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Effect of crystallization on morphology–conductivity relationship in polypyrrole/poly(ε-caprolactone) blends

M. Ángeles Corres [a], Agurtzane Mugica [a], Pedro M. Carrasco [b], M. Milagros Cortázar [a,*]

[a] *Polymer Science and Technology Department, Faculty of Chemistry, UPV/EHU, P.O. Box 1072, E-20080 Donostia-San Sebastián, Spain*
[b] *Centre for Electrochemical Technologies (CIDETEC), Parque Tecnológico de Miramon, P8 Miramón 196, 20009 Donostia-San Sebastián, Spain*

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Abstract

Electrically conducting blends, based on polypyrrole (PPy) as the conductive polymer and poly(ε-caprolactone) (PCL) as an insulating polymeric matrix, were prepared by polymerizing pyrrole (Py) in its vapor state inside the PCL matrix. The roles of specific interactions between blend components as well as the crystallization of PCL matrix in the resulting morphology have been analyzed by Fourier-transform infrared spectroscopy (FTIR), thermo-optical analysis (TOA) and atomic force microscopy (AFM). The results indicate that PPy is located within both the intra and interspherulitic regions of the PCL matrix achieving a well-developed connected network. Compared with amorphous matrices, considerable conductivity (around 1 S/cm) was raised with the crystalline PCL matrix with only a relatively low level of the conductive polymer (~5%) in the blend.

Keywords: Atomic force microscopy (AFM); Conducting blends; Polypyrrole

1. Introduction

The poor mechanical properties of highly conductive polymers restrict their large-scale application. In an effort to obtain thermally processable conducting blends or composites, conductive polymers have been incorporated into insulating polymeric matrices by chemical synthesis or electropolymerization [1–7]. The conductive polymer content of a blend needs to reach the percolation threshold to cause the onset of electronic conductivity [1,3]. Conversely, it is desirable to minimize the concentration of the conductive polymer in the blend in order to avoid detrimental effect upon mechanical properties caused by incorporating rigid chains of the conductive polymer in the insulating matrix.

In some conducting polymer blends the interactions between components were found to play a strong role in determining morphology and conductivity of these materials [7]. It has been proposed that interactions between the blend components are responsible for semi-compatibilization thus promoting conducting networks at low level of conductive polymer [8]. In blends prepared by in situ polymerization, the low solubility of the monomer in the insulating matrix can make it difficult to prepare blends with sufficient conductivity for them to be useful materials. Taking into account that the level of electrical conductivity in these materials depends upon the concentration of the conductive polymer [9], specific interactions between the monomer and the matrix in which polymerization takes place would favor the solubility of the monomer in the host polymer.

Macroscopic properties in blends depend not only on the concentration and chemical structures of their components but also on microstructures developed during the blending. To obtain highly conducting polymer materials and to lower the percolation threshold, different morphologies have been developed by in situ polymerization within the lamellar microdomains of block copolymers [10,11] as well as inside the

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* Corresponding author. Tel.: +34 943018189; fax: +34 943015270.
E-mail address: mila.cortazar@ehu.es (M.M. Cortázar).

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void space of a (micro or nano) porous polymeric matrix [12–14] or inside interstitial domains of a crystallizable host matrix.

In particular, the crystallinity in the host polymer can drive the microstructure that the conductive polymer adopts in the matrix during the polymerization process. Hopkins and Reynolds [15] analyzed the electrical conductivity in blends prepared with polyaniline and an amorphous or a crystalline polyamide as insulating host. They observed that conductivity using a crystalline host is 10 times higher than when using the amorphous one. This result was related to the conducting network or pathway developed in polyaniline as a consequence of matrix crystallization. The authors propose the use of crystallization in the host as a method for controlling morphology and tuning the ultimate electrical properties of conducting polymer blends.

In spite of the technological importance of the conducting pathways upon the final conductivity of the materials, little attention has been paid to understanding the role of the crystallization process on the electrical conductivity of the resultant material. This work has attempted to observe the morphology developed in films formed with both a crystalline host and a conductive polymer. Poly(ε-caprolactone) (PCL) and polypyrrole (PPy) were used as the crystalline and conductive polymers, respectively. The major aim was to investigate how the electrical conductivity is related to the morphology created during film formation. Optical microscopy (TOA) and atomic force microscopy (AFM) were used to characterize the developed morphology whilst Fourier-transform infrared spectroscopy (FTIR) was used to analyze specific interactions in blends.

2. Experimental

The poly(ε-caprolactone) (PCL) was supplied in pellet form by Polysciences Inc., with a weight-average molecular weight ($\bar{M}_w$) of 49,000 g/mol, as measured by gel permeation chromatography (GPC) using polystyrene standards and tetrahydrofuran (THF) as eluent and applying adequate Mark–Houwink constants. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), employed as a 1 M solution in bidistilled water, was purchased from Panreac and used as the oxidant without any further purification. Methanol (CH_3OH), used to wash the final product, was also supplied by Panreac and employed without any further purification. Pyrrole (Py) was purchased from Aldrich and distilled prior to use.

The neat PCL films were cast in a spin coater from a PCL/THF solution (5 wt.%) on glass substrates. The electrically conducting PCL/PPy thin films were prepared by chemical oxidative polymerization of Py in the vapor state [16,17]. The polymerization was carried out exposing PCL films to Py vapors. The exposure time ranged from 2 to 15 min under ambient conditions preparing three different blends. The polymerization was concluded by dipping the films in an aqueous solution of 1 M $FeCl_3 \cdot 6H_2O$ for 1 h at −20 °C. The resulting film was washed thoroughly in CH_3OH until the residual solution became transparent before drying under vacuum at room temperature. The conducting polymer amount was estimated by means of the weight increase of the PCL films and the corresponding compositions in weight are PCL/PPy 95/5, 90/10 and 85/15.

The spherulite growth rate and crystalline morphology of PCL/Py films were analyzed by polarized light microscopy. To this purpose a Leitz Aristomet microscope equipped with cross-polarizers and a Leica photographic digital camera, model DFC 320, were employed. The radii of the spherulites were measured using the IM-1000 software. A Mettler FP80 programmable hot stage was used as the temperature controller. The crystallinity of PCL/Py films was destroyed by heating to 60 °C and after this treatment the films were maintained isothermically at 26 °C until the crystallization was completed. At higher temperatures, the crystallization process was very slow to be followed in a reasonable experimental time, specially for samples with high Py content, and on the other hand, lower temperatures are difficult to control with a Mettler FP80 programmable hot stage.

Fourier-transform infrared spectroscopy (FTIR) was employed to determine intermolecular interactions. The films used in this study were sufficiently thin to be within the absorption range (≤ 1) where the Lambert–Beer law is obeyed. In our case the films with a thickness less than 20 μm fulfill the required condition and such thicknesses were determined with a Duo-Check ST-10 apparatus. Infrared spectroscopic measurements were recorded on a Nicolet, model Magna 560 FTIR spectrometer at a resolution of 2 cm^{-1} and averaged over a minimum of 64 scans. Spectra recorded at elevated temperatures were obtained by using a Spectra-tech heating cell, with an accuracy of ±2 °C, mounted inside the sample chamber. In order to ensure equilibrium conditions at elevated temperatures, the infrared spectra were recorded after an annealing period of approximately 15 min at each temperature.

The polymer morphologies were also observed with an atomic force microscopy (AFM), model Digital Instrument Nanoscope IV. Measurements were carried out in tapping mode using a silicon cantilever. The height and phase images were acquired simultaneously. The scan sizes of the images obtained were from 15 μm to 250 nm and each image had a resolution of 512 × 512 lines.

The conductivity of the samples was measured by a standard four-probe technique (Miler Design & Equipment model FPP-5000 automatic resistivity meter) at room temperature with sample discs of 1.6 cm of diameter.

3. Results and discussion

3.1. Determination of intermolecular interactions

In blends, molecular interactions between components control the level of miscibility. Therefore, any interaction will have an influence on the homogeneity of the distribution of Py in the PCL matrix and consequently in the final dispersion of PPy in this matrix. The most likely center for specific interactions in these blends is hydrogen bonding involving the carbonyl group in PCL and the −NH− group in Py [18].

This is confirmed from FTIR spectra studies for PCL/Py blends, prior to their chemical oxidative polymerization, as well as for PCL/PPy blends after such a polymerization.

Fig. 1 shows the infrared spectra corresponding to the carbonyl stretching region (1660–1820 cm^{-1}) for pure PCL, pure Py and a PCL/Py 90/10 blend, respectively. Neat PCL shows a carbonyl stretching band while pyrrole shows no absorption in this region. Therefore, any variations observed in this region should be directly attributed to those changes in the carbonyl-group environment of PCL, such as the formation of hydrogen bonds. At room temperature, PCL shows a band centered at 1725 cm^{-1} corresponding to the free crystalline carbonyl vibration and a shoulder around 1735 cm^{-1} attributed to free amorphous carbonyl vibration. When PCL is heated at 110 °C a completely amorphous polymer is obtained and only the band assigned to free amorphous carbonyl groups ($\sim$1735 cm^{-1}) is observed. By blending pyrrole with PCL, a new band appears at about 1715 cm^{-1}, which presumably was induced by the formation of the polyester pyrrole intermolecular hydrogen bond [19,20].

Fig. 2 illustrates the spectra corresponding to the carbonyl stretching region for PCL/PPy 90/10 blends at different temperatures after the polymerization of Py was carried out. A band centered at 1735 cm^{-1} corresponds to stretching vibrations of free carbonyl groups and a shoulder at around 1700 cm^{-1} is assigned to carbonyl groups bonded to the –NH– groups of PPy. Furthermore, it is shown in Fig. 2 that, on increasing the temperature of the blend the intensity of the band assigned to the associated stretching carbonyl group decreases because the number of hydrogen bonds at elevated temperatures is diminished [18]. Comparing the infrared spectra of PCL/Py (Fig. 1) and PCL/PPy (Fig. 2), it is concluded that the level of the intermolecular interactions between PCL and PPy is lower than the number of hydrogen bonds in PCL/Py blends. Although the polymerization process decreases the intermolecular interactions between the blend components, the remaining hydrogen bonding interactions will play considerable role on the morphology of PCL providing a more homogeneous distribution of PPy in the crystallizable matrix and consequently favoring the conductivity of the PCL/PPy blend [7,15].

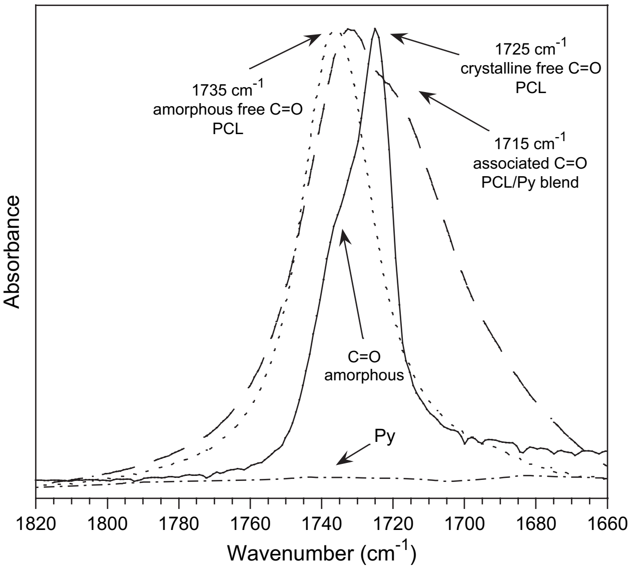

Fig. 1. FTIR spectra in the carbonyl stretching region of PCL, Py and PCL/Py blends: (- — - —) Py, (— — —) crystalline PCL, (···) amorphous PCL and (—) PCL/Py 90/10 blend.

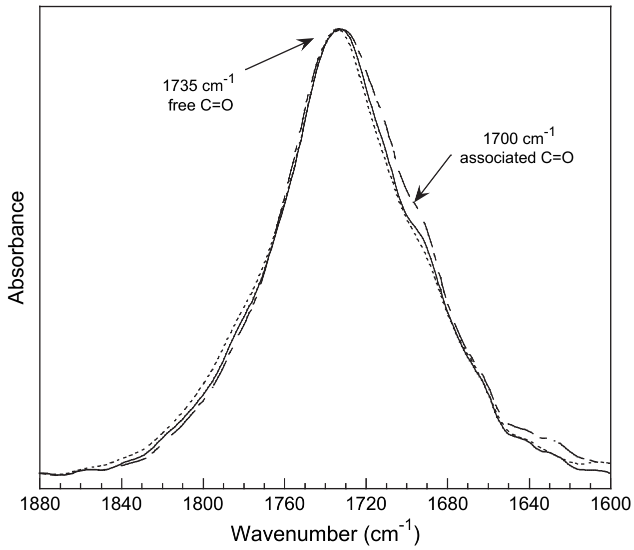

Fig. 2. FTIR spectra in the carbonyl stretching region of PCL/PPy 90/10 blends: (- — - —) 100 °C, (—) 150 °C and (···) 200 °C.

3.2. Morphology and spherulite growth rate

Under optical microscopy the pure PCL and PCL/Py 95/5 blends display a spherulitic morphology with a "Maltese cross" birefringent pattern as can be seen in Fig. 3a. By increasing the Py content in the blends (Fig. 3a–c), the spherulites lose gradually the Maltese cross pattern and exhibit a less regular texture, most likely [21,22] as a consequence of the progressive presence of uncrystallizing material in the interlamellar or interfibrillar intraspherulitic regions. The radii of PCL/Py spherulites against time are also given in Fig. 3. For all blend compositions investigated in this work it was found that the spherulite radius does not increase linearly with time.

The spherulite growth rates, G, for neat PCL and PCL/Py blends can be obtained from the variation of the spherulite radius with time. A constant growth rate was observed for the pure crystalline polymer, however in blends, G decreases when the crystallization time increases (Fig. 3a–c). Moreover, upon addition of Py to PCL causes a depression in the G values (Fig. 3a–c). In blends, the rate of spherulite growth is primarily governed by the composition of the melt at the growth front [23]. Thus, the experimental results shown in Fig. 3 suggest that the concentration of PCL crystallizable molecules at the growth front decreases during the crystallization process. This means that, during the crystallization, a proportion of the Py molecules is segregated increasing the

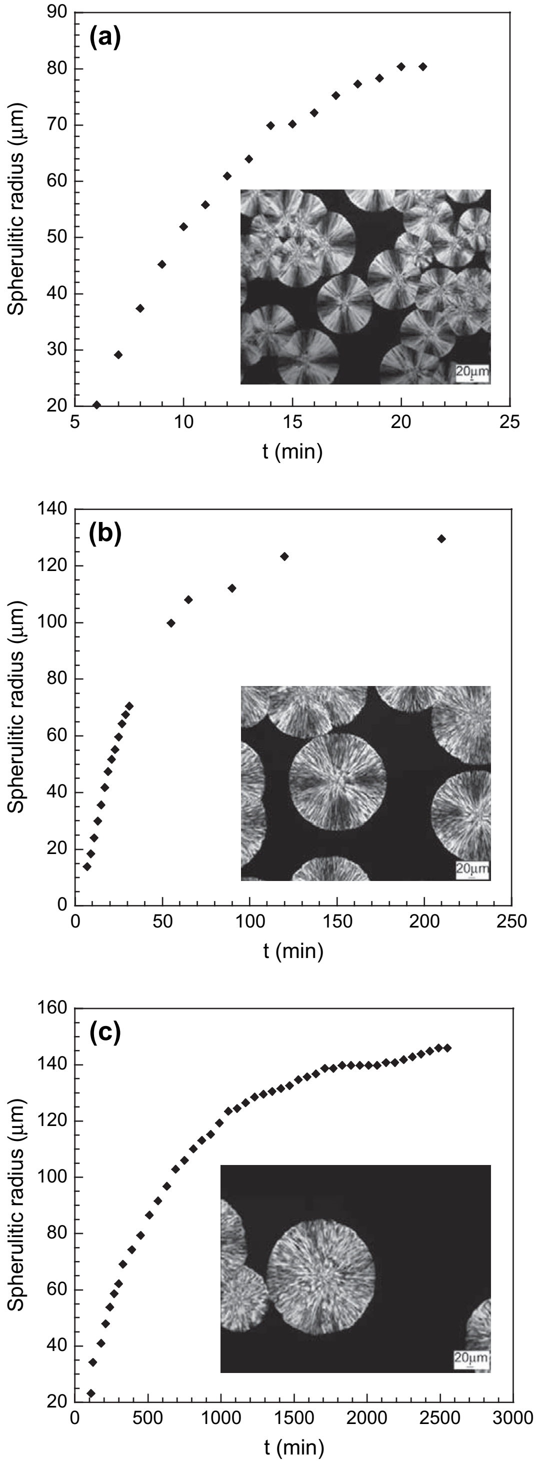

Fig. 3. Spherulitic growth of PCL/Py blends at 26 °C and its polarizing optical micrographs of spherulites isothermally crystallized: (a) PCL/Py 95/5, (b) PCL/Py 90/10 and (c) PCL/Py 85/15.

concentration of Py in the growth front. Therefore, additional time is necessary for crystallization to be completed in mixtures containing high amounts of Py.

According to the results shown in Fig. 3 it can be expected that Py is located in the interlamellar or interfibrillar intraspherulitic regions as well as in interspherulitic ones. The ordering get by Py during the crystallization process will presumably be maintained when polymerization takes place. However, this assumption requires proof.

3.3. The PPy distribution in the PCL matrix

Fig. 4 displays a comparison between morphologies developed in neat PCL and in PCL/PPy blends obtained using atomic force microscopy (AFM). It can be seen that PPy is homogeneously distributed in the host matrix and does not show PPy agglomerates in isolated domains (Fig. 4b). Greater magnification of the surface of PCL/PPy film (Fig. 4c) shows that PPy nanoparticles are spherical and, on average, as large as 70 nm in diameter. Nevertheless, the interspherulitic regions (as indicated via the arrows in Fig. 5) comprise part of the PPy, formed from Py segregated during the crystallization process. It was reported that in polyaniline–camphorsulfonic acid (PANI–HCSA)/nylon6 systems, the PANI–HCSA salt component was rejected from the interlamellar regions and the salt mainly resides in interspherulitic regions [15]. However, as it can be observed in AFM micrographs for PCL/PPy 90/10 blend (Fig. 4b), the conductive polymer is not just concentrated in interspherulitic regions. It is possible that the specific interactions between Py and PCL prevent Py from being completely excluded from the growing spherulites, which remain in the same place when polymerization of Py occurs.

The above results suggest that the crystallization of PCL drives PPy to develop a more ordered microstructure thus favoring the formation of a connected network of small particles of PPy, which presumably will increase the electrical conductivity of the conducting/crystallizable polymer blends.

3.4. Measurements of electrical conductivity

The electrical conductivity, as well as being sensitive to the morphology [24,25], has been shown to be sensitive to the concentration of the conductive polymer in the blend [14,15,26]. Thus, the variation of PCL/PPy blend conductivity with PPy concentration reached a maximum of around 1 S/cm. Practically no changes in conductivity were observed beyond a 5% PPy concentration.

The conductivities determined for PCL/PPy blends are comparable to those measured by Hopkins and Reynolds [15] for mixtures where the conductive polymer was blended with crystalline hosts. These values are much higher than those obtained for similar PPy concentrations in amorphous hosts such as poly(vinyl acetate) (PVAc), polystyrene (PS) or poly(vinyl chloride) (PVC) (10^{-4}–10^{-1} S/cm) [14,27–29]. This result is attributed to the formation of more organized conducting pathways, as was shown in the AFM micrographs for the blend containing the crystalline host.

4. Conclusions

The morphology developed by the crystallization of the PCL/Py blend was analyzed by microscopy. It was found

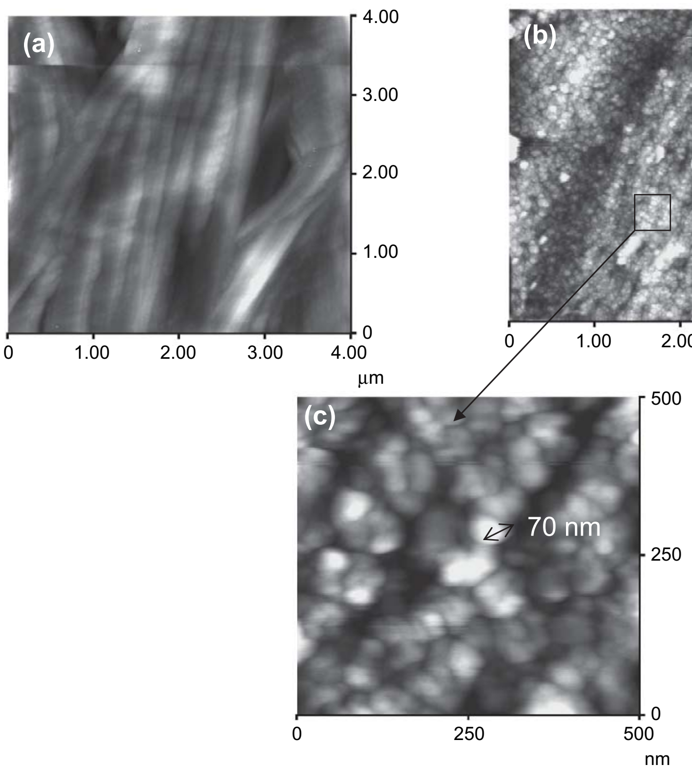

Fig. 4. Morphology of PCL and PCL/PPy 90/10 blends observed by AFM at different scan sizes: (a) PCL, (b, c) PCL/PPy blend in the intraspherulitic region.

that the crystallization process drives pyrrole into the intra and interspherulitic regions, and when pyrrole polymerization takes place, this allows the formation of conducting PPy networks in the blend. Furthermore, the favorable intermolecular interactions, i.e. the hydrogen bonds between PCL and Py, prevent the formation of isolated domains of PPy, achieving high electrical conductivity using small amounts of conductive polymer.

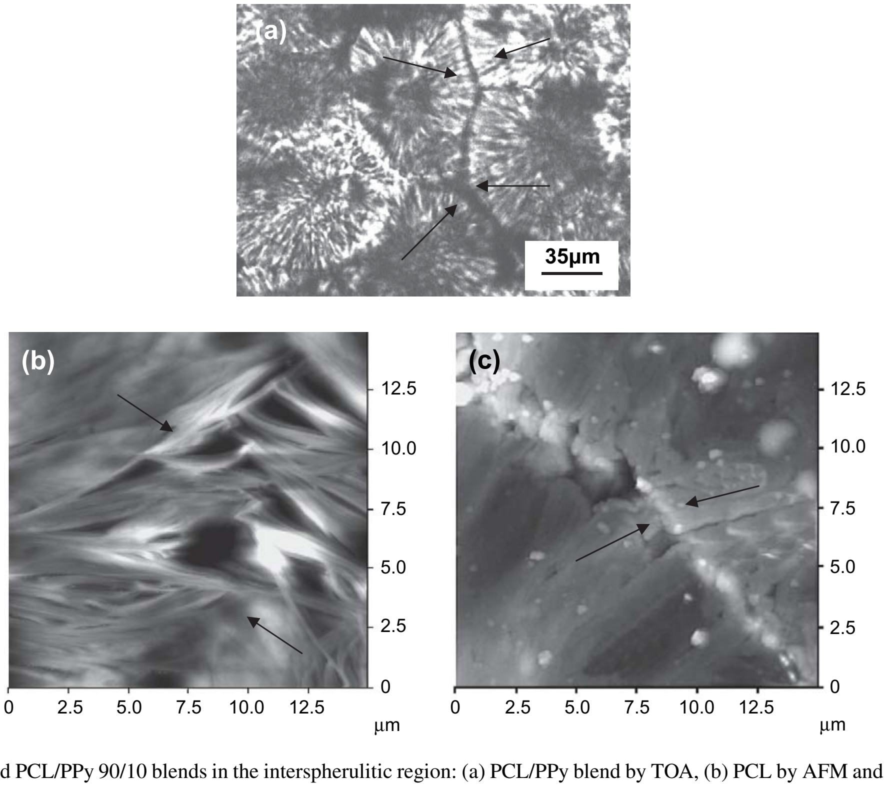

Fig. 5. Morphology of PCL and PCL/PPy 90/10 blends in the interspherulitic region: (a) PCL/PPy blend by TOA, (b) PCL by AFM and (c) PCL/PPy blend by AFM.

One of the most noteworthy finding in our research indicates that by combining a conductive polymer with another conventional, insulating, crystallizable polymer, it is possible to manipulate the electrical properties of the resulting material. In other words, by controlling the crystallization process of the insulating polymer, modification of the morphology of the blend becomes possible. Thus, the conductive component can be highly dispersed in the blend, maintaining high connectivity between the conductive particles and consequently, enhancing the electrical conductivity of the material using small amounts of the conductive polymer.

Therefore, it was shown that the electrical conductivity is highly sensitive to the location of the conductive polymer within the insulating polymeric matrix. As great variety of matrix polymers can be used to form materials of this kind, which offer the desired electrical and mechanical properties, extensive work still needs to be done to gain full understanding of the factors that are essential in the design of the morphology of these conducting materials. To this goal, factors such as the crystallization rate, the mobility of the conductive component as well as the interactions between the conductive polymer and the crystallizable matrix, among others, should be studied.

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