape modification, thus changing the CPC phase morphology. Nevertheless, for PBT/PEBAX-CB, the points surrounded by an ellipse in Fig. 2, corresponding to a processing temperature of 280°C for different screw speeds, diverge from the linear law represented by solid lines. This unexpected increase of resistivity can result from an increase of PEBAX viscosity due to partial cross-linking of macromolecules and/or degradation as also observed during rheological measurements.

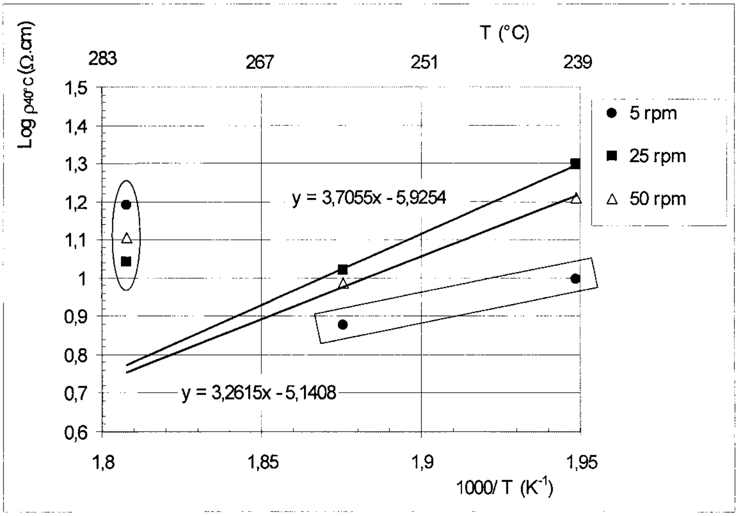

Fig. 2. ARRHENIUS plots of resistivity versus extrusion temperature and screw speed for PBT60/(PEBAX-40CB)40 (solid lines correspond to linear regressions y=a.x-b).

Influence of Screw Speed on Resistivity

From Fig. 2, it can be noticed that at 240°C and 260°C increasing screw speed from 25 to 50 rpm decreases room temperature resistivity. Like it was found for PBT/PE-CB and PBT/EEA-CB CPC, an increase of shear stress has a cumulative effect with an increase of processing temperature. The resulting resistivity decrease can be explained by a viscosity decrease favoring CB concentration at the interface. Nevertheless, this interpretation doesn't apply for $\Omega = 5$ rpm. In fact in Fig. 2, the points surrounded by a rectangle show that a conductivity enhancement can be achieved for very low screw speed. This suggests that more conductive structures can exist in PBT/PEBAX-CB that can be damaged by to important shear stress.

Morphology of Blends

As resistivity variations often come from changes in the conductive pathway characteristics, it is valuable to be able to display the CPC morphology as a function of processing conditions.

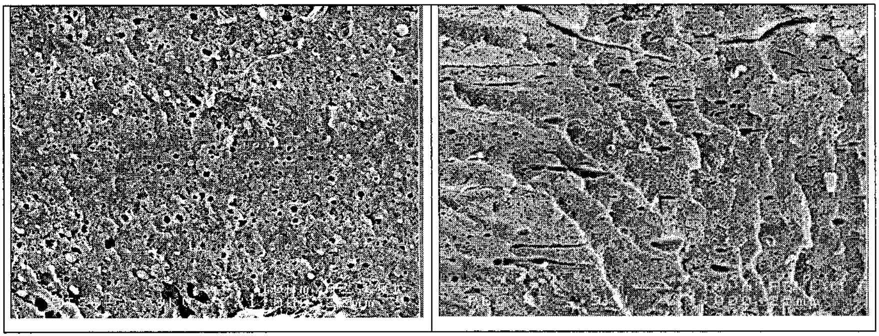

Fig. 3: S.E.M. pictures of PBT/PEBAX-CB, processing temperature $T_p = 260°C$.
a) Left : screw speed of Ω=5 rpm .b) Right : screw speed of Ω=50 rpm. (magnification x 1000).

S.E.M. pictures of Fig. 3 a) and b) represent respectively the morphologies of the CPC for low screw speed and high screw speed with a processing temperature of T_p=260°C. In Fig. 3 a), conductive channels have diameters comprised between 2 and 4μm and tubular shape. In Fig. 3 b), three populations of channels can be identified considering their diameter and shape: $0.5<\phi<1.5\mu m$ tubular, $2<\phi<6\mu m$ tubular and $\phi>10\mu m$ lamellar. These morphological differences could be pleaded to explain the electrical properties variations previously discussed, but it was also shown that for PBT/EEA-CB CPC, morphologies with EEA-CB lamellar shape channels were associated with higher conductivity CPC. This means, that the main parameter responsible for conductivity enhancement in diphasic CPC is not phase morphology. A more important contribution seams to be brought by CB concentration at the interface due to an aggregation process, which was also deduced from studies on the percolation threshold in a previous work.[11]

Conclusion

The investigation of electrical properties of PBT/PEBAX-CB blended by extrusion with different processing temperatures and screw speeds shows rather different features compared to other systems like PBT/PE-CB or PBT/EEA-CB. Increasing processing temperature and screw speed decreases CPC resistivity only for T_p=240 & 260°C and Ω=25 & 50 rpm. For T_p=280°C an increase of resistivity is observed probably due to PEBAX degradation and/or reticulation.

Surprisingly the better conductivity is achieved for Ω=5 rpm suggesting that PEBAX-CB can form high conductivity structures that may be destroyed by high shear rate. More than phase morphologies, carbon black distribution within the CPC appears to be the main parameter responsible for CPC electrical properties. These results evidence that the control of process parameters is essential to reproduce and optimize electrical properties.

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