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Effect of conducting fillers on the microstructure and electrical conductivity of thermoplastic polymer composites

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Summary

This paper reports on the synthesis and characterization (electrical, mechanical, thermal and dynamic mechanical) of electrically conducting polymer composites based on thermoplastic matrices (low density polyethylene (LDPE) and polypropylene (PP)) and two conducting fillers: iron particles (Fe) and carbon black (CB). The addition of Fe allows the easy incorporation of higher amounts of CB. Results suggest that the electrical and mechanical properties of these materials are improved by the presence of both fillers being necessary the addition of CB to achieve interesting values of conductivity. On the other hand, the crystalline structure of the polymer matrix is gradually reduced with the incorporation of both fillers but Fe by itself does not affect the geometry of growing crystals.

Introduction

Conducting polymer composites based on a polymer matrix and dispersed conducting particles are an interesting class of materials used in a wide variety of industrial applications such as antistatic media, corrosion resistant materials and bipolar plates for fuel cells [1-3]. The fillers (carbon black CB, graphite or metal particles) provide the bipolar plate with the electrical conductivity required to collect the current while the polymer gives them the mechanical resistance necessary for the assembly of the different elements. Thus, conducting filled polymer composites can offer a combination of inexpensive material and economical processing.

The composite electrical conductivity is generally characterized by its dependence on the filler fraction. At low filler loadings, the conductivity is very close to that of the pure polymer matrix; at some critical loading (percolation threshold) the conductivity increases several orders of magnitude due to the particles come in contact with each other and a continuous conductive network through the composite begins to form.

Most of the specialized literature focuses on composites containing a single filler, mainly CB due to its low cost, small particle size and capacity to form aggregates within the polymer matrix [4-6]. This last characteristic results in the formation of a continuous conducting network responsible for interesting conductivity values at low CB levels. Nevertheless, it is difficult to prepare composites with CB percentages higher than 35% by using conventional mixing and molding techniques. A method to overcome this problem consists of the incorporation of two conducting fillers [7,8].

This paper presents the results of conducting composites based on low density polyethylene (LDPE), polypropylene (PP) and a mixture of two conducting fillers: carbon black (CB) and iron particles (Fe) in different concentrations and with a total filler percentage up to 50%. The effect of mixing fillers and composite concentration on electrical conductivity, dynamic mechanical, mechanical and thermal properties is studied. The purpose is to discern if mixed fillers afford appreciable advantages over single fillers, specially about electrical conductivity and processing.

Experimental

Materials

Two different polymers were used as matrix materials. Low density polyethylene (LDPE) (Alcudia PE-017) with a melt flow index (190ºC, ISO1133) of 7 g/10min and polypropylene (PP) (Isplen PP-099 K2M) with a melt flow index (230ºC, ISO1133) of 55 g/10min both from Repsol Química. The conducting fillers used were carbon black (CB) Vulcan XC-72 supplied by Cabot India Ltd. with a particle diameter of 29 nm, aggregate density 1.8 g/cm^3, nitrogen absorption special surface area of 254 m^2/g and a platicizer absorption value DBP (dibutyl phtalate) of 188 mL/100g and iron particles (Fe) from Merck with a particle size of 10 μm. Both fillers were used as received.

Composite preparation

The samples were melt-mixed in a Haake Rheomix 600 at 115ºC for LDPE samples and 140ºC for PP composites, keeping the blend in the chamber for 15 minutes to ensure optimum dispersion of the components. Rotor speed was 90 rpm. Composite composition and nomenclature assigned are listed in Table I.

After the mixing process, test specimens were prepared using a Collin hydraulic press at 50 bar and 145ºC (LDPE systems) and 200ºC (PP systems).

Analysis methods

Mechanical experiments were performed at room temperature under standard conditions in an Instron 4301, using 0.5 kN and a crosshead speed of 50 mm/min. Five specimens were measured in each case. The tensile modulus E was determined from the slope of the initial part of the stress vs strain curve.

Differential Scanning Calorimetry (DSC) studies of the composites were carried out on a Mettler TA 4000 to characterize melting and non-isothermal crystallization behaviour. The samples were heated at 10ºC/min from room temperature to 125ºC for LDPE systems and to 180ºC for PP systems and kept for 5 minutes to eliminate thermal history. Then the samples were cooled to room temperature at different cooling rates 2, 5, 10 and 20ºC/min. Non-isothermal crystallization data were analyzed using Avrami's equation.

Table 1. Composite compositions, electrical conductivity and Young modulus

SAMPLE	LDPE wt (%)	PP wt (%)	Fe/CB wt (%)	total filler wt (%)	σ ($S\cdot cm^{-1}$)	E (MPa)
LDPE	100	-	0/0	0	$1.29\cdot10^{-8}$	178.9
LDPE-30	70	-	30/0	30	0.03	235.8
LDPE-40	60	-	20/20	40	0.10	415.4
LDPE-50	50	-	10/40	50	1.39	812.0
PP	-	100	0/0	0	$1.60\cdot10^{-8}$	1648.3
PP-30	-	70	30/0	30	0.06	1659.9
PP-40	-	60	20/20	40	0.60	2577.8
PP-50	-	50	10/40	50	4.43	---

Dynamic Mechanical Analysis (DMA) was performed with a Mettler DMA 861-e analyzer. Samples were measured in the tensile mode at a deformation frequency of 1 Hz, from -75ºC to 115ºC. The heating rate used was 3ºC/min.

Conductivity measurements were carried out at room temperature using the four-probe technique with a Hewlett-Packard HP 6614 C dc power supply and two Hewlett-Packard HP 34401 A multimeters controlled by a computer. The amplitude of the dc signal was 0.1 V and geometry of the samples was 30 mm large, 3 mm width and 1 mm thick. Five specimens were measured for each composite.

Results and discussion

Microstructural analysis

Mechanical properties

The stress-strain curves of the different samples are shown in Figure 1a. In the case of LDPE based systems those containing lower filler percentage than percolation threshold and Fe as unique conducting filler behave mechanically of very similar form to unfilled polymer. However, when CB percentage is increased and percolation threshold is reached the break elongation decreases dramatically (Figure 1b). With regards to the PP systems, in the case of pure polymer and the composite with lower filler content a yielding mechanism is observed with the formation of a well-defined neck (Figure 1a). This tendency to yield decreases and even it reaches the point of disappearing when increasing the filler percentage and CB is also added to the system. Unlike LDPE systems, in general composites of PP deform uniformly until break at a stress and strain similar to those of unfilled polymer (Figures 1b and 1c).

With regard to the Young modulus an increase is observed when increasing filler concentration (Table I) which corresponds to PP based composites the highest values although the sample with greater filler percentage (PP-50) has not been able to test for being a brittle material.

In general the mechanical properties of these materials, except elongation at break for LDPE based composites, are improved by the presence of both fillers, important factor to be considered for its potential application as bipolar plates in fuel cells.

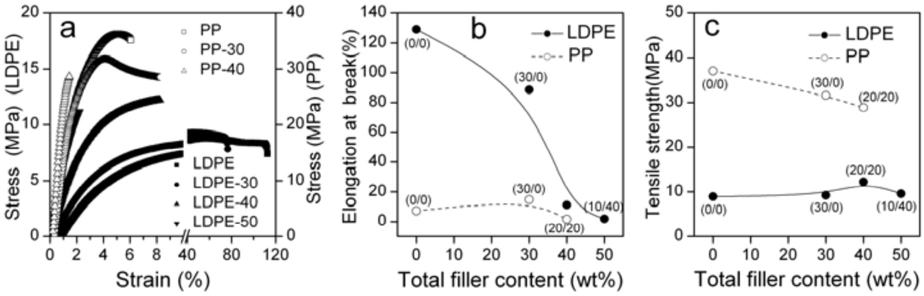

Figure 1. Mechanical properties of different composites

Thermal Analysis

The non-isothermal crystallization data of the composites were analyzed using the Avrami equation $\alpha(t)=1-\exp(-kt^n)$ where $\alpha(t)$ is the weight fraction of crystallized material at time t, k represents the rate constant of the crystallization process and n is the Avrami exponent which depends on the type of nucleation taking place and the growth geometry. The n and k values were obtained from the slopes and intercepts, respectively when plotting $\log\{-\ln[1-\alpha(t)]\}$ against log t for each cooling rate taking into account that time and temperature are related by means of cooling rate ($T=T_0+\beta t$). The kinetic data were collected below conversions of 30%.

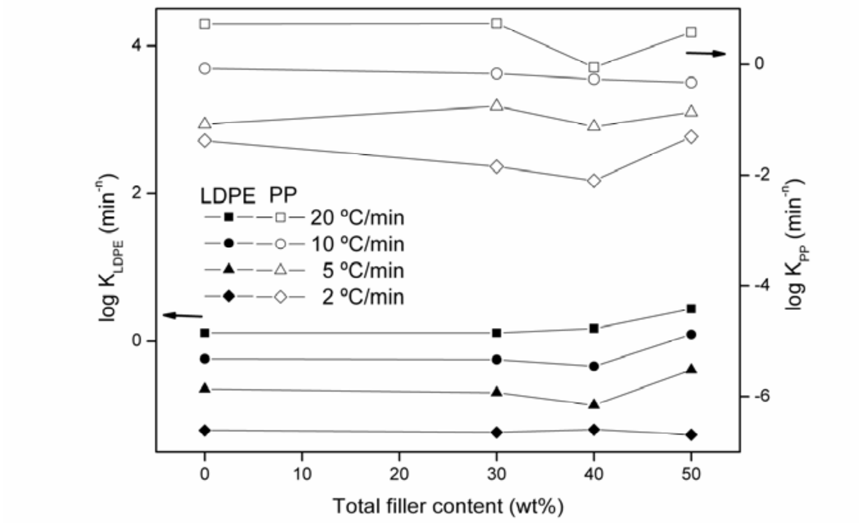

Figure 2. Crystallization rate constant as a function of total filler content for LDPE and PP based composites at different cooling rates

Figure 2 shows the rate constant of the non-isothermal crystallization process as a function of total filler content for the different experimental cooling rates and composites. In both systems no important variations were observed. Log k remains practically constant over the whole composition filler range.

With respect to the growth geometry of the crystalline LDPE or PP entities, interpreted through the value of Avrami's exponent, Figure 3 represents n as a function of filler concentration for the different composites. As it is shown, the geometry of the crystals is not modified when Fe is the only conducting filler present in the system. Nevertheless when in addition to Fe CB is incorporated, variations are observed, more pronounced when the CB content is of 40%.

On the other hand the effects are different depending on the polymer matrix. In the case of LDPE the growth geometry seems to be of bidimensional type for the pure polymer and the composite with only Fe to three-dimensional when CB is also incorporated into the blend.

In the case of composites based on PP the values of n diminish to high total filler percentage and again Fe by itself does not affect to the geometry of growing crystals.

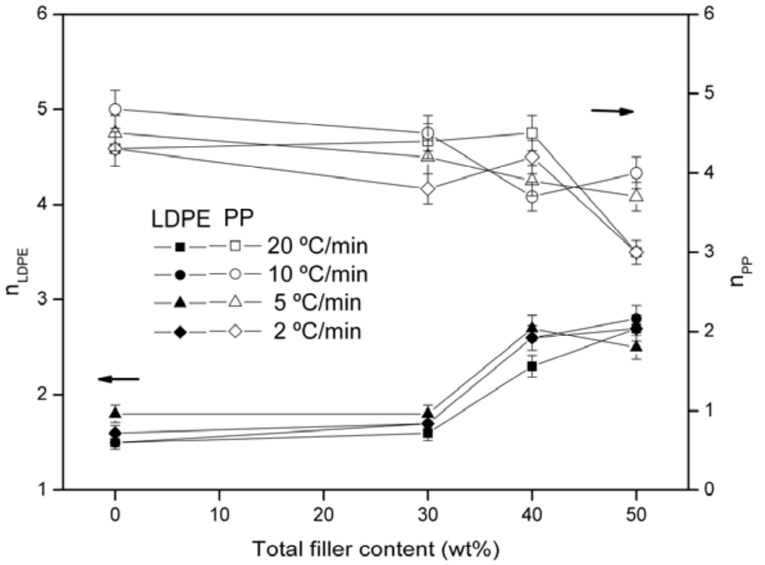

Figure 3. Avrami's exponent as a function of total filler content for LDPE and PP based composites at different cooling rates

With an increase in filler content either the crystallization or the melting temperatures change slightly as it is shown in Figure 4 where curves have been normalized in order to compare the results. In addition the profiles of both the exothermic and endothermic peaks become increasingly smaller when two fillers are added. These demonstrate morphological variation of the polymer matrix with both fillers incorporation. The crystalline structure is gradually reduced leading to an increase in the amount of imperfect crystals or amorphous portion.

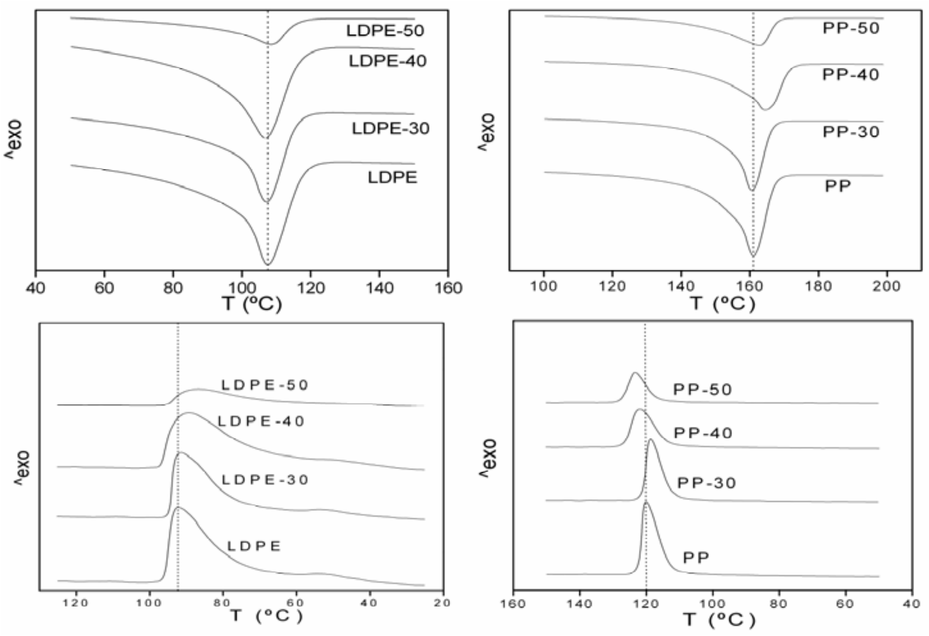

Figure 4. Melting and crystallization DSC thermograms of LDPE and PP based composites

Dynamic Mechanical Analysis

Dynamic mechanical measurements are believed to be a good method for gaining insight into the effects exerted by the filler on the polymer matrix. These effects are displayed as a variation in dynamic storage modulus (E'), a modification of the peak position and width of the relaxation spectrum as a consequence of filler-polymer interaction. Each peak marks a transition which is interpreted as the released of a restricted movement either in the polymer chain or in lateral groups.

Figure 5 display the temperature dependence of dynamic storage modulus (E') and loss modulus (E'') for LDPE and PP composites. Values of E' for filled samples consistently decrease at different rates as the temperature increases. With regards to LDPE composites the incorporation of the conducting fillers causes an increase of the dynamic storage modulus (E') in all the interval of temperatures studied. From room temperature the system with greater total filler percentage (PE-50) shows the highest E' with respect to pure polymer, detecting also for this composite a slight increase in the glass transition temperature that is not observed in the other cases.

For composites based on PP the incorporation of Fe as unique conducting filler reduces the value of E' with respect to neat polymer. When in addition CB is added to the system its stiffness increases in all the temperature interval studied being greater for composite with more elevated concentration of filler (PP-50). Furthermore for this system the appearance of the dynamicmechanical relaxations spectrum (E'') changes indicating important changes in the microstructure of this composite.

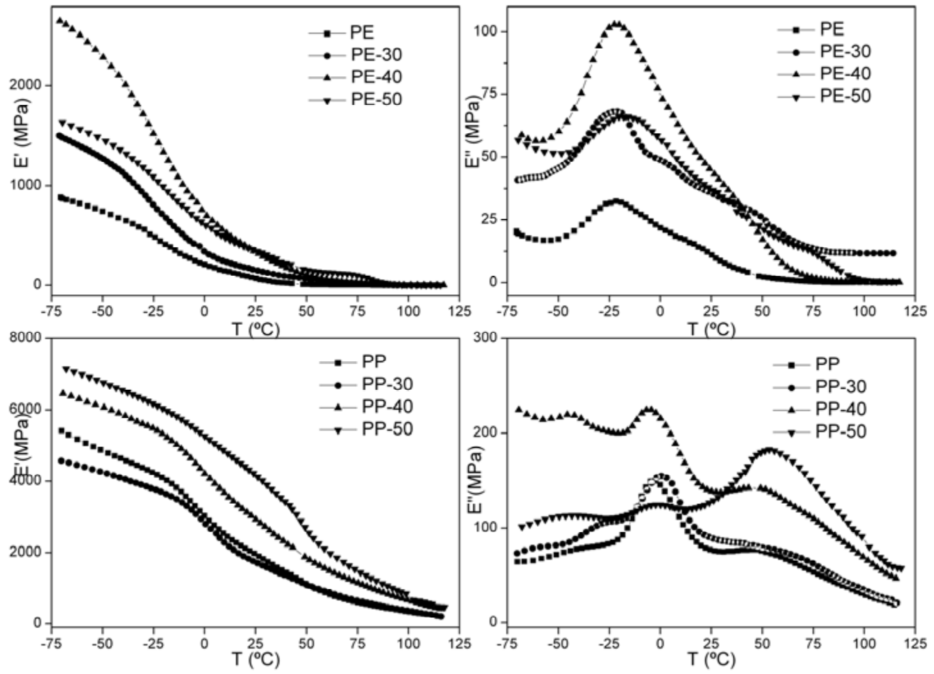

Figure 5. Dynamic storage modulus (E') and loss modulus (E'') as a function of temperature for LDPE and PP based composites

Electrical analysis

Conductivity

The composite conductivity was obtained from five different measurements of each sample. The conductivity variation with respect to total filler concentration is displayed in Figure 6 for LDPE and PP composites.

The conductivity increases with increasing filler content and it is necessary the presence of high percentages of CB to obtain values of conductivity higher than 10^{-1} S·cm^{-1} and therefore acceptable for bipolar plate application (Table I).

The stepwise change of conductivity takes place in composites containing both fillers and is thought to be a result of the formation of an interconnected structure of CB. It can be regarded as electrical percolation which means that a high percentage of electrons is permited to flow through the material due to the creation of an interconnecting conductivity pathway. Because of the small size and high specific surface, CB particles are favorable for self aggregation and easily form three-dimensional networks in a polymer matrix whereas metal Fe particles are too large to create sufficient contacts. Therefore the role of Fe particles is to allow the incorporation of greater amount of CB to the system (until a 40%) and to facilitate the flow channels processing than for enhancing the electrical conductivity of the material.

Comparing both polymer matrices, the highest values of conductivity are obtained for composites based on PP.

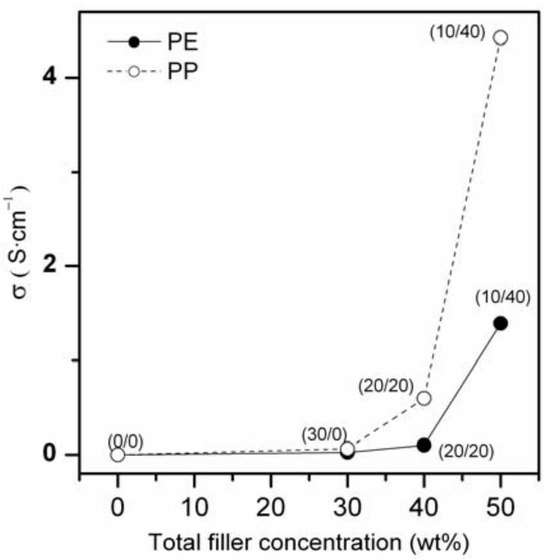

Figure 6. Electrical conductivity as a function of total filler content for LDPE and PP based composites

Conclusions

Electrical conductivity increases with increasing filler content; it is necessary the presence of CB to achieve values of conductivity higher than 10^{-1} S·cm^{-1} . Comparing both polymer matrices, the most notable results are obtained for composites based on PP. In general the mechanical strength of the polymer composites is improved by the presence of both fillers (Fe + CB). The samples with Fe particles as unique filler behave mechanically of similar way to unfilled polymer.

The results of the thermal study indicate that the particles of Fe are not able to modify the geometry of crystals in growth. On the contrary, the incorporation of both conductive fillers to the polymer matrix gives rise to microstructural modifications, reducing the crystalline phase and increasing the amorphous phase of the polymer. These modifications are also observed in the mechanodynamic spectrum of the composites with greater percentage of total filler.

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